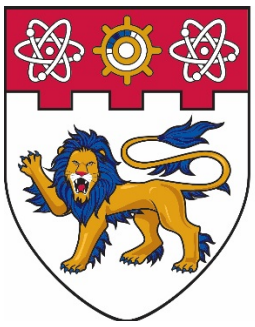

NANYANG TECHNOLOGICAL UNIVERSITY
SINGAPORE

THE PRODUCTION AND BIOTRANSFORMATIONAL CHANGES OF SOLUBLE MICROBIAL PRODUCTS (SMPs) AND ITS EFFECTS ON ANAEROBIC WASTEWATER TREATMENT

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A thesis submitted to the Nanyang Technological University in partial fulfillment of the requirement for the degree of Doctor of Philosophy

2020

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Authorship Attribution Statement

This thesis contains material from 4 papers published in the following peer-reviewed journals in which I am listed as an author.

The contents in Chapter 2 is published as Y.N.A. Soh, C. Kunacheva, R.D. Webster, D.C. Stuckey, Identification of the production and biotransformational changes of soluble microbial products (SMP) in wastewater treatment processes: A short review, *Chemosphere*, **251**, 126391 (2020).

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- Prof Stuckey and Prof Webster provided the initial direction and edited the manuscript drafts.
- Dr Kunacheva proofread the manuscript drafts
- I am the main author of this manuscript.

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- Prof Stuckey provided the initial project direction and edited the manuscript drafts.
- Dr Kunacheva co-designed the study with Prof Stuckey. Dr Kunacheva prepared the samples and carried out the solid phase extraction and gas chromatography-mass spectrometry in Advanced Environmental Biotechnology Centre (NEWRI) while I was the assistant in this work.
- Dr Le developed the liquid-liquid extraction method in Advanced Environmental Biotechnology Centre (NEWRI).

- I was in-charge of the data analysis from the gas-chromatography-mass spectrometry, and preparation of part of the sections on methods and results in the manuscript.

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- Prof Stuckey and Prof Webster provided the initial direction and edited the manuscript drafts.

- Dr Kunacheva assisted in setting up the bioreactor and the design of the experiment.
- I discussed the objectives this study with the professors, set-up and carried out the experiment, performed the data analysis and prepared the manuscript.

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Summary

Effluent quality has been an important factor in the regulatory requirement for discharge of effluent from wastewater treatment plants. Characterization of effluents from both aerobic and anaerobic processes has shown that soluble microbial products (SMP) produced by microorganisms during biological treatment constitute the major proportion of the residual chemical oxygen demand (COD), and this can be up to 100%. Over the past twenty years, advancements in SMP analysis have allowed for their chemical characterization with increasing specificity, however, these advances are still not widely used in the study of anaerobic wastewater treatment systems. Hence, this study aims to examine: the biotransformational changes in soluble microbial products (SMPs), and the trends in their formation and disappearance during anaerobic wastewater treatment; the effects of feed macronutrients on the SMPs produced and their effects on membrane fouling, and; finally, evaluating SMP production in full-scale wastewater treatment plants. An anaerobic baffled reactor (ABR) was used because this type of reactor "splits" the biological reactions (trophic groups) into their constituent parts, as opposed to a continuously stirred tank reactor (CSTR), and hence enables us to monitor the production and degradation/ biotransformation of the SMPs down the reactor over time.

The samples collected were extracted by sequential solid phase extraction (SPE) and liquid-liquid extraction (LLE), followed by untargeted analysis using gas chromatography coupled mass spectrometry (GC-MS) and liquid chromatography coupled tandem quadruopole time-of-flight (LC-Q-ToF). The first part of the study on the biotransformational changes of SMPs found the net production of alkanes and alkenes during the pseudo steady-state operation of an anaerobic baffled reactor set at a 24-hour hydraulic retention time (HRT). Previous work reported that the 'recalcitrant' phthalate esters are degradable, and a literature search found earlier studies proving that they are products of marine algae. This again showed that such 'recalcitrant' microbial products are degradable but are dependent on reactor time (HRT) and conditions (solids retention time-SRT). In terms of the impact of the change in carbon and nitrogen source (macronutrients) in the bioreactor feed on the production of SMPs, the

results obtained do not show any obvious changes in the physical parameters routinely monitored for reactor performance (such as COD removal, and volatile fatty acid - VFA production). However, the chemical analysis using chromatographic methods coupled to mass spectrometry revealed underlying biochemical changes over a period of 24 hours after the change in the macronutrients in the feed. One significant finding is that a switch from an organic to an inorganic nitrogen source induced an inhibitory effect on glucose metabolism shown by an increase in the quantity of aliphatic aldehydes produced, which are reaction intermediates of the glucose metabolic pathway, and the 'disappearance' of alkanes. A considerable amount of work in the past which has examined fouling in membrane bioreactors were conducted in aerobic systems, but limited information has been available on anaerobic systems. The foulants were characterised in the past using liquid chromatography coupled oraganic carbon detection and organic nitrogen detection (LC-OCD-OND) and excitation-emission matrix (EEM), and these only showed the presence of polysaccharides and proteins. This lack of information led to the detailed chemical characterization of membrane foulants in this study, which has not been reported before. The untargeted scanning using LC-Q-ToF of the extracted membrane foulants found that the compounds detected were in the range of 200 – 799 Da, other than colloids and larger sized particles. A majority of compounds in the foulant were identified as fatty acids and their conjugates, and steroids and their derivatives. Finally, we reported on the characterisation of SMPs in the samples collected at various points of the full-scale industrial wastewater treatment plant, which is an area with limited information in the literature. The chemical characterisation showed some degree of similarity to the SMPs detected during the transient states of the lab-scale bioreactor operating on synthetic feed, while there was a small number of similar compounds primarily comprised of long-chain alkanes and phthalates.

Abbreviations

ABR	Anaerobic baffled reactor
APHA	American Public Health Association
BAP	Biomass-associated products
ChEBI	Chemical Entities of Biological Interest
COD	Chemical oxygen demand
CSTR	continuously stirred tank reactor
Da	Daltons (unit of measurement for molecular weight)
DBPs	Disinfection by-products
DCM	Dichloromethane
DOC	Dissolved organic carbon
EAWAG-BBD	Swiss Federal Institute of Aquatic Science and Technology - Biocatalysis/ Biodegradation Database
EPS	Extracellular polymeric substances
ESI	Electrospray ionisation
GC-MS	Gas chromatography coupled mass spectrometry
HMDB	Human Metabolome Database
HPLC	High performance liquid chromatography
HRMS	High resolution mass spectrometry
HRT	Hydraulic retention time
KEGG	Kyoto Encyclopedia of Genes and Genomes
LC-OCD-OND	Liquid chromatography coupled organic carbon detection-organic nitrogen detection
LC-Q-ToF	Liquid chromatography coupled quadrupole-time-of-flight
LLE	Liquid-liquid extraction
m/z	Mass to charge ratio
MW	Molecular weight
NIST	National Institute of Standards and Technology
OLR	Organic loading rate
ORP	Oxidation-reduction potential
RI	Retention index
RT	Retention time

SAMBR	Submerged anaerobic membrane bioreactor
SEC	Size-exclusion chromatography
SMP	Soluble microbial products
SPE	Solid phase extraction
SRT	Sludge retention time
TMP	Transmembrane pressure
TOC	Total organic carbon
UAP	Utilisation-associated products
UASB	Upflow anaerobic sludge blanket
USEPA or EPA	United States Environmental Protection Agency
VFA	Volatile fatty acids
VSS	Volatile suspended solids
WWTP	Wastewater treatment plant

Chapter 1

Introduction

The increasing importance of addressing the issues of water scarcity and pollution of water sources due to industrialization and urbanization, has triggered the growth of research and development of modern wastewater treatment systems. The entire treatment flow involves physical, chemical and biological processes, with biological process being the secondary treatment, which consists of the important role of removing organic pollutants from the influents of various sources. These biological processes can be classified as aerobic and anaerobic, each with its own advantages and disadvantages. Aerobic biological treatment was developed a century ago, and was the process of choice for dilute wastewaters, while anaerobic digestion was used solely for sludge digestion of primary and waste activated sludge. However, in the last 20 years further research found that anaerobic treatment possessed more attractive and crucial advantages over aerobic processes. Aerobic processes experience problems of high energy consumption for aeration of the reactor; the release of oxides of nitrogen (N_2O-a potent greenhouse gas) and carbon dioxide (air pollution); and production of large amounts of waste sludge (~40% of the COD converted to waste biomass) which requires an additional step to treat and then dispose of it. Anaerobic processes on the other hand do not require aeration, and the only energy required is the recycling of biogas for mixing of bioreactor contents, while methane gas is generated (a component of the biogas which can be used as an energy source onsite), and the solids generated is approximately 90-96% less than aerobic treatment greatly reducing the need for sludge treatment and disposal. For these reasons, the development of anaerobic treatment technology has started to be integrated into secondary treatment processes to improve the overall efficiency, reduce energy use and solids disposal. Since the development of anaerobic treatment systems, the focus has been on the rate and degree of bioconversion, the effects of the nutrients available, and the robustness of the system in response to variable flows and organic loads (Speece, 1983).

One of the key goals of wastewater treatment is to achieve sufficiently low effluent chemical oxygen demand (COD, an indicator of the amount of organic and inorganic matter present in a sample calculated by the degree of oxidation), which must comply with increasingly tight environmental legislation. The fundamental basis of biological wastewater treatment is the breaking down (catabolism) of complex molecules in the influent into the simplest forms of organic carbon, carbon dioxide (and methane in anaerobic systems). The three stages of anaerobic catabolism are acetogenesis, acidogenesis, and methanogenesis, and in these processes hydrogen gas is generated (McCarty & Smith, 1986). Thermodynamically, the conversion of complex molecules first into volatile fatty acids (VFA) and subsequently to methane via synergistic reactions are favourable and should totally convert these organics to carbon dioxide and methane. However, there is still a substantial amount of effluent COD despite considering the biogas generated, VFAs and residual feed COD due to incomplete conversion of influent substrates. Later studies identified the effluent COD as extracellular polymeric substances (EPS, or ECP in some more recent journals), which are polymers generated during cell lysis or released by the cells due to stresses from the external environment (such as temperature and pH of the bioreactor). Further investigation of this group of compounds found that they not only consisted of 'polymeric substances', but also other organic compounds which resulted from substrate metabolism, cell growth and decay. It is generally agreed that soluble microbial products (SMPs) can be broadly classified as biomass-associated products (BAP-due to cell lysis) and utilization-associated products (UAP-which are produced during catabolism/anabolism) (Laspidou & Rittmann, 2002), and that there is a higher molecular weight range of soluble compounds which are largely the proteins/polypeptides, polysaccharides and lipids, and their fragments (Barker & Stuckey, 1999; Jarusutthirak & Amy, 2007; Ni et al., 2011). Clearly, UAP refers to the compounds generated by cells from the biotransformation of the influent, for instance lipids forming an additional layer around the cell during sudden change in cell environment such as temperature and pH, while BAPs are intrinsically produced by the cells during cell death and lysis. From previous studies carried out in our group, there is another group of compounds which were detected during HRT shock loads (Kunacheva et al., 2017c), and the sudden onset of

extreme conditions such as very low or high pH (Kunacheva et al., 2017b). Furthermore, advanced detection methods such as gas chromatography- and liquid chromatography-mass spectrometry allows identification, or at least partial identification, of these compounds (unravelling the chemical classes these compounds belong to) (Kunacheva & Stuckey, 2014; Pico & Barcelo, 2015).

Historically, the studies on detection of compounds found in wastewater before, during and after the various treatments were focused on targeted analysis such as pharmaceutical compounds, pesticides and drugs (endocrine disruptors and antibiotics). These often miss the unexpected reaction intermediates and possible emerging contaminants that may be present. As such, current studies have not totally understood the origin of all the components in the effluent COD (besides VFA and residual feed). Microbial products of individual species had been studied in numerous lab-scale experiments but the synergistic effects of a mixed culture, which is usually the case for anaerobic digestion systems, was not considered. In addition, studies on the effects of macronutrients and their effects on the composition of SMPs are also very limited. The overall aim of this study was, therefore, to close this knowledge gap of the existence of SMPs in mixed cultures, how their composition changed with time and varying influent composition, and how these changes in SMPs affected membrane fouling.

This thesis is organized as follows:

Chapter 2 – Review of previous studies on the detection of SMPs, the degradation and biotransformation of SMPs and their implications on the environment, and the occurrence of functional natural products. This leads to the main objectives and scope of this study.

Chapter 3 – Description of the methods adopted to achieve the objectives of this study.

Chapter 4 – A study on the trends observed in SMP composition down the length of a compartmentalized anaerobic baffled reactor fed with synthetic wastewater (controlled influent) using.

Chapter 5 – Investigation of the differences or similarities in SMP composition due to changes in the macronutrients, i.e. carbon and nitrogen sources.

Chapter 6 – Addressing the effects of SMPs on membrane fouling.

Chapter 7 – This section of the study aims to put the identification of SMPs closer to its application in actual full-scale treatment plants. The samples being analysed were collected from an industrial scale wastewater treatment in Singapore, and a comparison of the SMPs produced from it was made with those from a lab-scale bioreactor treating synthetic wastewater.

Chapter 8 – A summary of the findings from this study and suggestions for future research.

Chapter 2

Literature review

2.1 Introduction

This chapter presented a review of the fundamentals obtained by previous studies that had been carried out with regards to the production of soluble microbial products (SMPs), and their characterization methods, and implications of SMPs generated during biological treatment processes. Due to the increasing interest in the development of membrane bioreactors, the control of membrane fouling has become an important area of research into what are the causes of membrane fouling, and the role of SMPs in this area. The availability of nutrients also affects the efficiency of biological treatment processes. Micronutrients such as metals (trace concentrations) play an important role in the performance of bioreactors, and changes in the influent composition (carbon and nitrogen sources) should also have significant effects on the performance of bioreactors since they are the main components and biodegradation targets.

2.2 The definitions of SMPs

While the exact definition of SMPs remains debatable, it generally refers to the group of organic compounds released by microbial cells into their extracellular environment during cell metabolism and lysis. A small fraction of these organics make up a significant portion of the effluent chemical oxygen demand (COD) from biological wastewater treatment processes (Kunacheva & Stuckey, 2014; Laspidou & Rittmann, 2002; Mesquita et al., 2010).

A variety of organic compounds, not present in the influent, have been detected in the effluents from biological wastewater treatment processes. This group of organic compounds, ranges from simple molecules to macromolecules such as proteins, polysaccharides and lipids, and even larger polymers up to 1.5 million

Da, are found in bioreactors and their effluent due to cell activity, i.e. substrate metabolism and cell degradation (Kunacheva & Stuckey, 2014). The effluent COD has been known to comprise up to 17% of extracellular polymeric substances (EPS), excluding volatile fatty acids (VFAs) and compounds in the influent (Aquino, 2004; Aquino & Stuckey, 2008; Barker & Stuckey, 1999; Laspidou & Rittmann, 2002; Namkung & Rittmann, 1986), hence it is an important consideration for assessing performance of the bioreactor. The amount of SMP can be estimated by the following equation:

SMP (as COD) = soluble effluent COD - [VFA (as COD) + residual substrate (as COD)]

where, VFA (as COD) = 0.35(formate) + 1.07(acetate) + 1.51(propionate) + 1.82(butyrate + isobutyrate) + 2.04(valerate + isovalerate); residual substrate (as COD) = 1.07(glucose) (Aquino & Stuckey, 2008; Barker & Stuckey, 1999)

This estimation can be used in systems where glucose is the sole substrate. In this thesis, meat extract and peptone were added as nitrogen source, and these two substrates contribute to the substrate COD as well, hence the concentration of SMPs is estimated by soluble effluent COD excluding VFAs (as COD).

Over 30 years ago SMPs were broadly categorised into two groups; utilization associated products (UAP) which refers to the compounds produced during metabolism of the feed inside the cell, and subsequently excreted into the bulk phase, and biomass associated products (BAP) which are associated with biomass decay (Namkung & Rittmann, 1986; Noguera et al., 1994), and released due to cell lysis and consist of cell wall fragments, especially EPS which are not bound to the surface of cells (EPS were found to be excreted by cells as its natural response to changes in its external environment to enhance cell wall integrity) (Barker & Stuckey, 1999; Namkung & Rittmann, 1986). Radiolabelled-carbon (^{14}C) was used in attempts to differentiate between UAPs and BAPs in simplified bioreactor models (Barker & Stuckey, 2001; Namkung & Rittmann, 1986), and further studies involving other process conditions and bioreactor models, and consideration of microorganism communities would bring greater insights into the reasons behind the production of SMPs.

The SMPs detected by previous studies include alkanes, alkenes esters, acids, alcohols and carbonyl compounds (most probably metabolic intermediates), nitrogenous compounds (those not detected in the feed, hence are degraded or transformed feed compounds), cell membrane lipid fragments, and cell signaling molecules (Kunacheva et al., 2017a; Tipthara et al., 2017). Another group of rare and lower concentration compounds detected was found to be antibiotics and plant metabolites, based on a literature search and database matching. Earlier research had reported that SMPs are compounds that can be degraded over time, and hence one of the limiting factors is the hydraulic retention times of conventional processes which are usually not long enough for the degradation to proceed to completion (Schiener et al., 1998). These compounds while usually environmentally harmless, might accumulate when released into the environment, or undergo further chemical reactions in downstream processes (aerobic process, disinfection process – chlorination, UV, ozonation) and form disinfection by-products (DBPs) which could be more toxic to the environment (Liu & Li, 2010; Liu et al., 2014; Shah & Mitch, 2012), or other recalcitrant chemical compounds that pose a danger to the environment (endocrine disruptors, for instance). The cell-signalling (Frezza, 2017; Mukherjee & Bassler, 2019) and higher molecular weight compounds detected might also contribute to or become constituents of membrane foulants in a membrane bioreactor.

2.3 Occurrences of SMPs in biological wastewater treatment processes

Besides the classification of SMPs by bacterial phases mentioned in the previous section of this chapter (Namkung & Rittmann, 1986; Noguera et al., 1994), another classification derived by Chudoba (1985) and based on the organic compounds produced from activated sludge systems into three categories: excreted as a result of their interactions with the environment, produced through substrate- and growth-associated, and released due to cell lysis and degradation (Chudoba, 1985). From these three categories of SMPs, the production of microbial products is mainly due to the substrate available, the operating

conditions, and their intrinsic growth and decay. Some of the factors of SMP production are described in the following sub-sections.

2.3.1 Bioreactor operating conditions

One of the first few studies on the effects of organic loading rate (OLR; set at 0.25 and 0.5 g/L per day in this study), sludge retention time (SRT; controlled at 15, 25, and 40 days) and reactor feed concentrations (glucose at 10 L/day and acetate at 5 mL/day) on SMP production was carried in anaerobic chemostats with a working volume of 3 L; effluent SMP concentration was calculated by the equation in section 2.2). The results showed that the percentage of SMPs in effluent soluble COD increased with increasing SRT and OLR, with an average of >85% (Kuo et al., 1996).

The review by Barker and Stuckey (1999) summarized that the optimum range of organic loads in which minimum effluent SMP concentrations can be achieved was 0.3±1.2 g COD per gram mixed-liquor suspended solids per day (g MLSS·day) or 0.2±0.8 g BOD/g MLSS·d (Barker & Stuckey, 1999); at high organic loads, the sludge becomes overloaded and hence is not able to remove all the organics at the controlled HRT; at low organic loads, it becomes underfed and cell decomposition becomes more dominant, releasing the organic cell components into solution (Baskir & Hansford, 1980; Pribyl et al., 1997). An optimum SRT of approximately 25 days for anaerobic systems was also reported, for effluent SMPs to be kept at a minimum. Prolonged sludge age generally results in contribution of organic matter from biomass decay to total SMP concentration. With shorter SRT, there would be higher substrate utilization hence higher UAP composition in the effluent SMP. Therefore an optimum SRT reduces the production of UAP, and more effectively degrade the organic matter (Kuo et al., 1996).

Lower temperatures also resulted in the increase in SMP production in an ABR operating at 25ºC (Nachaiyasit & Stuckey, 1997) and an aerobic MBR at 11-15ºC (Drews et al., 2007). However, additional studies on different temperature ranges

and bioreactor configurations will be required to find out more about the relation between SMP production and operating temperature.

Work was carried out previously by our group on the effects of different HRTs (Kunacheva et al., 2017c) and influent pH (Kunacheva et al., 2017b) on the performance of a 3-L SAMBR. The increase in total concentration of SMPs (with reference to integrated peak area of the chromatograms from GC-MS) corresponded to the increase in effluent COD and VFA during the initial sampling after the HRT decreased stepwise from 12h through 1h. The change in influent pH from 7 to 5 resulted in a shift of MW distribution towards the lower MW range, and shift to the higher MW range when the influent pH was changed from 7 to 11. The effects of pH on the operation of the SAMBR was delayed as compared to the effects of HRT on the same SAMBR, with one of the main reasons being the high buffer capacity of the synthetic feed (containing sodium bicarbonate and potassium dihydrogen phosphate).

2.3.2 Substrate

The formation of SMPs and EPS is not only dependent on operational parameters, but also on feed composition. A study of the difference in SMP production in acetate-fed and glucose-fed chemostats by Kuo et al (1996) (section 2.3.1) reported that the SMP concentration was always higher in the glucose-fed chemostats (Kuo et al., 1996). The authors explained this by the higher free energy (ΔG^o) of glucose (ΔG^o = -17.73 kJ/eeq) compared to acetate (ΔG^o = -3.54 kJ/eeq), calculated from the chemical equations below, and hence the more spontaneous conversion of glucose. In addition, they stated that the nutrient availability factor is important since glucose can be taken up by acetogens, acidogens and methanogens, while acetate uptake occurs only selectively by the acetoclastic methanogens.

$$\frac{1}{24}\ C_6H_{12}O_6 \rightarrow \frac{1}{8}\ CH_4 + \frac{1}{8}\ CO_2 \qquad \Delta G^0 = -17.73 \text{ kJ/eeq}$$

$$\frac{1}{8}\ CH_3COO^- + \frac{1}{8}\ H_2O \rightarrow \frac{1}{8}\ CH_4 + \frac{1}{8}\ HCO_3^- \qquad \Delta G^0 = -3.54 \text{ kJ/eeq}$$

Previously, the carbon:nitrogen:phosphorus ratio of the influent was studied with the aim of investigating the efficiency of biological processes (Tezuka, 1990). Arabi and Nakhla (2008) studied the changes in molecular weight and hydrophobicity of the protein- and carbohydrate-based SMPs and EPSs generated under different influent protein/carbohydrate ratios in submerged aerobic MBRs (Arabi & Nakhla, 2008). Their results showed that there is an increase in both protein and carbohydrate SMPs and EPSs as well as hydrophobicity with high protein/carbohydrate ratio influents, and hence higher fouling rates. Ferrer-Polonio et al (2018) also carried out a similar test evaluating the effect of different food/microorganism ratios on a sequencing batch reactor (SBR). The characterization methods used were the BCA and anthrone methods for 'protein' and carbohydrate analysis, respectively (Ferrer-Polonio et al., 2018).

With the advancement in analytical methods, there has been an increasing number of studies on the effects of various organic carbon and nitrogen types on process and effluent quality (Guo et al., 2011; Hao et al., 2016; Ly et al., 2019; Ly et al., 2018; Maqbool et al., 2019). As far as we are aware, the existing studies reported the effects of macronutrients on the performance of bioreactors and the production of effluent organic matter (Ly & Hur, 2018; Ly et al., 2019), but only achieved broad classification of SMPs using EEM-PARAFAC (characterization by the detection of functional groups) and SEC (characterization by molecular weight), and were not fully accountable for the biochemical reactions that occurred in the duration of the experiments.

Another recent study in our group on varying the carbon and nitrogen sources during anaerobic digestion revealed that the addition of ammonium chloride in place of peptone and meat extract as the nitrogen source, and replacing glucose with sucrose, significantly increased the amount of low MW SMPs, and decreased proteinaceous compounds and carbohydrates in anaerobic batch set-ups (Le & Stuckey, 2017). Currently, there are very limited studies on the effects of the macronutrients on the formation of SMPs in anaerobic wastewater treatment, although it is known that SMPs will change, but the extent of change and their effects on bioreactor performance is not known.

2.4 Impact of SMPs in biological wastewater treatment

The advantages of using membrane bioreactors (MBR) over conventional wastewater treatment methods include improved effluent quality and a smaller footprint, and the added advantages of low sludge production and methane generation in the case of anaerobic MBRs. However, the challenges of MBRs lies in their scaling up, and controlling membrane fouling which affects the flux, and hence the efficiency of MBRs and their operational costs (Stuckey, 2012; Zhou et al., 2016). Extensive work has been carried out to explain the reasons behind the fouling of membranes, such as the deposition of colloids on the membrane surface, but more recently the research focus has shifted towards the identification of SMPs and EPS being the major source of foulants (Arabi & Nakhla, 2008; Drews, 2010; Zhou et al., 2016). Lesjean et al (2005) ran two industrial-size membrane bioreactors of different biological process, pre- and post- denitrification, in parallel and found a clear linear increase in fouling rate with increases in polysaccharide concentrations measured by liquid chromatography coupled organic carbon detection (LC-OCD) (Lesjean et al., 2005).

Considerable research work has been conducted to explain the fouling caused by SMPs, EPS, proteins and carbohydrates in reactor systems (Arabi & Nakhla, 2008; Drews, 2010; Jarusutthirak & Amy, 2006; Malamis & Andreadakis, 2009), hydrophobicity (Lee, 2003), gelling properties (Wang & Waite, 2009), and particles of various molecular weights (Meng et al., 2011) in aerobic systems, but there is limited information on anaerobic systems.

The occurrence of SMPs in bioreactors and their effluents not only affects the system in which they are being generated, for instance contributing to membrane fouling in MBRs, they can also affect the effluent quality of downstream processes, i.e. whether the SMPs can be removed, are they precursors of DBPs, or will they transform into a more recalcitrant compound. Since the effect of SMPs on effluent quality and membrane biofouling have been a concern in the development of wastewater treatment systems, it is important to understand more about the evolutionary purpose for their existence, the metabolism and biotransformation of such compounds, and the possible intermediate compounds

formed (which may or may not be detectable due to the highly unstable nature of many reaction intermediates). To date the use of gas chromatography coupled to mass spectrometry (GC-MS) has been a common method used for chemical characterisation of low MW SMPs (Aquino, 2004; Kunacheva et al., 2017b; Kunacheva et al., 2017c; Trzcinski & Stuckey, 2010; Wu & Zhou, 2010; Zhou et al., 2009), while liquid chromatography coupled to mass spectrometry (LC-MS) or even high accuracy LC-MS has been used for scanning and targeted analyses of higher MW and more polar compounds (Petrovic et al., 2004; Quintana et al., 2010; Wille et al., 2010). These chemical characterisation studies were carried out on a single-stage reactor, and only the end products (effluent SMPs) and their quantities were reported (Trzcinski & Stuckey, 2010). The following sub-sections discusses the significant work carried out on the advancement of SMP characterisation methods over the years, and the transformations and biotransformational changes of organic substances reported.

2.5 Detection and characterization of SMPs

The initial interest in the analysis of SMPs in wastewater treatment systems mainly arose from; their contribution to effluent COD (an important measure of water quality), being potential DBP precursors, and their role on membrane fouling in membrane bioreactors. The accumulation of SMPs in membrane bioreactors (MBRs) leading to membrane fouling is attributed to the retention of SMPs by the membrane itself. However, earlier studies which attempted to characterise the foulant mainly used colorimetric methods (COD, modified Lowry for ‘protein’ quantification, Dubois phenol-sulfuric acid for ‘polysaccharide’ quantification) and molecular weight (MW) distribution which only allowed for broad and poorly chemically distinguishable characterisation (Huang et al., 2011; Rojas et al., 2005; Rosenberger et al., 2006; Shin & Kang, 2003). Recently, the development of advanced analytical methods took characterisation of SMPs to another level where identification, or at least partial identification, became possible.

Other than colorimetric methods, earlier research characterised SMPs primarily by MW distribution. Namkung and Rittmann using ultrafiltration (10 kDa, 1 kDa and 500 Da) with stirred cells (Model 8010, Amicon Corp, Lexington, Mass) found that the MW of more than 70% of the effluent SMPs (phenol as the only carbon source) to be more than 1000 Da (Namkung & Rittmann, 1986), but the identity of the SMPs remained unknown. Parkin and McCarty measured the soluble organic nitrogen content from untreated wastewater in comparison to that treated using activated sludge. Their results from gel filtration chromatography showed that 50-60% of the soluble organic nitrogen and COD were less than 1800 Da. However, recently two critical evaluations of colorimetric methods for protein and carbohydrate quantification by Le at al. (2016) showed how many false positive results were obtained using the Lowry, phenol-sulphuric acid, and other colorimetric methods and kits. The authors used spiked samples with typical interfering solutes such as alkanes, alkenes, acids, aromatics and glucose, which are often present in wastewater or feed for evaluation of the 'protein' measurement methods, and a series of monosaccharides, their derivatives and other forms of glycol-compounds, and inter-assays to prove the reliability of colorimetric methods that had been used for carbohydrate analysis (Le et al., 2016). Results clearly showed the inaccuracy of the quantification method using glucose as the calibration standard due to the differences in the reactivity of the various types of saccharides and saccharide derivatives to the reagents.

Although conventional methods (COD, modified Lowry, Dubois phenol-sulfuric acid), total organic carbon (TOC) analysis, and MW distribution are still being used to crudely analyse the presence of SMPs, techniques such as excitation-emission matrix (EEM) fluorescence spectroscopy (Tian et al., 2011b) are starting to reveal more characteristics of the SMPs. Advances in analytical methodology finally allowed the identification and quantification of some low molecular weight (MW) compounds. One such analytical tool that has been widely used is gas chromatography coupled mass spectrometry (GC-MS), which has commercial chemical compound libraries available for compound identification. This is also the main advantage of using the GC-MS for qualitative analysis of SMPs as this class of compounds is comprised of unknowns, and therefore matching them to reference compounds is essential to identify the

compounds present in the samples. Qualitative and/or quantitative analysis of aqueous samples using GC-MS usually requires a sample extraction step such as the widely used solid-phase extraction (SPE), or liquid-liquid extraction (LLE), and others such as solid-phase microextraction (Bean et al., 2012), headspace injection (Citron et al., 2012), and purge-and-trap (Huybrechts et al., 2000) depending on the characteristic of the group of compounds that are of interest. Gaseous samples can be analysed using thermal desorption coupled to GC-MS (Rodriguez-Navas et al., 2012). The accurate identification of the compounds is highly dependent on the mass spectral information (fragmentation pattern) and the availability of chemical standards. Until recently, the best possible identification we can get is through estimation using mass spectral libraries and the retention indices (retention time of unknown relative to retention time of straight chain alkane standards) (Kunacheva et al., 2017a).

Aquino (2004) used SPE and GC-MS for the detection of SMPs in a mixed culture anaerobic reactor effluent and found that most of the compounds identified were aromatics, while the balance belonged to other families of hydrocarbons, such as alkanes and some nitrogen and sulphur-containing compounds. Di-2-ethylhexyl phthalate (DEHP), a recalcitrant plasticizer, was also quantified and found to be in the high concentration range of approximately 3 mg/L even allowing for the leaching from the plastic reactor and tubing. The author reported that rough quantification of the compounds identified accounted for approximately 8% of the CSTR effluent COD, and approximately 12% of the MBR supernatant COD. However, repeatability of compound detection and identification was low (between experiments), implying the possibility of change in the liquid phase SMPs reactor compositions when the samples are collected at different times (Aquino, 2004).

However, the applicability of GC-MS requires the analyte(s) to be sufficiently volatile and thermally stable, and hence the range of compounds which can be detected is still limited with regards untargeted analysis. Schummer et al. (2009) used derivatisation to improve the GC compatibility of the chemicals of interest; derivatisation agents, N-(t-butyldimethylsilyl)-N-methyltrifluoroacetamide (MTBSTFA) and N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA),

demonstrated increased sensitivity in the detection of polar compounds using GC-MS (Schummer et al., 2009). Alternatively, the researchers have considered liquid chromatography for analysing such compounds which are more polar.

Earlier attempts to characterise a broader MW range of SMPs by Aquino (2004) using matrix assisted laser desorption ionisation coupled time-of-flight mass spectrometry (MALDI-ToF) experienced problems with an unstable matrix, which gave off a distinct spectra below 700 Da; the peaks in the 470-500 Da range and higher in the sample spectra were not found in the matrix spectra (Aquino, 2004). Mesquita et al (2010) later proposed using MALDI-ToF for characterising high MW SMPs as well, using a different matrix which comprised of α-cyano-4-hydroxycinnamic acid (CHCA) and sinapinic acid both dissolved in 50% acetonitrile and 0.05% trifluoracetic acid, and liquid chromatography coupled tandem ion trap-time-of-flight mass spectrometry (LC-IT-ToF) for the detection of non-volatile compounds in the effluents from both aerobic and anaerobic systems. Although the results presented only show mass/charge ratios, and no further profiling information, it demonstrated that the Lowry method, which has all along been the standard method for protein analysis, have been detecting 'proteins' which could probably be peptide fragments or polypeptide chains of molecular weights higher above 80 kDa These compounds are beyond the 20 kDa – 80 kDa working range of MALDI-ToF (Mesquita et al., 2010). Currently, there is no method for MALDI-ToF sample screening yet, but this technique has been used for targeted analysis such as for; the aerobic biodegradability of synthetic polymers poly(vinylpyrrolidone) (Trimpin et al., 2001) and polycaprolactonediol (Rivas et al., 2016), lipopolysaccharide biosurfactant production by *Bacillus subtilis* isolated from petroleum sludge (Vater et al., 2002), detection of the bacteria *Enterococcus* spp. isolates from environmental samples (to trace the source of bacteria) by comparison with the peptide mass fragmentation pattern of the database (Giebel et al., 2008), an alternative method for trace analysis of perfluorinated compounds in environmental water samples (Cao et al., 2011), structural elucidation of polysaccharides in membrane bioreactors to determine the cause of membrane fouling (Kimura et al., 2012).

Advances in analytical methods have allowed for the partial identification of SMPs, however, the pool of compounds formed is very large, ranging from macromolecules such as polypeptides and polysaccharides to the simple hydrocarbons of around 100 Da. Characterization of SMPs by MW found that the distribution was bimodal, with the majority of compounds having MWs of less than 1000 Da or greater than 10 kDa (Kuo & Parkin, 1996). Hence, these characteristics require a combination of several analytical methods to identify many of the SMPs present in sample matrices (up to 2 kDa). In recent years, the development of high-resolution mass spectrometry (HRMS) with increased sensitivity and mass accuracy, has enabled more in-depth analysis of unknown samples and their biological and abiotic transformation products. The software developed for acquisition and data analysis enabled the derivation of possible molecular formulae from the accurate mass measurements. The studies reviewed by Pico and Barcelo (2015) focused on anthropogenic micropollutants and the detection of their transformation products. Such studies are becoming important with the ever-increasing emergence of contaminants, typically pharmaceuticals, personal care products (generically known as PPCPs), and halogenated compounds from new materials developed for industries which have been found in water bodies (Pico & Barcelo, 2015). Although this does not deal directly with microbial products, they serve as a good reference for future research on the formation and possible routes for the biotransformation of natural products in mixed culture systems. More recently, Tipthara et al (2017) demonstrated the use of ultrahigh pressure liquid chromatography coupled to HRMS in an attempt to identify the more polar components of SMPs with molecular weights up to 2000 Da. Details of the findings using this method of analysis are discussed in the next section (Tipthara et al., 2017).

2.6 Transformation of SMPs

The conclusions drawn by research groups which have carried out qualitative analyses on these SMPs, are that chemical compounds which have increased in concentration after treatment are recalcitrant, and those not detected in the final effluent are biodegradable. However, viewed from a different perspective, the

compounds with increasing concentrations over time could be the degradation or metabolic products of another solute (Babu & Wu, 2010; Chen, 2004; Gavala et al., 2003a; Gulde et al., 2016). Wu and Zhou pointed out the possibility that acidogens were primarily responsible for SMP production, whereas methanogens only removed SMPs, after analysing samples collected at different depths from a full scale upflow anaerobic sludge blanket (UASB) treating anaerobic wastewater (Wu & Zhou, 2010). However, Kunacheva et al (2020) recently reported that both fermentative bacteria and methanogens were capable of producing SMPs, and those SMPs with a MW in the range of 30 Da to 580 Da had up to 71% similarity (Kunacheva et al 2020). One explanation for the different findings in the two studies could be the synergistic effects of the microbial community in the bioreactor, whereby individually they produce similar SMPs but the production kinetics of each changes when both are functioning in a mixed system.

SMPs have been widely accepted as the pool of organic compounds released by microbial cells into their extracelluar environment due to cell metabolism and lysis, and many of these compounds have been known to eventually biodegrade (either aerobically or anaerobically) (Laspidou & Rittmann, 2002; Schiener et al., 1998) but due to process and/or feed conditions, and influence from the external environment, the biodegradability and their production changes as well based on the considerable past literature. In the following part of this review, the focus is on the chemical analysis of microbial products and their possible or identified transformation products in various wastewater treatment systems, and fundamental studies using batch cultures and pure strains.

2.6.1 Targeted analysis

Although targeted analysis might end up with the analyst detecting only what they want to detect, i.e. reducing the chance of finding novel compounds, it is a more direct approach for developing a highly sensitive method of detection.

2.6.1.1 Phthalate esters

Trzcinski and Stuckey (2010) used GC-MS results to compare the performance of two submerged anaerobic membrane bioreactors (SAMBRs) treating the organic fraction of municipal solid waste (OFMSW) leachate containing

phthalates, with the SAMBRs operated at SRT of 30 and 300 days and temperatures of 20 ºC and 35 ºC. Their results showed the presence of di-2-ethylhexyl phthalate (DEHP) as well; to confirm that the phthalates detected were not leached from the reactor material/tubing, a set of control experiment was set up in which plastic from the reactor, and tubing, were soaked in ultrapure water for a few weeks under the same operating conditions as the SAMBRs. GC-MS analysis did not identify DEHP in the control samples, and the concentration of DEHP was observed to have doubled as the feed passed through the anaerobic reactor. This suggested that the phthalates detected could be a biosynthetic product or metabolite of unknown compounds (Trzcinski & Stuckey, 2009b, 2010). Phthalate esters have been known to be synthesised in biological systems, but their biological origin, i.e. biosynthesis, remains unknown (Chen, 2004). Some studies had proven that DEHP and di-butyl phthalate are biosynthesised by the red alga *Bangia atropurpurea,* and some freshwater algae and cyanobacteria, and these phthalate esters are secreted into the extracellular media under stressed conditions (Babu & Wu, 2010; Chen, 2004). Their toxicity to the methanogenic process was measured by biogas production (Owen et al., 1979) as methane production is an indication of methanogenic activity, which is an important stage in anaerobic processes. Anaerobic toxicity of DEHP had been analysed in several studies, and was proven to inhibit methanogenesis and is toxic at an average concentration of above 100 mg/L; and the purpose for their synthesis was for enhancing the integrity of cell membranes, and also a protective mechanism for some variations of bacterial species (Babu & Wu, 2010; Benotti et al., 2009; Chen, 2004; Gavala et al., 2003b; Oconnor et al., 1989; Trzcinski et al., 2012).

With regards to the occurrence of plasticizers in the environment and their persistent nature, the focus has been on their biodegradability and removal in treatment systems. Phthalate esters are known to be plasticizers often detected in the environment such as in landfill leachates, and have been listed as environmental pollutants due to their endocrine-disturbing properties when ingested by humans, and their long half-lives of up to 2000 years for DEHP (Gao & Wen, 2016). Since there are a few studies which have found the de novo synthesis of phthalates, more emphasis on biological water treatment conditions such as temperature, pressure, pH, and the interaction between different

microbial communities in mixed microbial systems on the production of phthalate esters might be useful in future research on controlling the presence of phthalates in the environment and after treatment processes.

De-esterification was understood to be the main degradation process of phthalates under both anaerobic and aerobic conditions (Shelton et al., 1984). Liang et al (2007) demonstrated the mineralisation of dimethyl phthalate in a UASB operating at mesophilic conditions through conversion to monoester phthalate then phthalic acid; the two intermediates were identified using HPLC (Liang et al., 2007). Kleerebezem et al (1999) had earlier conducted several studies which focused on the anaerobic biodegradation pathway of phthalic acid through benzoate, concluding that this is the rate-determination step for the complete conversion of phthalates to methane and carbon dioxide under anaerobic conditions (Kleerebezem et al., 1999a, b, c; Kleerebezem et al., 1999d). Further studies conducted by the group suggested that the biodegradation of different phthalate isomers (*ortho*-, *para*-, and *meta*-phthalic acid) were by specific microorganisms (Kleerebezem et al., 1999a). A suspected intermediate, carboxycyclohexane, was detected by GC during the investigation of biodegradation of phthalates in the fermentation process (methanogens had been inhibited at the start of the experiment) (Kleerebezem et al., 1999b). From the measurement of the amount of hydrogen present, and the conversion energetics of benzoate to acetate and benzoate to carboxycyclohexane, the authors suggested that both processes can proceed simultaneously to a certain limit. The possibility of carboxycyclohexane being an intermediate of other processes remained as the authors themselves stated that their experiments were not able to prove that yet.

Recent studies on the metabolism of the facultative anaerobe, *E. coli,* revealed the prokaryotic biosynthesis of ubiquinone via the chorismate pyruvate lyase (CPL) reaction whereby chorismate is converted to 4-hydroxybenzoate (4-HB), followed by hydroxylation-oxidation (anaerobic-aerobic), reduction, and alkylation reactions in that order. The enzymes involved in the intermediate anaerobic processes were found to be hydroxylases. The authors have thus proven the feasibility of ubiquinone biosynthesis through both aerobic and anaerobic

pathways despite ubiquinone being more often related to aerobic growth, and menaquinone to anaerobic growth (Aussel et al., 2014; Meganathan, 2001).

2.6.1.2 Nitrogenous compounds

Gulde et al (2016) monitored and elucidated the biotransformation pathway of 19 selected micropollutants with amine functional groups in activated sludge systems using high resolution LC-quadrupole-orbitrap mass spectrometer (Q Exactive, Thermo Scientific) and summarised the observed reactions in Figure 2. The postulated biotransformation products were detected through targeted analysis, while the non-targeted scanning mode was used to discover additional compounds that might form. Compounds were deemed identified by; a significant signal-to-noise ratio, reasonable peak shape, were non-detectable or negligible in control experiments, showed concentration increasing/decreasing trends, and isotopic pattern recognition using a library (Compound Discoverer 1.0 and Sieve 2.2 by Thermo Scientific). Further structural elucidation was carried out using the software through isotopic patterns of parent ion and daughter ions in tandem mass spectra. Confirmation of structural elucidation results was by mass spectra of commercially available or synthesized reference compounds. Subsequent quantification of the disappearance of parent compounds and appearance of confirmed/suspected biotransformation products was then carried out to arrive at the compounds' biotransformation pathways. Additional experiments on the possibilities of back-transformation, where the metabolites are converted back to their parent compound, were also carried out for certain types of reactions such as *N*-oxidation and *N*-acylation (Gulde et al., 2016).

2.6.1.3 Potential precursors of disinfection by-products (DBPs)

With advances in the detection and characterisation of SMPs which allows for identification of the organic compounds, some were found to be potential precursors of DBPs as they undergo degradation and/or biotransformation when they react with post-treatment disinfection agents such as chlorine, to form chlorinated compounds (Liu & Li, 2010; Liu et al., 2014). Therefore, it is important to identify and characterize the SMPs involved in these processes,

which can then in turn improve wastewater treatment efficiency and effectiveness, and at the same time reduce environmental damage.

The detection and characterization of biodegradation and biotransformation of potential organic precursors of DBPs in wastewater by chlorination was studied by Liu and Li (2010). Aerobic batch set-ups in a 20^{o}C temperature-controlled incubator consisted of ultrapure water (produced by Milli-Q water purifier) spiked with humic acid, tannic acid, glucose, starch, glycine, and bovine serum albumin (BSA) chosen to represent the organic components, mainly carbohydrates and proteins, found in municipal wastewater in general. Experiments using filtered (0.45 μm) influent (raw sewage) and secondary effluent from a full-scale activated sludge process treating municipal biological sewage were carried out in parallel to the spiked models to monitor organic biodegradation and DBP formation potential by chlorination. Aerobic biodegradation proceeded in a 20^{o}C incubator and samples were collected on Days 1 to 5, 7 and 10. Sodium hypochlorite (NaOCl, 3 to 5 mg/L of free chlorine) was added to 100 mL of filtered (0.45 μm) samples, and these chlorinated samples were incubated for 7 days at pH 7, 25 ± 0.5 ^{o}C in the dark. Excess chlorine was then quenched and the DBPs were extracted using methods from the Environmental Protection Agency (EPA). The extraction of DBPs was carried out using liquid-liquid extraction with methyl-*tert*-butyl ether (MTBE) followed by targeted analysis using a GC with an Agilent DB-35MS column coupled to an electron capture detector (ECD) (according to EPA Method 551.1, USEPA 1995 and modified EPA Method 552.3, USEPA 2003). The authors found significant concentrations of seven DBPs, namely; chloroform (CF), di- and tri-chloroacetic acid (DCAA and TCAA), chloral hydrate (CH, a type of haloacetaldehyde), trichloropropanone (TCP), and nitrogen-containing compounds dichloroacetonitrile (DCAN) and trichloronitromethane (TCNM) (Liu & Li, 2010). As the authors concluded, SMP formation might be the cause of the increase in formation potential of DBPs during chlorination. The results of the dynamic studies of the transformation of SMPs in filtered water samples into DBPs after the addition of sodium hypochloride and incubation for 7 days showed an increase in DBP production, although there was still no initial chemical characterization of SMPs in the filtered water used in the test (Liu et al.,

2014).

The transformation pathway to nitrogenous disinfection by-products has been reviewed by Shah and Mitch as toxicological research has proven these compounds to be more toxic compared to those of the carbonaceous family (Shah & Mitch, 2012). The review summarised the transformation pathways due to disinfection as: oxidation of amines to nitro 3+ functional group; chlorination and chloroamination of primary amines, amino acids, dipeptides, and nucleic acids to form chloramines and chloropicrin; chlorination of nitrites to $ClNO_2$ and N_2O_4 nitrating agents.

2.6.1.4 Cell-signalling molecules

The production of extracellular polymeric substances has been understood to be due to microbial responses to changes in their external environment, such as extreme temperatures or pH. This group of compounds had been classified into tightly-bound and loosely-bound, and are potentially released during cell lysis. Also, under normal conditions microbial interactions result in the release cell-signalling compounds in which the microorganisms 'communicate' between a range of genera.

Bacteria which contributed to quorum-sensing were found to be involved in the production of diketopiperazines (DKPs), which are compounds comprising two amino acid moieties. Experiments have shown that the extracts of *Pseudomonas aeruginosa* grown in *Luria-Bertani* (LB) broth contains both cyclo($_D$-Ala-$_L$-Val) and cyclo($_L$-Pro-$_L$-Tyr), which were either synthesized directly from primary metabolites, or as a result of bacterial peptide metabolic reactions (Gu et al., 2013; Holden et al., 1999). Two recent reviews have also summarised the cell-signalling properties of cell metabolites such as lactate and intermediates of fatty acid oxidation (Frezza, 2017; Haas et al., 2016).

2.6.1.5 Amino acids and analogues

There has been considerable interest in the utilization of amino acids by bacteria as early as the late 1950s, and these earlier discoveries of novel metabolic pathways of amino acids by anaerobic bacteria was summarized by Barker in

1981 with the conclusion that different bacterial species exhibit different methods of biotransformation of the acids . In the field of medical toxicology, much effort had been made by Smith and Rosazza, and Testa et al in elucidating the biotransformation of pharmaceutical drugs using microbial models to mimic mammalian metabolism, which subsequently led to the compilation of the biochemistry of drug metabolism in the body (Smith & Rosazza, 1983; Testa & Kramer, 2006, 2007, 2009).

Deppe et al summarised and found that fructosamines are ubiquitous in nature, from the non-enzymatic reaction between reducing sugars and amino acids or proteins (glycation reaction). Due to the cell-damaging properties of fructosamines, cells developed enzymes which degrade them. Under different environments and substrates present, a variety of enzymes and their respective catabolic pathways have been proposed, such as fructosyl amino acid oxidases found in fungi *Aspergillus* and *Penicillium*, and bacteria *Arthrobacter*, *Pseudomonas* and *Corynebacterium* which proceed by oxidation and generate amino acids, glucosone and hydrogen peroxide. This could have resulted in the existence of fructosamine degradation products, such as in water bodies (Deppe et al., 2011).

2.6.2 Untargeted analysis

One of the earlier methods of SMP characterisation was by molecular weight distribution, which until now serves as useful supporting data, particularly in the study of membrane fouling (Ly et al., 2019; Zhou et al., 2016). Schiener et al (1998) studied the production of SMPs in an anaerobic baffled reactor (ABR), and highlighted the relationship between SMP composition and biodegradability, and the reactor operating parameters, namely temperature, hydraulic retention time (HRT) and organic loading rate (OLR) (Schiener et al., 1998). Their results showed that the composition of SMPs measured in the same bioreactor operating under the same conditions over time can be substantially different. The authors attributed this finding to the change in biomass bed structure over the time of sampling, and in turn this caused changes in the pH and reactor “dead space” within the system. The authors also found a net increase in SMPs in the effluent with decreasing temperature and decreasing HRT (higher OLR). The conversion

of substrate COD to SMPs in the first compartment of the ABR varied from 26% to 48%, where 48% was more than twice that converted previously in a CSTR which was fed with glucose as the substrate. This is due to the design of the ABR which resembles a plug flow reactor, with the resulting elevated substrate concentrations and low pH measured in the first ABR compartment. Characterisation of SMPs in this study was conducted by MW fractionation using membrane filters of various pore sizes and then HPLC, and it was found that the distribution of SMP MWs was bimodal, i.e. high concentrations at the lower end of 1 kDa, and at the higher end of 100 kDa. The HPLC results of the high MW fraction hydrolysate identified it as a heteropolysaccharide consisting of monosaccharides and amino sugars; 9% of the total hydrolysate remained unknown.With this observation, and previous work which focused on the microbial communities in the different compartments of an ABR, it is postulated that the SMP composition might also change with changes in microbial communities in the bioreactor, as well as over time (Chen et al., 2016; Ziganshin et al., 2019).

Wu and Zhou (2010) reported using dichloromethane (DCM) for extraction followed by GC-MS and found long chain alkanes, esters, acids, aromatic compounds and amides at 17.7%, 17.4%, 12.4% and 4.6% of the total compounds identified in an upflow anaerobic sludge bed (UASB) reactor treated raw distillery wastewater, respectively, and 3.1% long chain alkanes, 1.3% acids, 3.2% amides and 1.2% alcohols in the effluent from an anaerobic bioreactor fed with raw purified terephthalic acid (PTA) wastewater. The authors also found 0.3% phthalates in treated PTA wastewater, but these were attributed to non-biodegradable compounds, or intermediates from the feed (Wu & Zhou, 2010). This suggests that certain bacterial species in mixed culture might be able to produce phthalates, as discussed above, and studies have found phthalate-producing marine algal cultures, cyanobacteria and freshwater algae (Babu & Wu, 2010; Chen, 2004).

The LC-Q-ToF metabolite and lipid profiling method by Tipthara et al (2017) mentioned earlier in this review identified compounds based on mass error (compared to the mass of the suggested compound), similarity of isotopic and

fragmentation patterns calculated by the algorithm of an analytical program, Progenesis QI, and extensive library searches of databases such as the Human Metabolome Database (HMDB), a structural database for *Escherichia coli*, Chemical Entities of Biological Interest (ChEBI) database, LIPID MAPS, and Kyoto Encyclopedia of Genes and Genomes (KEGG). The authors classified the compounds detected in samples collected at 4h and 48h as 'intermediates' and 'end products'. It is known that the general degradation/metabolic pathway of bioreactor influents follow the scheme shown in Figure 2.1, and that intermediates are putatively produced during the fermentation process, which is consistent with the conclusion from a study on SMP production by Wu and Zhou (Wu & Zhou, 2010). Lipids and their derivatives are collectively identified as cell membrane lysis products, while other metabolites and amino acid residues are generally from bacterial metabolic activities, and released into extracellular media over time (Tipthara et al., 2017).

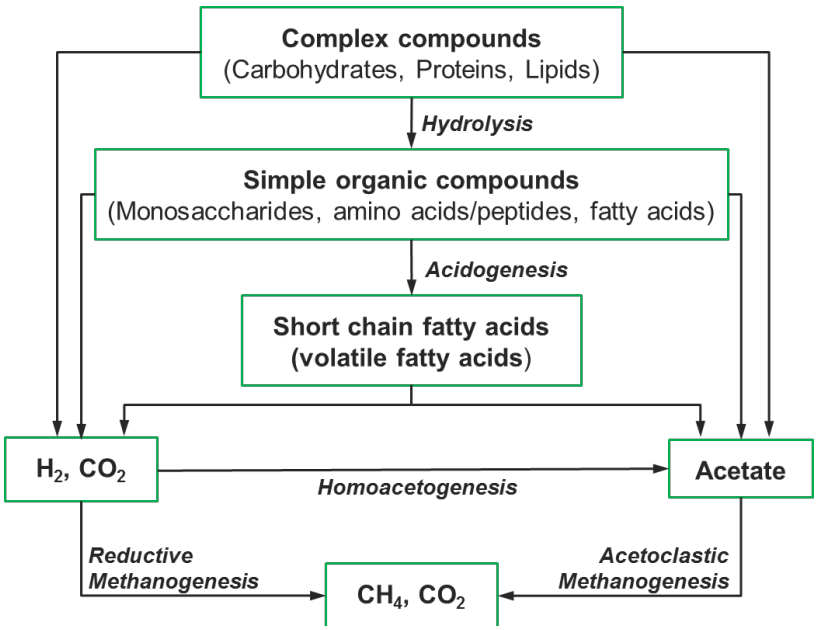


Figure 2.1 Schematic of fermentation and methanogenesis process in anaerobic systems (modified from (McCarty & Smith, 1986))

Biotransformation products of amine-containing micropollutants have shown that certain bacterial metabolic pathways in activated sludge systems are comparable to that of mammalian systems, while there are still other metabolic routes that are not reported yet, and also many other factors to consider like the bacterial community in the mixed culture system used for the experiments (Gulde et al., 2016). This information can be useful in monitoring the efficiency of the

bacteria, and explaining the occurrences of certain compounds at specific time points, however, results might not be repeatable due to the changing nature of microbial communities in mixed culture systems, as in an ABR with slight variations in operational conditions in different compartments (Schiener et al., 1998). As discussed in the earlier part of this section, the variation in SMPs detected along the depth of UASB reactors suggested that the microorganisms that carry out fermentation and the methanogens might play different roles in terms of SMPs; the former appearing to contribute more to its production, while the latter more to its consumption (Wu & Zhou, 2010; Zhou et al., 2009).

(Jacquin et al., 2018) studied the changes in the dissolved organic content in an activated sludge membrane bioreactor system with a high nitrogen concentration in the influent (urine) using three-dimensional excitation-emission spectroscopy, and liquid chromatography coupled to organic carbon and nitrogen detection (LC-OCD) and UV absorption spectroscopy at 254 nm. The concentrations of humic substances, acidic and neutral low molecular weight organic compounds were found to have significantly reduced (62% to 84% in general) inside of the MBR as compared to the influent; it was explained that these compounds largely underwent biotransformation. The production of biopolymers was proven by the LC-OCD results, and these were likely to have accumulated in the MBR supernatant over time despite the decrease observed between day 40 and day 66 of the sample collection period. This was explained by the change in the kinetics of consumption and accumulation within the biological system since substrate limitations during that period could have led to biopolymer consumption due to food shortages; hence these biopolymers can be considered as UAPs which was consistent with that reported by Jiang et al and Tian et al (Jiang et al., 2008; Tian et al., 2011a; Tian et al., 2011b). On the other hand, the humic substances were found to have increased in this period, and therefore were related to BAPs as observed by (Maqbool et al., 2017). The 3-dimensional electron emission microscopy (3D-EEM) intensity maps also showed the disappearance and appearance of certain functional groups (3D-EEM measures the emissions from functional groups attached to chemical compounds) when comparing the MBR influent and supernatant, which meant that there were compounds consumed and formed during the process. However, Ruscalleda et al. reported a different

observation where the humic substances and protein-like compounds were associated with UAPs and BAPs, respectively, in an Anammox system (Ruscalleda et al., 2014). This shows that the SMPs produced in different operating systems proceeded via different mechanisms, and further research into the microbial communities might reveal more about the mechanism of SMP formation and transformation in relation to the feed types (Le & Stuckey, 2017).

Experiments conducted by Le and Stuckey were carried out in batch reactors for 35 weeks. This initial work provided insights into the less explored influence of macronutrients (glucose, sucrose, fructose, ammonium and urea) on the production of SMPs at MWCO 2 kDa, 3.5 kDa, 7 kDa and 10 kDa. The researchers found that biodegradation tends to first mineralize oxidized hydrocarbons, leaving reduced aliphatic compounds at a higher concentration in general, and thus plausibly 'persisting' in the system. This in turn revealed a new aspect of the dynamics of these organic compounds and whether their 'persistence' is due to their intrinsic molecular structures, or because the environment in which they exist limits their rate of decay, therefore appearing to be "recalcitrant". As such, it might be considered that the oxidised hydrocarbons (such as alcohols, aldehydes, ketones, acids and esters) can be more easily adsorbed onto or by microorganisms, with hydrophilicity being the difference between them and the reduced aliphatic compounds (such as alkanes and alkenes).

2.7 Summary of literature review

- From the research work reviewed above, it is clear that effluent SMPs are inevitable as they are produced by microorganisms during metabolism and lysis, presumably for an evolutionary purpose, although at present most of these are unknown.

- Furthermore, some of the SMPs produced can be completely mineralised, as in the case of the phthalates, but this depends strongly on the rate of reaction, environmental conditions, and the microorganisms present.

- There has been growing interest in the transformation mechanisms of

organic materials that may be formed during the treatment of wastewater from varying sources, but the experiments designed for the studies focused on specific contaminants, typically anthropogenic, such as antibiotics, personal care products, illicit drugs, pesticides, perfluorinated compounds and other recalcitrant industrial products. This is due to the ever-increasing production of such compounds which eventually end up in wastewater treatment systems and natural water bodies.

- The release of organic matter by cells into their surrounding environment due to cell stress and presence of pathogens has been known, and from there it developed into isolation of pure strains to study in greater detail the formation pathways of natural products in response to changes in their surroundings. Another driving force for pure culture studies has been for the purpose of extracting useful natural products such as antibiotics.

- Nevertheless, studies in the biotransformation of microbial products in mixed cultures are rare due to the wide spectrum of compounds involved, and requires untargeted analysis with limited background knowledge readily available despite knowing that these organic compounds have the potential to form more recalcitrant molecules. Hence there is a need to further explore the methods for the detection and identification of SMPs and their biotransformational products, and the effects they might have in wastewater treatment systems.

- In view of this change in SMP composition due to changes in influent, the mechanism of membrane fouling in anaerobic membrane bioreactors can be further understood by chemical analysis of the composition of the membrane fouling layer under different feed conditions, and hence provide fundamental knowledge for future work involving the optimization of MBR processes.

2.8 Objectives and scope of study

Based on the literature review above, the aim of this research was to fill in the research gaps on the composition and occurrences of SMPs in anaerobic systems,

the changes in SMPs with changes in macronutrients in the feed, and their effects on membrane fouling. Hence, the main objectives of this thesis were as follows:

1. To investigate the formation, biotransformation/degradation of compounds detected in a bioreactor during anaerobic wastewater treatment process;

2. To determine the changes in the production of SMPs with different feed compositions;

3. To assess the effects of SMPs on membrane fouling;

4. To analyse the changes in SMPs in a full-scale wastewater treatment plant treating industrial wastewater, and compare the SMPs produced with that produced in a lab-scale bioreactor treating synthetic wastewater.

Due to the broad spectrum of SMPs, their production and their effects on the various stages in the entire wastewater treatment process, the scope of work for this study is defined (as highlighted) in Figure 2.2 to achieve the aim of this work.

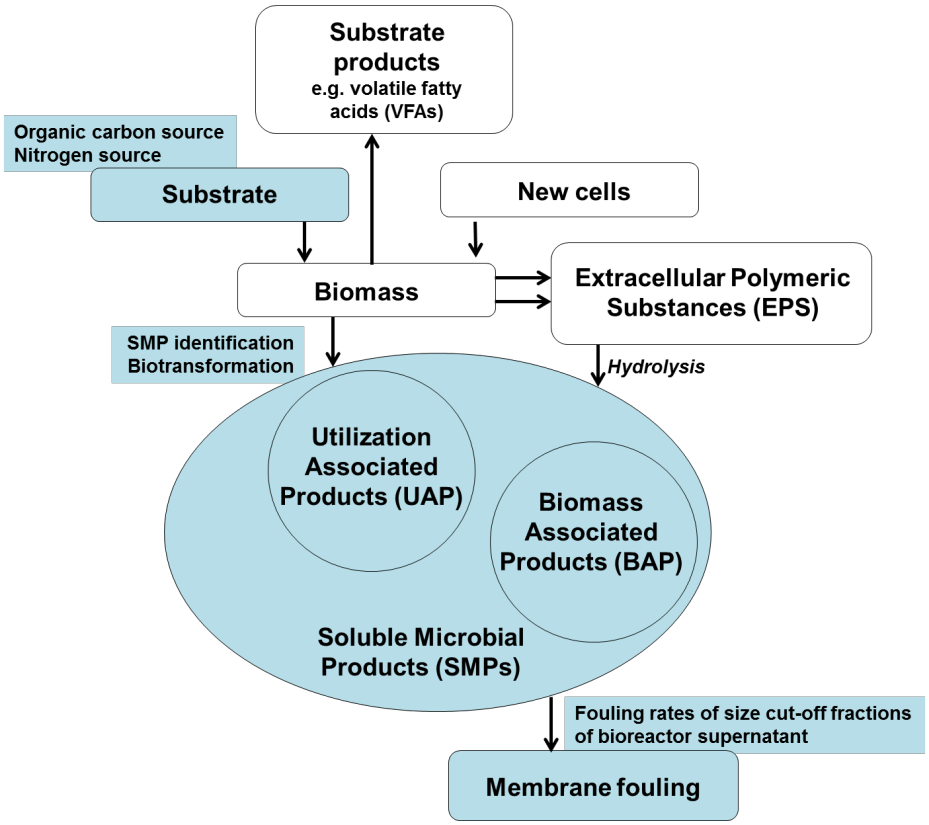


Figure 2.2 Diagram of the production of SMPs and EPS in a heterotrophic biological wastewater treatment system. The highlighted areas are the scope of this thesis.

In addition to the lab-scale studies, samples were collected from the industrial wastewater treatment process plant in Jurong Water Reclamation plant for SMP analysis. The process from which samples were collected consisted of a UASB followed by an aerobic MBR. The changes in the composition of SMPs were compared to that detected from the lab-scale experiments using synthetic feed.

Chapter 3

Materials and Methods

3.1. Introduction

This chapter presents the preparation of seed sludge and feed composition of the bioreactors used in the experiments, and the common analysis methods for bioreactor monitoring and analysis of SMPs which were used throughout the study. The methodologies specific to the experiment were described in their respective chapters.

3.2. Cultivation of sludge and synthetic feed for anaerobic bioreactors

Seed sludge for the anaerobic reactors was obtained from a digester in a municipal wastewater treatment plant (Ulu Pandan Water Reclamation Plant, Singapore). The sludge was sieved to remove particulate impurities, other than sludge, and cultivated in a 5-L batch-fed completely stirred tank reactor. The seed sludge was fed once a week in a fill-and-draw mode. The synthetic feed consisting of glucose, meat extract and peptone, supplemented with essential metal nutrients (Table 3.1). A concentrated stock media of 40 gCOD/L was prepared and diluted to the desired concentration before use.

The description and operating parameters of the bioreactors used for the experiments are described in detail in their respective chapters (Chapter 4 – Anaerobic Baffled Reactor (ABR), Chapter 5 – Submerged Anaerobic Membrane Bioreactor (SAMBR))

Table 3.1 Synthetic feed components (Grobicki & Stuckey, 1991; Zhou et al., 2016)

	Components	40 gCOD/L of concentration stock media
Organics	Peptone	8.2 g
	Meat extract	2.7 g
	Glucose	27.3 g
Metal nutrients	$CoCl_2.6H_2O$	24.4 mg
	$FeCl_2.4H_2O$	160.8 mg
	$MnCl_2.4H_2O$	7.68 mg
	$Na_2MoO_4.2H_2O$	3.84 mg
	$NiCl_2.6H_2O$	4.64 mg
Buffer	K_2HPO_4	819.2 mg
	$NaHCO_3$	66.6 g

3.3. Analysis of general parameters

3.3.1 Volatile suspended solids (VSS)

Biomass concentration was estimated by measuring its VSS; a 5 mL sample (duplicate) was added to a pre-weighed foil tray and heated for 2 hours in an oven pre-set at 105ºC (Memmert, Model UM500) to allow for the evaporation of water. The weight of the dried sample was recorded for the total suspended solids (TSS). The sample tray was then placed in a furnace (Nabertherm, Model P330) to heat at 550ºC for 1 h for the combustion and evaporation of the organic fraction. The tray was then weighed again and VSS was calculated by (APHA, 1992):

TSS (mg/L) = weight after 105ºC heating (mg/5mL) * 5000 mL/L (Eqn 1)

VSS (mg/L) = TSS (mg/L) - weight after 550ºC heating (mg/5mL) * 5000 mL/L (Eqn 2)

All samples were left to cool in a desiccator before weighing. The coefficient of variance for 5 identical samples was within ±5%.

3.3.2 pH

Offline measurement of pH was carried out using a pH meter (Mettler-Toledo SevenCompactTM S220); online pH monitoring in bioreactor was by a pH probe

(Mettler Toledo, M300). The probes were calibrated with buffer solutions of pH 10, pH 7, and pH 4. The measurements were accurate to within ± 0.02.

3.3.3 Chemical Oxygen Demand (COD)

The COD was determined based on the 'closed reflux, colorimetric method' as described in section 5220-D of APHA Standard Methods (1992) (APHA, 1992). The reagents were prepared and stored before use. Potassium dichromate(VI) ($K_2Cr_2O_7$) (Merck) was dried at 105ºC before use. The $K_2Cr_2O_7$ digestion solution was prepared by adding 10.216 g of $K_2Cr_2O_7$ for high range COD (100 – 1000 mgCOD/L) measurement (1.022 g for low range (0 – 100 mgCOD/L) COD, 167 mL of concentrated sulphuric acid (H_2SO_4) (Merck) and 33.3 g of mercury (II) sulphate ($HgSO_4$) (Alfa Aesar) to 500 mL of distilled water. The solids were stirred well to dissolve completely, and the mixture was then left to cool to room temperature before diluting to 1000 mL. The sulphuric acid reagent was prepared by adding silver sulphate (Ag_2SO_4) (Alfa Aesar) to concentrated H_2SO_4 (Merck) at 5.5 g silver sulphate/kg sulphuric acid and stirred at room temperature overnight until all the solids dissolved.

The COD protocol consisted of the addition of 1.5 mL of $K_2Cr_2O_7$ digestion solution and 3.5 mL of sulphuric acid reagent to 2.5 mL of sample/diluted sample (filtered with 0.45µm nylon syringe filters for soluble COD) in COD glass tubes. The tubes were tightly sealed and properly mixed before reflux in a COD reflux digester (Model ECO 16, VELP Scientifica) at 150ºC for 2 h. After cooling to room temperature, the samples were analyzed on a UV/Vis scanning spectrophotometer (Shimadzu UV-2600) at a wavelength of 600 nm for high range COD and 420 nm for low range COD.

Potassium hydrogen phthalate (Reagencon Diagnostics Ltd.) was used to prepare standard solutions in the range 10 – 1000 mg/L. The detection limit was 5 mg/L and the standard deviation based on duplicates was within ±5%.

3.3.4 Volatile Fatty Acids (VFAs)

VFAs were measured using a Shimadzu Prominence Ultra-fast Performance Liquid Chromatography (UPLC, SPD-20AD) equipped with an Aminex® HPX-

87H (300 mm × 7.8 mm) column and diode array detector (DAD, SPD-M20A). The UPLC run took 25 minutes at isocratic flow of 0.8 mL/min, column temperature kept at 55 ºC, with 0.005 M H_2SO_4 as the mobile phase (Guerrant et al., 1982). A total of seven VFAs including formic, acetic, propionic, iso-butyric, butyric, iso-valeric and valeric acids (VFA Standards Mix, 10 mM each, AccuStandard) were quantified at 210 nm (retention time ± 0.05 min). The lower limit of detection was 0.5 mM (millimolar, concentration (in mM) = concentration (in mg/L)/molecular weight (mg/mmol)), the coefficient of variance of five identical samples was within ±2%.

3.3.5 Biogas volume and composition

Biogas was collected using gas-sampling bags, and its composition (methane, oxygen, nitrogen, and carbon dioxide) was determined using gas chromatography with a thermal conductivity detector (GC-TCD) (Shimadzu GC-2014) equipped with a select permanent gases/CO_2 column (Agilent J&W Column, CP7429, 60 m × 0.53 mm × 30 µm) for gas separation (retention time ± 0.01 min). The carrier gas was helium at a flow rate of 156 mL/min, and the column temperature, injector temperature, and detector temperature were set at 35ºC, 40ºC, and 100ºC, respectively. The coefficient of variance (CV) for biogas composition of five identical samples was within ± 2%. Gas volume was measured from gas-sampling bags using a gas pump with a gas flow meter (gas volume ± 0.1 L).

3.4. Characterisation of SMPs

Various methods have been developed for the characterization of SMPs, as discussed in the literature review (Chapter 2), and the advantages of mass spectrometry in comparison to other characterisation methods for the identification, or at least classification, of chemical compounds. In this study, two methods developed previously by our research group were used to cover the widest range possible. However, there is a limitation to the method of untargeted analysis: chemical compounds derived from the analysis are considered only “partially” identified, especially for LC-Q-ToF, since it is not possible to obtain

all the chemical standards required for confirmation of the exact chemical compound detected.

A general pre-treatment step before sample extraction was centrifugation followed by filtration through 0.45 µm glass fiber filter to remove sludge and other larger particles which may clog the extraction cartridge and the analytical instrument. The amount of sample used for extraction followed by the chromatographic coupled mass spectrometry analysis depended on the COD of the sample. This is to prevent under/over-loading of the extraction cartridges and the instruments. To avoid contamination, all glassware used in this study was washed with tap water, cleaned with ultrapure water and rinsed with acetone. During the procedure, all apparatus was made of glass to avoid contamination.

3.4.1. Gas chromatography coupled mass spectrometry (GC-MS)

This method developed for the analysis of SMPs covered the retention and extraction of non-polar compounds (hexane) to mid-polar to polar compounds (methanol), and the GC column selected (RTX-5MS, Restek) was for wide range polarity compounds analysis.

Pre-filtered samples were loaded into two conditioned solid phase extraction (SPE) cartridges (Waters Oasis® HLB, Waters, Milford, USA) in series at a flow rate of 10 mL/min using a peristaltic pump (Watson-Marlow 120U). The tubing of the pump was rinsed with methanol (5 min) followed by ultrapure water (10 min) prior to sample loading. The cartridges were then eluted with 2 mL of methanol, acetone, dichloromethane and hexane in sequence. The GC-MS injection volume was optimised at 3µL for dichloromethane and hexane, 2µL for methanol, and 1µL for acetone, to prevent split peaks.

The SPE eluate was collected for liquid-liquid extraction (LLE) using a mixed chloroform/hexane/ dichloromethane solvent in equal parts to extract any compounds from the SPE breakthrough, if any. LLE was carried out at room temperature; the eluate from SPE (volume used depends on COD of the individual samples) was poured into a separating funnel followed by the extraction solvent mixture. The funnel was sealed and agitated vigorously for one minute with periodic venting to release the pressure. The funnel was left to stand

until there was an obvious separation of organic and aqueous layers. The organic layer was collected into a conical flask, and this extraction was repeated another two times. Moisture content was removed from the combined organic extracts using anhydrous sodium sulfate (gently swirl, then stand for 2-5 minutes). After filtration to remove the sodium sulfate, the solvent was evaporated using a rotary evaporator; possible losses of highly volatile compounds could be expected due to evaporation. The dried contents were reconstituted in 1-mL dichloromethane (measured using a glass microsyringe) and transferred into analysis vials for GC-MS. A 2 µL aliquot was injected into the GC-MS system directly.

The instrument parameters were set as follow: splitless injection at 280 ^{o}C, and the GC program used was according to a published SMPs analysis method, 50 ^{o}C hold for 7 minutes, increase to 325^{o}C at a rate of 7 ^{o}C/min, hold at 325 ^{o}C for 14 minutes, total run time of 60.2 minutes. Mass fragmentation was by electron ionization at 70 eV, MS interface was set at 230 ^{o}C, 12 minutes solvent cut-time, mass-to-charge (m/z) scan range from 30 to 580, tuning parameters were optimized as per autotune results performed monthly (Kunacheva et al., 2017a).

GC-MS interpretation was carried out using Shimadzu GC-MS Solution software equipped with the NIST 11 library. C_{10}-C_{40} *n*-alkane standards (all even, 50 mg/L each in hexane, Restek) were used as peak position markers by their retention indices to support the most likely identity of the analyte peaks (Figure 3.1, Table 3.2). All the suggested compounds had a more than 85% similarity index compared to the standard mass spectra from the NIST 11 library. For some of the peaks, only partial identification was possible due to the possibilities of isomers, such as positional isomers of alkanes which gave very similar mass spectra, but classification into their chemical groups was possible due to their distinctive fragmentation pattern. The iconic fragmentation patterns and fragments are shown in Figure 3.2.

The integrated peak area was used for comparison of the concentration of the compounds at specific retention times and were estimated using the *n*-alkane standard at concentrations 0 mg/L, 0.5 mg/L, and 1 mg/L in hexane. A close approximation of the concentrations instead of exact concentrations were calculated using the alkane standards calibration curve, since the GC-MS was

operated in scan mode and obtaining all the standard compounds to obtain individual calibration curves was not practical in this case.

3.4.2. Liquid chromatography coupled tandem mass spectrometry (LC-MS-MS)

The LC-MS-MS method used in this study was an ultrahigh performance liquid chromatography coupled to quadrupole time-of-flight (LC-Q-ToF). The higher MW compounds, and those which are more polar, are not sufficiently volatile for detection using GC-MS, and hence the LC-Q-ToF method was adopted for this purpose. This set of extractions and the detection procedure from Tipthara et al (2017), with slight modifications, provided information on the more polar metabolites (inclusive of protein and polysaccharide fragments), and the lipid fragments which may be present. The extraction method gave two distinct layers – an organic layer which had lipids, and an aqueous layer which had the polar metabolites (Tipthara et al., 2017).

ACQUITY UPLC with a 2777C autosampler (Waters, USA) coupled to a Xevo G2-XS QToF mass spectrometer (Waters, Manchester, U.K.) was used. All sample injections were in triplicate, at low energy collisions of 4 V and 6 V for extracts of polar metabolites and lipids, respectively. Secondary collisions with a high collision energy ramp was not used in this method since the fragmentation complicates the library search because in most cases there is more than one precursor ion at one retention time. Secondary fragmentation assumes all masses present to be from the same analyte, resulting in possible error in the library search. The mass range for full scan acquisition was set at m/z 50 to 1200 for polar metabolites and m/z 50 to 2000 for lipids. High mass accuracy was achieved by lock mass correction using leucine enkephalin (m/z 556.2771 in ESI positive mode and m/z 554.2615 in ESI negative mode). The LC-Q-ToF settings are described in Table 3.3.

Although chemical standards were not available, four metabolites libraries ChEBI, HMDB, *E. coli* metabolites and LipidMaps were used for identification of the compounds. Identification was based on the overall score which comprises a mathematical derivation from the isotope similarity and mass error. Due to the

limited literature available for microbial product identification in mixed culture systems, the libraries used for compound identification were mainly consolidated from experiments in human metabolomic studies. Hence, a substantial level of data interpretation by the author's experience and previous studies by other research groups were used in the discussions below.

Table 3.2 Alkane standards, from method validation (Kunacheva et al., 2017a)

Compound Name	Chemical Formula	Molecular Weight	Retention Time (min)	R^2	IDL (mg/L)	IQL (mg/L)	Retention Index
Decane	$C_{10}H_{22}$	142	12.15	0.999	0.026	0.087	1015
Dodecane	$C_{12}H_{26}$	170	17.16	0.999	0.017	0.056	1214
Tetradecane	$C_{14}H_{30}$	198	21.96	0.999	0.019	0.064	1413
Hexadecane	$C_{16}H_{34}$	226	25.7	0.997	0.02	0.066	1612
Octadecane	$C_{18}H_{38}$	254	29.03	0.997	0.015	0.05	1810
Eicosane	$C_{20}H_{42}$	282	32.04	0.996	0.02	0.068	2009
Docosane	$C_{22}H_{46}$	310	34.78	0.997	0.022	0.073	2208
Tetracosane	$C_{24}H_{50}$	338	37.3	0.991	0.017	0.055	2407
Hexacosane	$C_{26}H_{54}$	366	39.62	0.995	0.013	0.042	2606
Octacosane	$C_{28}H_{58}$	394	41.77	0.993	0.014	0.046	2804
Triacontane	$C_{30}H_{62}$	422	43.78	0.994	0.016	0.054	3003
Dotriacontane	$C_{32}H_{66}$	450	45.66	0.99	0.015	0.051	3202
Tetratriacontane	$C_{34}H_{70}$	478	47.51	0.991	0.01	0.033	3401
Hexatriacontane	$C_{36}H_{74}$	506	49.72	0.99	0.014	0.046	3600
Octatriacontane	$C_{38}H_{78}$	534	52.59	0.981	0.011	0.038	3800
Tetracontane	$C_{40}H_{82}$	562	56.45	0.984	0.054	0.182	3997

Note: IDL= Instrument Detection Limit; IQL= Instrument Quantification Limit; R^2 = correlation coefficient for a five-point calibration comprising of standards at 0, 0.1, 0.2, 0.5, and 1 mg/L.

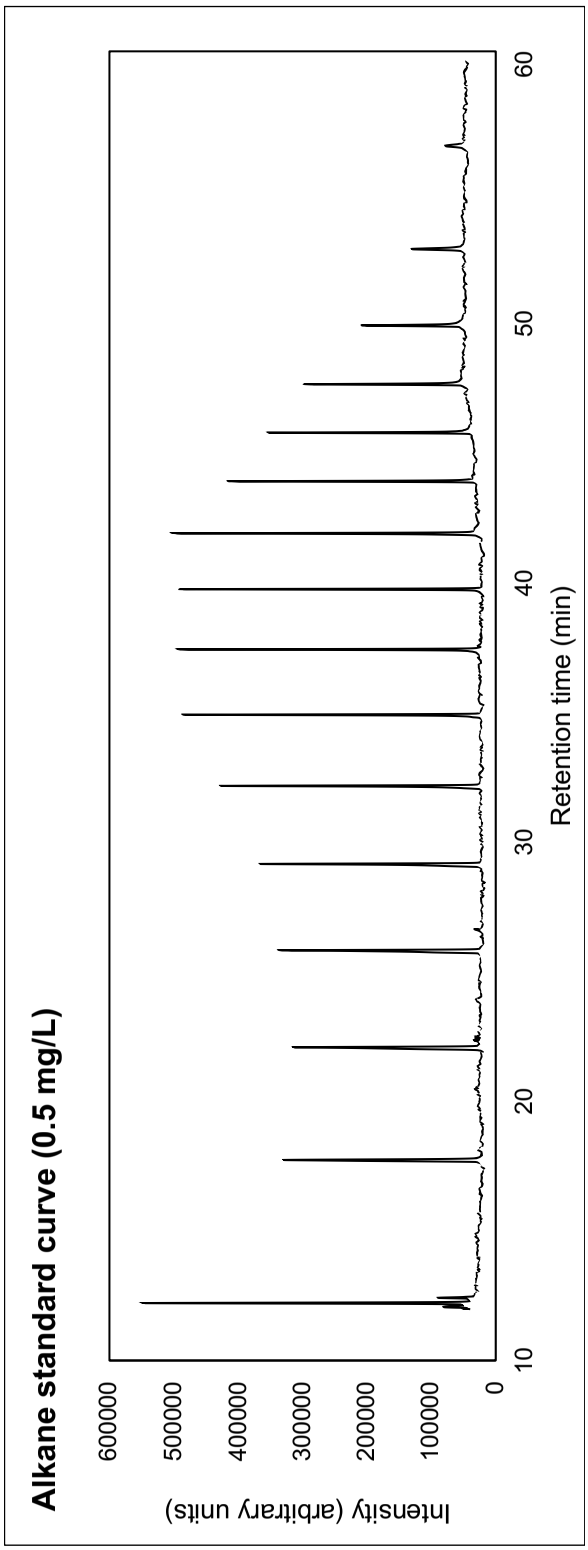
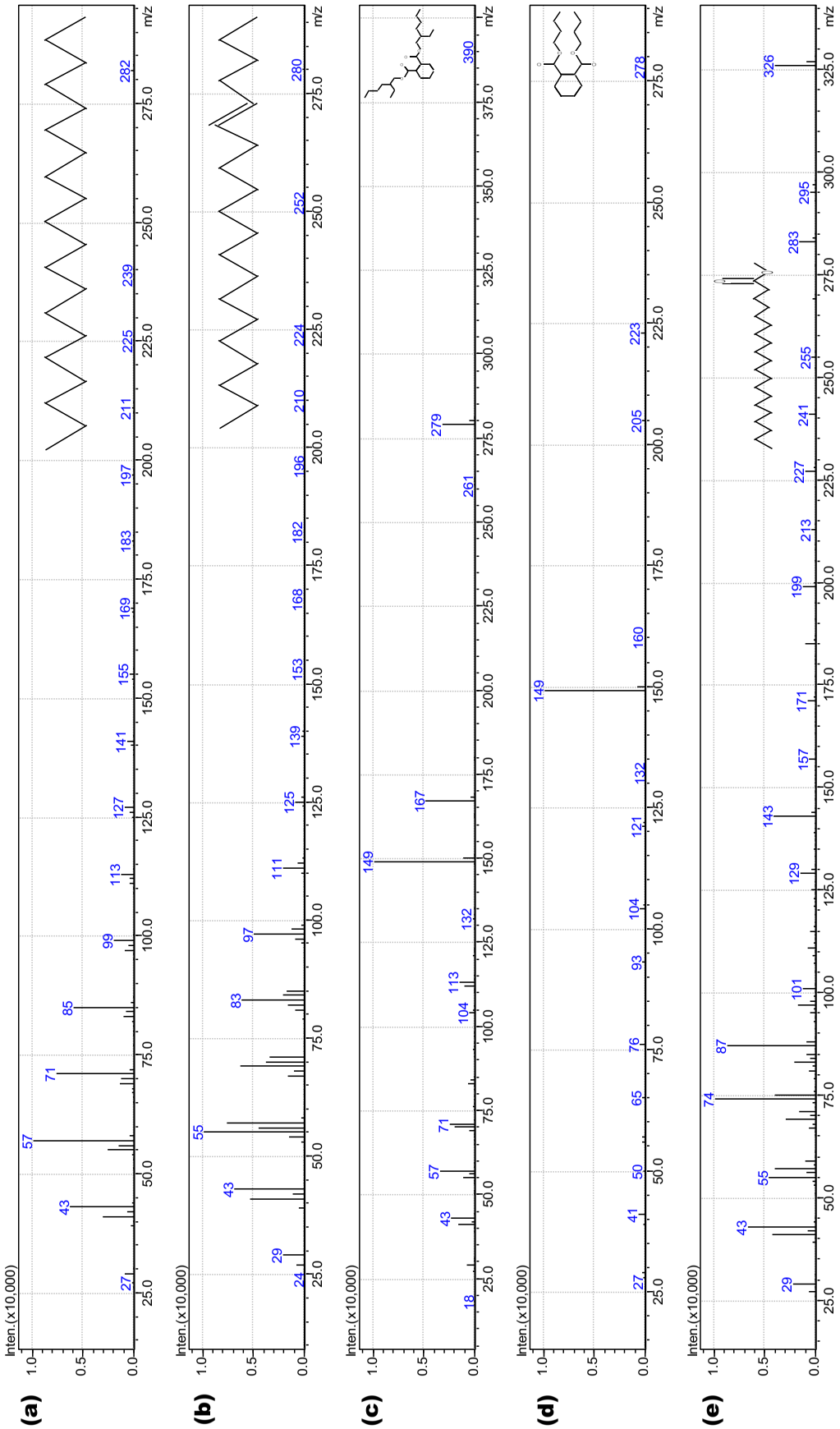
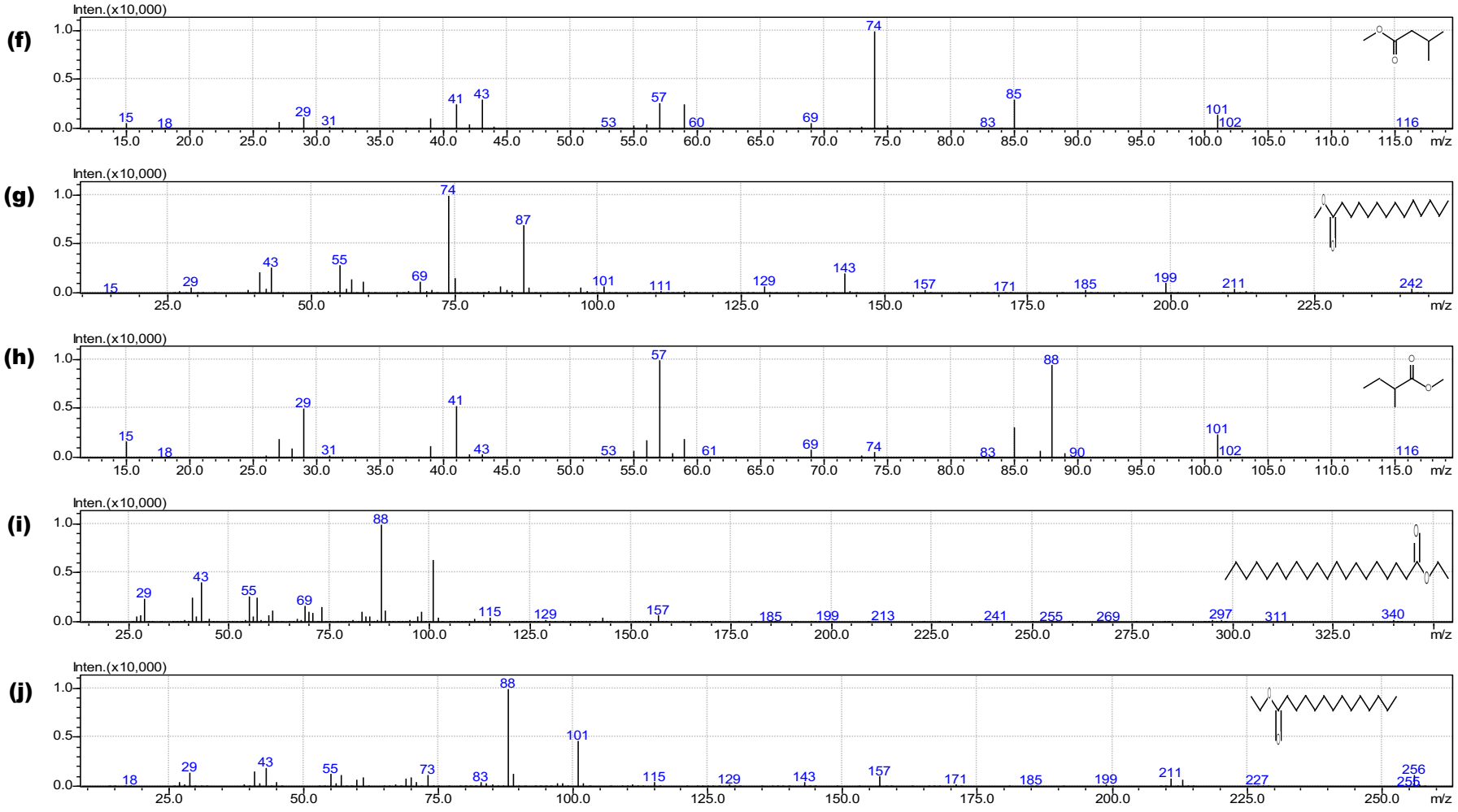


Figure 3.1 Chromatogram of alkane standards (0.5 mg/L, in hexane) injection


(a)
(b)
(c)
(d)
(e)
Inten.(x10,000)
m/z


(f)
Inten.(x10,000)
1.0
0.5
0.0
15
18
29
31
41
43
53
57
60
69
74
83
85
101
102
116
15.0
20.0
25.0
30.0
35.0
40.0
45.0
50.0
55.0
60.0
65.0
70.0
75.0
80.0
85.0
90.0
95.0
100.0
105.0
110.0
115.0
m/z
(g)
Inten.(x10,000)
1.0
0.5
0.0
15
29
43
55
69
74
87
101
111
129
143
157
171
185
199
211
242
25.0
50.0
75.0
100.0
125.0
150.0
175.0
200.0
225.0
m/z
(h)
Inten.(x10,000)
1.0
0.5
0.0
15
18
29
31
41
43
53
57
61
69
74
83
88
90
101
102
116
15.0
20.0
25.0
30.0
35.0
40.0
45.0
50.0
55.0
60.0
65.0
70.0
75.0
80.0
85.0
90.0
95.0
100.0
105.0
110.0
115.0
m/z
(i)
Inten.(x10,000)
1.0
0.5
0.0
29
43
55
69
88
115
129
157
185
199
213
241
255
269
297
311
340
25.0
50.0
75.0
100.0
125.0
150.0
175.0
200.0
225.0
250.0
275.0
300.0
325.0
m/z
(j)
Inten.(x10,000)
1.0
0.5
0.0
18
29
43
55
73
83
88
101
115
129
143
157
171
185
199
211
227
255
256
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200.0
225.0
250.0
m/z

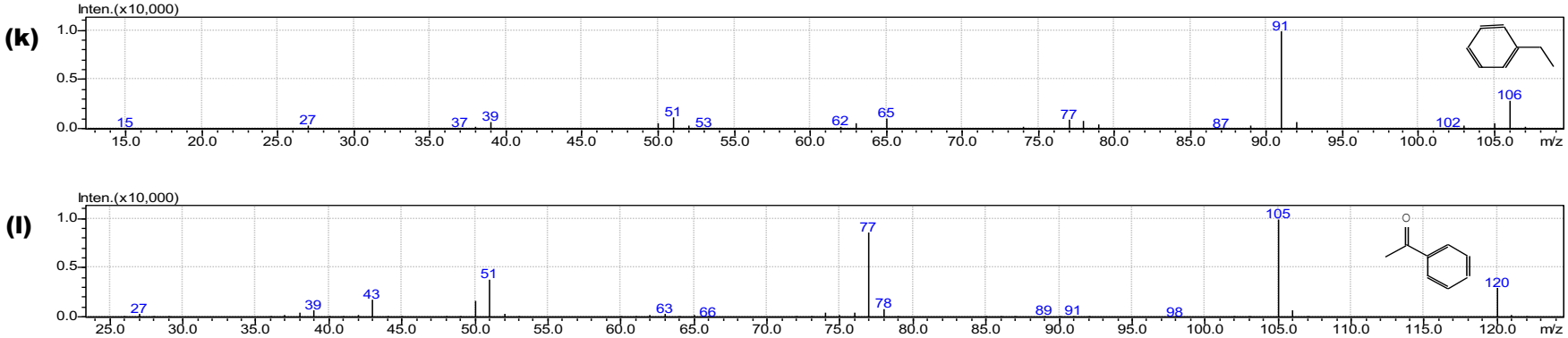


Figure 3.2 Examples of mass fragmentation patterns (a) alkane, (b) alkene, (c, d) phthalates with characteristic m/z 149, (e, f, g) methyl esters with characteristic m/z 74, (h, i, j) ethyl esters with characteristic m/z 88, benzene substituted compounds with characteristic (k) m/z 91 of $[C_7H_7]^+$and (l) m/z 77 of $[C_6H_5]^+$.

Table 3.3 LC-Q-ToF settings

	Polar Metabolites (aqueous fraction)	**Lipid (organic fraction)**
MW range analysed	50 Da – 1200 Da	50 Da – 2000 Da
UPLC conditions		
1. Column	Waters ACQUITY UPLC HSS T3 column (2.1 × 100 mm, 1.8 μm); 40 °C	Waters ACQUITY UPLC CSH C18 column (2.1 × 100 mm, 1.7 μm); 55 °C
2. Mobile phase	A: water with 0.1% formic acid; B: acetonitrile with 0.1% formic acid	A: Water:IPA:ACN, (v/v) 2:1:1, 5mM Ammonium Acetate, 0.05% Acetic Acid, 20uM Phosphoric Acid; B: IPA:ACN, (v/v) 1:1, 5mM Ammonium Acetate, 0.05% Acetic Acid
3. Elution gradient (time, % mobile phase A, flowrate in ml/min)	0.0 min, 99% A, 0.6 0.10 min, 99% A, 0.6 10.00 min, 45% A, 0.6 10.15 min, 35% A, 0.61 10.30 min, 25% A, 0.63 10.45 min, 15% A, 0.67 10.60 min, 5% A, 0.75 10.70 min, 0% A, 0.8 11.00 min, 0% A, 1.0 11.55 min, 0% A, 1.0 11.65 min, 99% A, 1.0 11.70 min, 99% A, 0.9 11.80 min, 99% A, 0.8 11.90 min, 99% A, 0.7 12.00 min, 99% A, 0.65 12.10 min, 99% A, 0.61 12.15 min, 99% A, 0.6 12.65 min, 99% A, 0.6	0.0 min, 99% A, 0.6 0.10 min, 99% A, 0.6 2.00 min, 70% A, 0.6 11.50 min, 10% A, 0.6 12.00 min, 0.1% A, 1.0 12.50 min, 0.1% A, 1.0 12.55 min, 35% A, 0.9 12.65 min, 70% A, 0.8 12.75 min, 99% A, 0.7 12.95 min, 99% A, 0.6 13.25 min, 99% A, 0.6
ESI settings		
1. Capillary voltages	1.5 kV (positive); 1.0 kV (negative)	2.0 kV (positive); 1.5 kV (negative)
2. Cone voltage	20 V	25 V
3. Tempe-ratures	120 °C source temperature; 600 °C desolvation temperature	
4. Desolvation gas flow	1000 L/h	
MS conditions	4 V low collision energy	6 V low collision energy

Chapter 4

Composition and Changes in SMPs along an Anaerobic Baffled Reactor (ABR)

4.1. Introduction

As described in the literature (Chapter 2), SMPs include a wide range of complex organics, of which approximately 20% are extracellular polymeric substances (EPS), but exclude volatile fatty acids and compounds already present in the influent (although if the concentration of these compounds increase with time, then they are considered SMPs) (Aquino, 2004; Kunacheva & Stuckey, 2014). It is known that some effluent SMPs are degradable over time in both aerobic and anaerobic processes, however, their complete degradation is often limited due to their low hydraulic retention time (HRT) in the reactor (Kunacheva et al., 2017c). However, more fundamental work is needed to understand in depth more about SMP formation and degradation, and the reasons behind their persistent occurrence in effluent. This is important for the further development of anaerobic biological treatment methods to improve effluent quality and reduce the chances of DBP generation.

To track the simultaneous production/consumption of SMPs in anaerobic reactors (as assumed in McCarty and Rittmann's kinetic treatment of SMPs (McCarty & Rittmann, 2001)), it was decided that the anaerobic baffled reactor (ABR) would be more suitable as the flow is compartmentalised. Moreover, previous work on microbial ecology in an ABR had reported that the first few compartments contained microorganisms predominantly responsible for fermentation, while methanogens dominated the communities further down the system (Ban et al., 2013; Chen et al., 2016). SMP studies conducted to date using the ABR were only broadly analysed in terms of MW distribution and chemical composition using HPLC-UV-RID, which is susceptible to spectral interferences (Schiener et al., 1998). Although it was concluded that the SMPs produced were mainly below

a MW of 1 kDa, and higher than 100 kDa, the types of compounds remained unidentified.

Previous work reported 50 compounds with the highest integrated peak area from SPE-LLE-GC-MS in the bioreactor effluent (bioreactor was in 'steady-state' condition), 31 of which were alkanes and alkenes, and 7 were nitrogenous compounds which were also detected in the bioreactor feed (Kunacheva et al., 2017a). This work aims to characterise the SMPs down the length of the ABR in greater detail using more advanced analytical techniques, and identify the trend of production and catabolism of SMPs. This will give us greater insight into what kind of compounds were produced during metabolism/cell lysis, and what compounds are degraded, and from here trace the formation/disappearance trends of SMPs (useful for resource recovery). This could include compounds in the CSTR effluent which are the net result of production/consumption.

4.2. Materials and Methods

4.2.1. Chemicals

All chemicals used for sample preparation, chemical extraction and GC-MS were of GC-MS or LC-MS grade, purchased from Sigma-Aldrich, while Ultrapure water was obtained from a Milli-Q water process (Millipore Advantage A10). VFA Standards Mix Solution (formic, acetic, propionic, iso-butyric, butyric, iso-valeric and valeric acid) was of analytical grade and purchased from AccuStandard. The alkane standard mixture (C_{10} - C_{40}, all even, 50 mg/L each in hexane) for calibration of the MS was purchased from Restek. Glassware for sample preparation were rinsed with methanol prior to use.

4.2.2. Anaerobic baffled reactor (ABR)

An anaerobic baffled reactor (ABR) is a rectangular box divided into eight equal volume compartments (10-litre working volume) with verticle baffles, as shown in Figure 4.1 (Grobicki & Stuckey, 1991). Each compartment has an internal dimension of 5 cm by 13 cm by 28 cm (length by width by height), liquid depth

of 18 cm (height of the weir on the standing baffles separating one compartment from the next, and an overflow of cross section area 45.5 cm^2. The direction of flow is shown by the dashed arrows in Figure 4.1. The reactor was operated at room temperature (25 ± 1 ^oC) with a continuous feed.

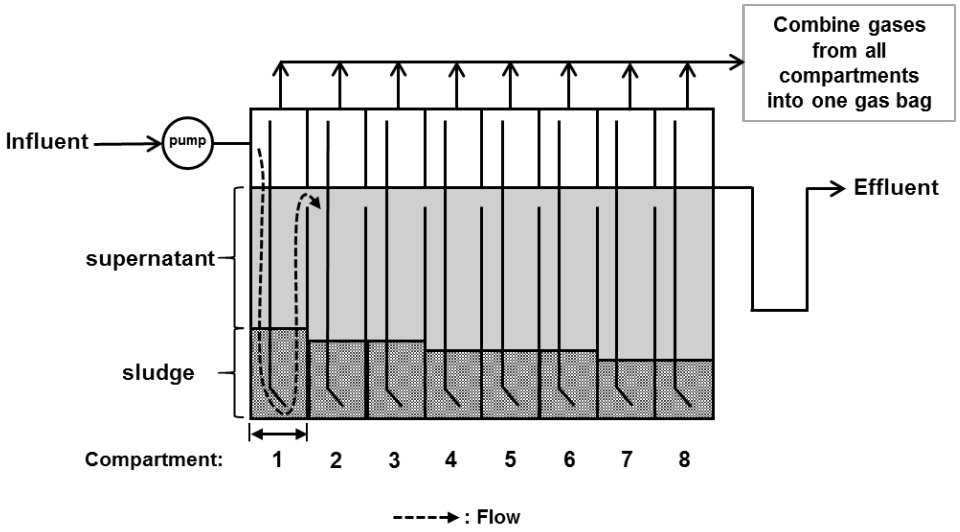


Figure 4.1 Schematic diagram of anaerobic baffled reactor (ABR)

A blank using ultrapure water was initially run continuously through the biomass free reactor for two weeks. The water was then extracted and analysed by GC-MS using the same procedure as for the samples to check that the reactor itself does not leach any solutes. The ABR was seeded with mixed sludge (cultivated in the batch-fed completely stirred tank reactor described in section 3.2) diluted to a volatile suspended solids (VSS) concentration of 4 g/L and initially fed 0.5 g COD/L of the buffered feed (components of the synthetic wastewater were presented in Table 3.1 of Chapter 3, with eighty times dilution to 0.5 gCOD/L for this initial phase of the experiment). The ABR was set to operate at a HRT of 24 h. To observe for variations in SMPs during the change in influent concentration, the influent concentration was subsequently stepped up to 2 g COD/L after 27 days. Supernatant from the ABR was collected from the overhead sampling ports of the respective compartments one week after the increase in feed concentration on Day 34, and subsequently on Days 56 and 96. By Day 96, the COD removal reached 84% which was close to its pseudo-steady state. The feed concentration was then further increased to 4 g COD/L and sample

collection was one week later (Day 120) and on Day 158. The samples were centrifuged to remove any solids and filtered through 0.45 μm nylon syringe filters for measurement of soluble COD and SPE. Subsequent filtration with 0.2 μm filters were carried out for HPLC for volatile fatty acid analysis.

4.2.3. General parameters

Methane gas production, volatile fatty acids (VFAs) and soluble COD from the ABR were monitored as a measure of reactor performance. The detailed procedure for monitoring of bioreactor was described in Chapter 3.

4.2.4. Qualitative analysis of SMPs

For compound identification, supernatant from the different compartments of the ABR were removed and filtered through 0.45 μm glass fiber filters. The samples collected for analysis were supernatant samples with a COD greater than 100 mg/L, so the volume used for SPE loading was 100 mL, and 10 mL of SPE eluent with 50 mL extraction solvent was used for LLE. The details of the extraction procedure, GC-MS and LC-Q-ToF analysis methods can be found in Chapter 3.

4.3. Results and Discussion

4.3.1. ABR performance (COD, VFA, and methane production)

COD, VFAs, and methane production were monitored in order to determine reactor performance. Analysis of the ABR with an initial influent of 0.5 g COD/L indicated that the VFAs in the bulk solution in the third compartment were close to zero (Figure 4.2), while the methane produced increased to a maximum of 76% in the same compartment (Table 4.1) after 27 days. However, the methane composition decreased slightly one week after the feed was increased to 2 g COD/L (maximum 70% in the 4th compartment and minimum 60% in the 8th compartment) on Day 28, but stayed in the range of 58% − 73% thereafter; carbon dioxide was found to be 23% − 25%, and nitrogen was 7% - 13% of the total gas composition. On days when samples were collected, the methane composition

was maximum in the 4th compartment on Days 34 (70%), 56 (67%), 96 (73%), 120 (72%), and 158 (70%). The compartment with the highest percentage of methane present suggested the most active stage of methanogenesis in the system.

COD removal efficiency was as high as 97% at 0.5 g COD/L, but decreased to 88% 2 days after the feed was increased to 2 g/L, and to 60% on Day 34 (first sampling, 7 days after the increase in feed concentration); a similar trend in COD removal was observed after the second increment of influent concentration; COD removals over time are shown in Table 4.1.

Table 4.1 Bioreactor monitoring during the day of sampling

Sample	Feed concentration (gCOD/L)	Average methane composition	Effluent COD (mg/L)	COD removal
Day 27	0.5	72%	11	97%
Day 34	2	64%	745	60%
Day 56	2	63%	614	66%
Day 96	2	70%	207	84%
Day 120	4	63%	1556	56%
Day 158	4	63%	453	88%

VFA analyses are shown in Figure 4.2; at 0.5 g COD/L, propionic acid was found in the first two compartments, but not from the 3rd compartment onwards. VFA production increased at 2 g COD/L, and the effluent still contained VFAs at a concentration of 556 mg COD/L (effluent COD = 614 mg/L), approximately 91% of the total soluble COD. However, the reactor approached a pseudo steady state by Day 96 where the total VFAs decreased down the reactor, with no butyrate and only 75 mg COD/L of propionate detected by the last compartment. When the influent concentration was doubled to 4 g COD/L (Day 120), the VFAs 24 hours afterwards showed a further 25% increase in the 1st compartment compared to those measured on Day 96. Subsequent compartments of the ABR showed fluctuations in total VFAs of not more than 20%, and although the last compartment had the lowest VFA concentration, it was still high (~1800 mg COD/L), and was comprised of acetate, propionate, butyrate and isovalerate.

Samples collected on Day 158 (39 days after the increase in feed concentration) showed a significant drop (approximately 80%) in VFAs in the 5th compartment, which then increased in the 6th compartment and were maintained at approximately 500 mg/L until the last compartment. This phenomenon was not observed in the samples collected on other days. The analysis of low and high MW SMPs in the 4th compartment showed a 20% increase in the total concentration of low MW compounds, and a 20% decrease in the total concentration of high MW compounds in comparison to that from the 5th compartment.

4.3.2. GC-MS analysis

The compounds detected were categorised into the various chemical groups: alkane, alkene, ester, acid, alcohol, aromatic compounds, nitrogenous compounds (denoted 'N' in Figures 4.3 a-e), and unknowns; other compounds detected but not categorised were grouped under 'others'. The number of each type of compound found and tentatively identified based on NIST 11 library similarity indices and retention indices were summarised in Table 4.2 and Figure 4.3. Suggestions of compounds identified included the possible isomers having the same elution time, for instance, 6-methyl-pentadecane/7-methyl-pentadecane/5-propyl-tridecane at retention time (RT) 24.079 minutes, 5-(E)-Tetradecene/4-(Z)-Tetradecene at RT 21.568 minutes; isomers with different retention times (distinctively separated peaks with same mass spectra due to the same features of the analyte), for example isomers of pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(2-methylpropyl)- detected at RT 30.879 and 30.922 minutes, and for unknown compound with m/z 91, 113, 141, 204 and 169 at RT 36.132 and 36.439 minutes.

Table 4.2 Total number of low molecular weight compounds detected from the respective ABR compartments on Day 34, 56, 96, 120, and 158 using GC-MS.

ABR compartment	Day 34	Day 56	Day 96	Day 120	Day 158
1	77	58	75	143	65
4	30	53	46	229	58
8	45	40	55	70	72

Samples analysed were from the 1st, 4th and 8th compartment of the ABR, with the 4th compartment having the highest percentage of methane produced. The total number of compounds in each compartment generally decreased from the first to the last compartment (Table 4.2, Figure 4.3). In terms of the 'quantity', the highest total concentration was in the 1st compartment, and decreased to the lowest concentration in the 4th compartment, before increasing again in the last compartment in the samples collected on Days 34 and 96. A decrease in concentration down the ABR was observed on Day 120 (24 hours after the increase in feed from 2 to 4 g COD/L). The same trend was observed in both the samples collected on Day 56 and Day 158, where the concentration decreased from the 1st to the 4th compartment, and then increased to its maximum in the last compartment. From the trend observed in these experiments, the low MW compounds tend to accumulate until the last compartment of the ABR when it is in a transient state (25-30 days after change in feed COD concentration, with reference to the COD removal efficiency); the lowest concentration of SMPs occurred in the 4th compartment of the ABR, where methane concentration was also observed to be at its highest. Thus, the increase in SMPs after the 4th compartment suggested a mixture of degraded and biotransformed influent compounds, and new SMPs generated. The drop in concentration and number of compounds to their lowest point in the 4th compartment also suggested the high activity of methanogens (percentage of methane was the highest in the 4th compartment (as discussed in Section 4.3.1)), which agrees with the findings of Wu and Zhou (Wu & Zhou, 2010). Early studies by McCarty & Smith had already explained the conversion of complex compounds (macromolecules, mainly proteins, carbohydrates, and lipids) into simpler molecules (such as monosaccharides, shorter peptides, and fatty acids), then to acetate, and finally to methane gas and carbon dioxide in anaerobic processes. The higher conversion rate of acetate into methane gas (from the higher percentage of methane gas in total biogas composition) enhanced the process of conversion of organic compounds in the system, which is reflected as a lower concentration of organic compounds in the 4th compartment compared to the first and last compartments (McCarty & Smith, 1986).

The full list of suggested compounds can be found in the Appendix (Table A1).

4.3.2.1. Nitrogenous compounds (denoted 'N' in the tables and figures)

A decreasing trend in nitrogenous compounds down the compartments was observed. From the compounds identified in all three sets of samples, some of the nitrogenous compounds, such as hexahydro-3-(2-methylpropyl)-pyrrolo[1,2-a]pyrazine-1,4-dione, 5,10-diethoxy-2,3,7,8-tetrahydro-1H,6H-dipyrrolo[1,2-a:1', 2'-d]pyrazine-5-pyrrolidino-2-pyrrolidone, 3-methyl-6-(phenylmethyl)-2,5-piperazinedione, *N*-acetyl-3-methyl-1,4-diazabicyclo[4.3.0]nonan-2,5-dione, and their isomers found in the influent were observed to first increase and then decrease down the reactor. These compounds were also found in the feed, which is comprised of meat extract (Merck) and peptone (Merck), or released from cells due to microbial metabolism as biomass associated products (BAPs). The biotransformation of nitrogenous compounds has been of interest as many active ingredients in pharmaceuticals contain an amine functional group which leads to the formation of more stable transformation products through reactions such as N-oxidation, N-dealkylation and N-acetylation (Gulde et al., 2016).

The Swiss Federal Institute of Aquatic Science and Technology - Biocatalysis/ Biodegradation Database (EAWAG-BBD) pathway prediction system is a tool to aid in the mapping of transformation pathways following a set of biotransformation rules, with reference to metabolic pathways reported in the literature. Using the EAWAG-BBD, one of the biotransformation products of 3-methyl-6-(phenylmethyl)-2,5-piperazinedione was predicted to be benzeneacetic acid, and it was found in the first compartment on Day 56 (during the transient state of feed concentration increment) and the last compartment of Day 120 sample (transient state of the second increment). The concentration (by integrated peak area) of benzeneacetic acid detected on Day 120 was 1.5 times higher than that on Day 56. This implied that benzeneacetic acid accumulates at the initial stages of a shock load (step increase in feed concentration), but then degraded over a period of up to 38 – 42 days since it was not detected in the samples collected on Days 96 and 158. Further metabolic pathway prediction by EAWAG-BBD showed the transformation of benzeneacetic acid into a diester and simpler hydrocarbons (EAWAG-BBD Pathway Prediction Results).

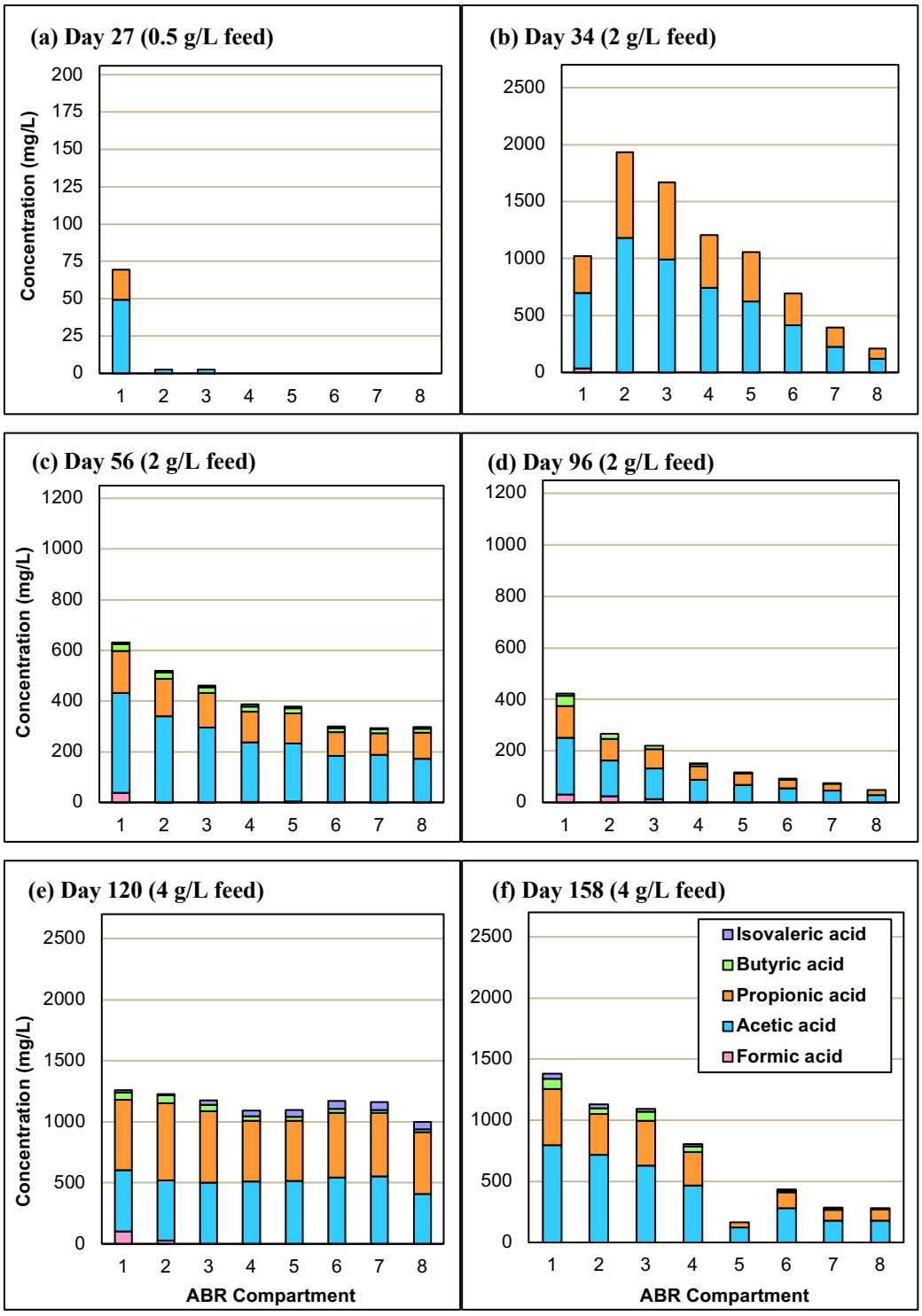


Figure 4.2 Concentration of the VFAs produced (mgCOD/L) before (a) Day 27 and during sampling days (b) Day 34, (c) 56, (d) 96, (e) 120, and (f) 158

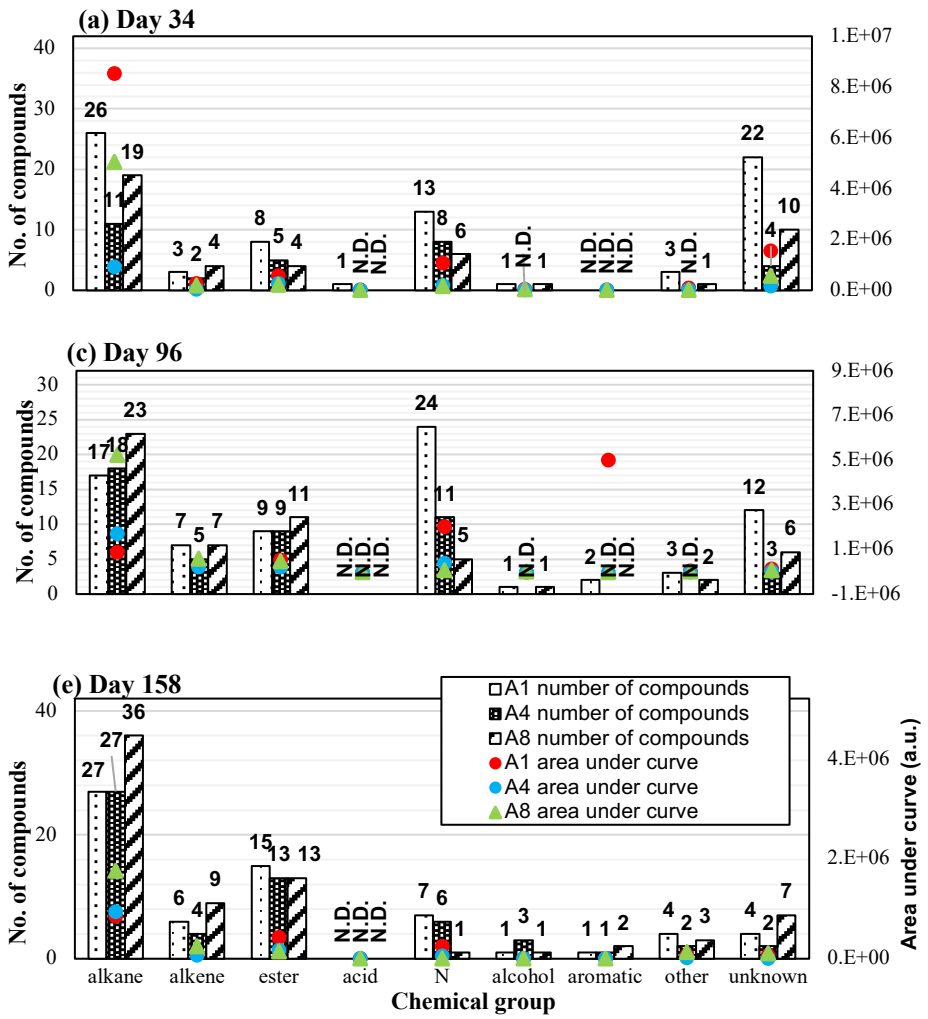
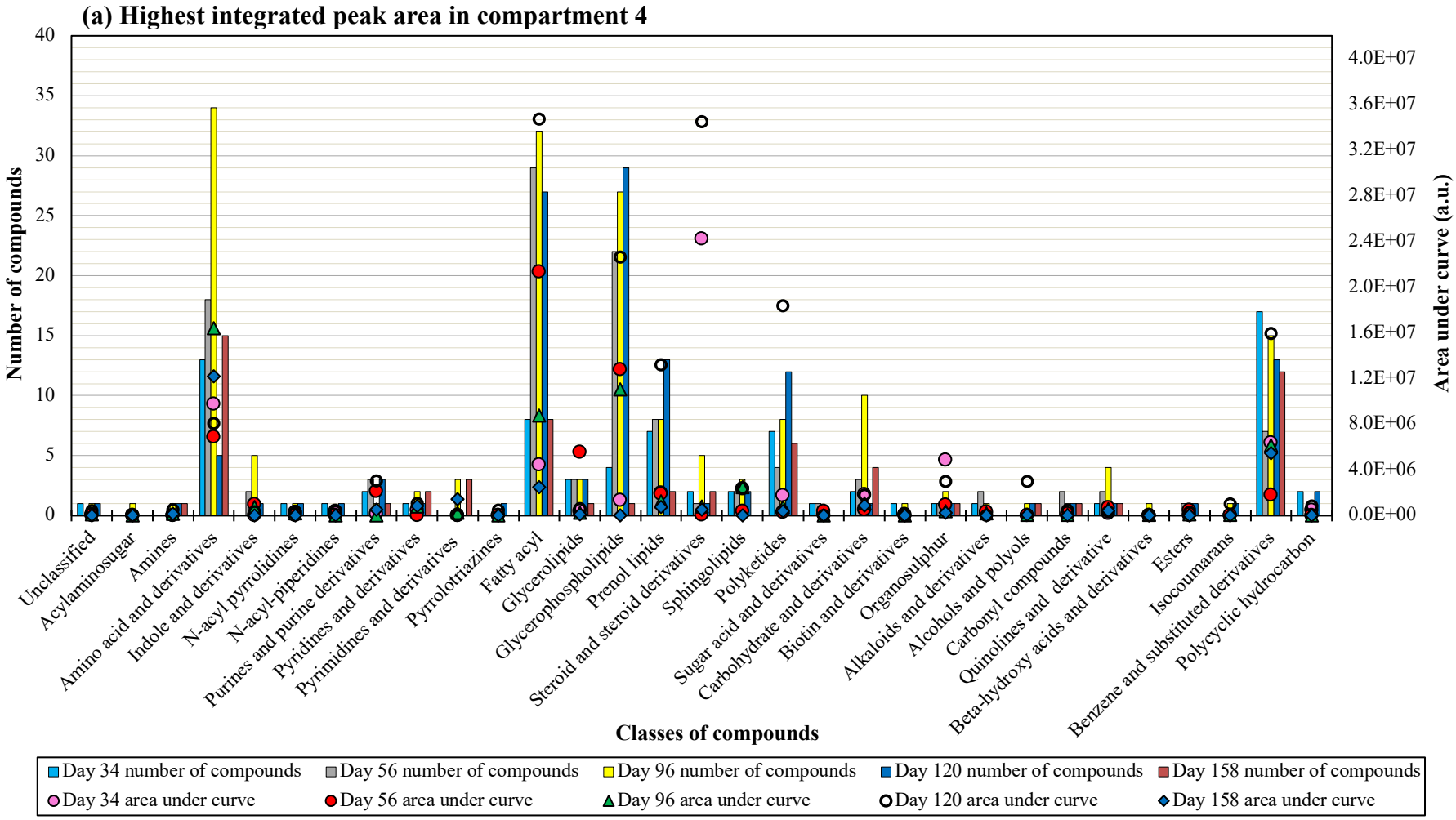
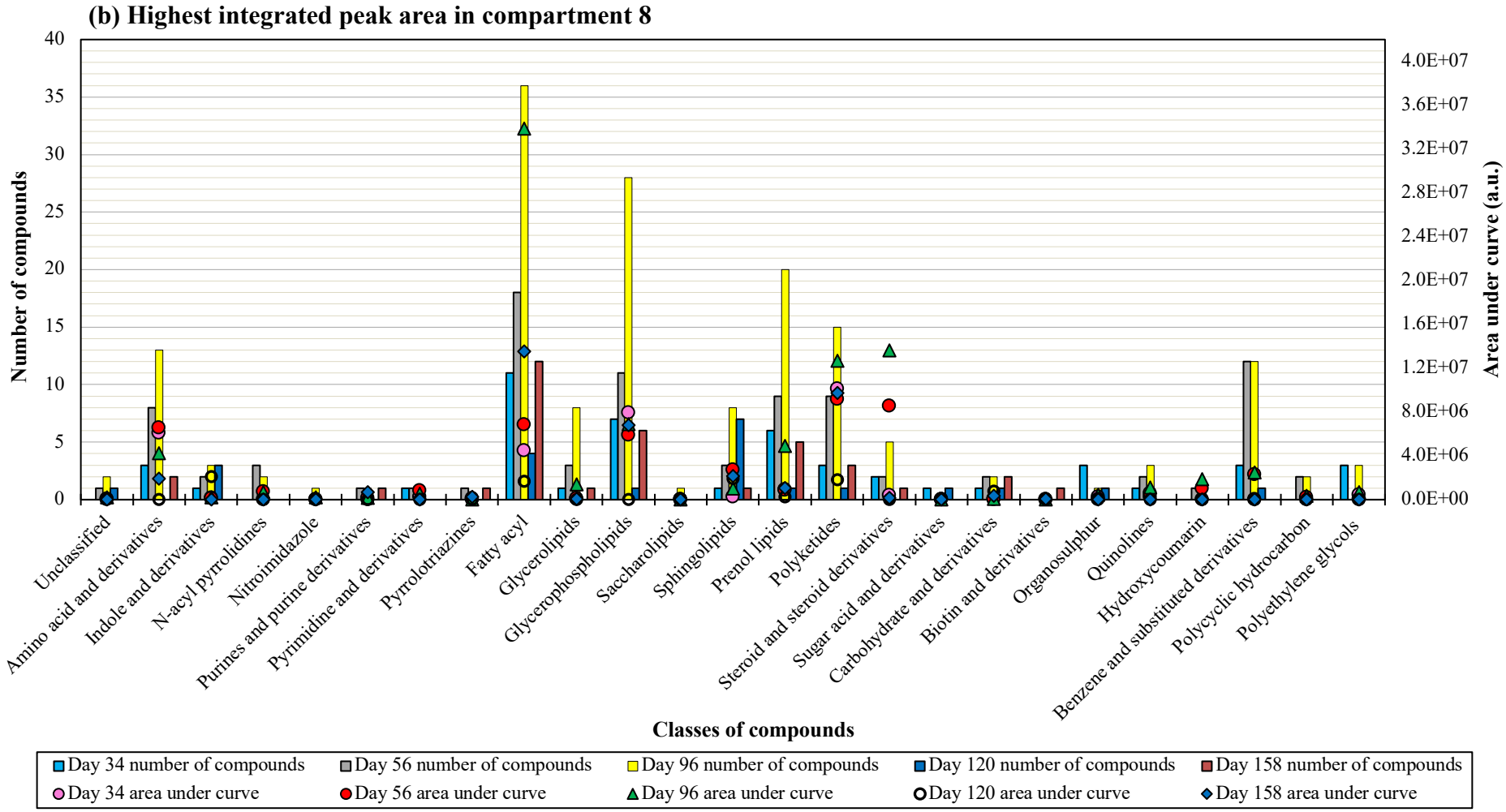


Figure 4.3 Number of compounds detected from GC-MS (bar chart) and area under curve (scatter plot) identified in ABR compartments 1, 4, and 8 (denoted A1, A4, and A8 respectively) using GC-MS for samples collected on Days (a) 34, (b) 56, (c) 96, where influent strength is 2 gCOD/L; Days (d) 120, and (e) 158, where influent strength is 4 gCOD/L; 'N.D.' refers to 'Not Detected'.


(a) Highest integrated peak area in compartment 4
Number of compounds
Area under curve (a.u.)
Classes of compounds
Unclassified
Acylaminosugar
Amines
Amino acid and derivatives
Indole and derivatives
N-acyl pyrrolidines
N-acyl-piperidines
Purines and purine derivatives
Pyridines and derivatives
Pyrimidines and derivatives
Pyrrolotriazines
Fatty acyl
Glycerolipids
Glycerophospholipids
Prenol lipids
Steroid and steroid derivatives
Sphingolipids
Polyketides
Sugar acid and derivatives
Carbohydrate and derivatives
Biotin and derivatives
Organosulphur
Alkaloids and derivatives
Alcohols and polyols
Carbonyl compounds
Quinolines and derivative
Beta-hydroxy acids and derivatives
Esters
Isocoumarans
Benzene and substituted derivatives
Polycyclic hydrocarbon
Day 34 number of compounds
Day 56 number of compounds
Day 96 number of compounds
Day 120 number of compounds
Day 158 number of compounds
Day 34 area under curve
Day 56 area under curve
Day 96 area under curve
Day 120 area under curve
Day 158 area under curve


(b) Highest integrated peak area in compartment 8
Number of compounds
Area under curve (a.u.)
Classes of compounds
Unclassified
Amino acid and derivatives
Indole and derivatives
N-acyl pyrrolidines
Nitroimidazole
Purines and purine derivatives
Pyrimidine and derivatives
Pyrrolotriazines
Fatty acyl
Glycerolipids
Glycerophospholipids
Saccharolipids
Sphingolipids
Prenol lipids
Polyketides
Steroid and steroid derivatives
Sugar acid and derivatives
Carbohydrate and derivatives
Biotin and derivatives
Organosulphur
Quinolines
Hydroxycoumarin
Benzene and substituted derivatives
Polycyclic hydrocarbon
Polyethylene glycols
Day 34 number of compounds
Day 56 number of compounds
Day 96 number of compounds
Day 120 number of compounds
Day 158 number of compounds
Day 34 area under curve
Day 56 area under curve
Day 96 area under curve
Day 120 area under curve
Day 158 area under curve

(c) Highest integrated peak area in compartment 4

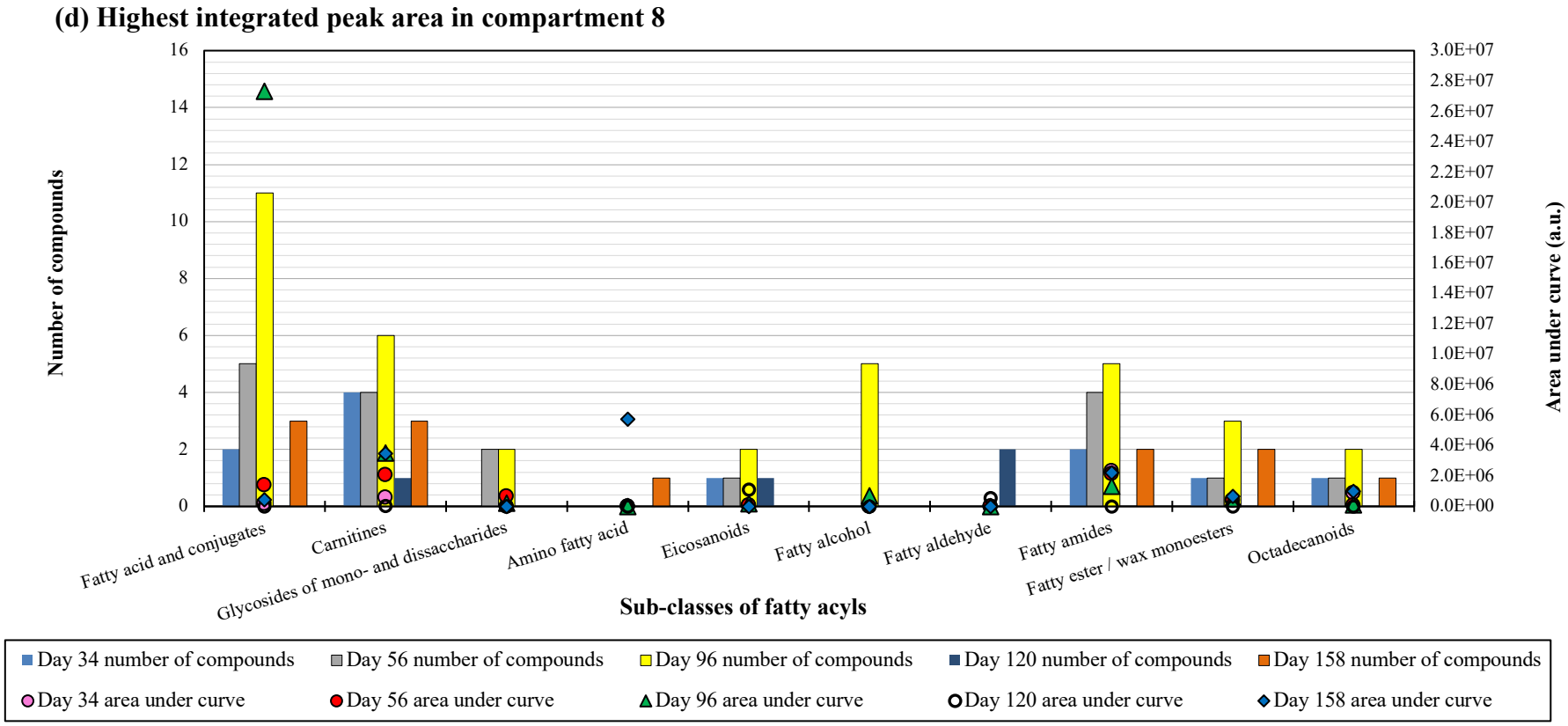


Figure 4.4 (a), (b) General classes of compounds and (c), (d) Sub-classes of fatty acyl; Number of high MW compounds (bar chart) and area under curve (scatter plot) identified in ABR compartments 1, 4, and 8 using LC-Q-ToF which was found to have highest area under curve in compartment 8; Samples were collected on Days 34, 56, 96, where influent strength is 2 gCOD/L; Days 120, and 158, where influent strength is 4 gCOD/L.

Table 4.3 List of compounds found to be at the highest concentration in ABR compartments 4 and 8.

Classes of compounds	highest concentration in ABR compartment 4	highest concentration in ABR compartment 8
Unclassified	√	√
Acylaminosugar	√	
Amines	√	
Amino acids and derivatives (dipeptides, oligopeptides, tripeptides, tryptamine and derivatives)	√	√
Indole and derivatives	√	√
N-acyl pyrrolidines	√	√
N-acyl-piperidines	√	
Nitroimidazole		√
Purines and derivatives	√	√
Pyridines and derivatives	√	
Pyrimidines and derivatives	√	√
Pyrrolotriazines	√	√
Fatty acyls - fatty acids and conjugates, eicosanoids, carnitines (fatty esters), glycosides of mono- and disaccharides, fatty amides, fatty alcohols, fatty aldehyde, octadecanoid, wax monoesters (fatty esters)	√	√
Glycerolipids - monoradylglycerol (MG), diacylglycerol (DG), diradylglycerol (ladderane)	√	√
Glycerophospholipids - glycerophosphoserines (PS), phosphoinositols (PI), diacylglycerophosphate (PA), phosphatidylglycerol (PG), phosphatidylcholine (PC), phosphatidylethanolamine (PE)	√	√
Sphingolipids - ceramides (Cer), N-acylsphinganines, sphingosines	√	√

Prenol lipids - C15-isoprenoids (sesquiterpenes), C18-steroids (estrogen) and derivatives, C20-isoprenoids (diterpenes), C30-isoprenoids (tritepenes), C40-isoprenoids (tetraterpenes), carotenoids, monoterpenoids, diterpenoids, hopanoids	√	√
Saccharolipids		√
Polyketides - chalcones (flavonoids), cinnamaldehyde (phenylpropanoids), flavones, flavonols, flavonoids and isoflavonoids, kavalactones (phenylpropanoids))	√	√
Steroid and derivatives - cholesterol and derivatives, vitamin D3 and derivatives	√	√
Sugar acid and derivatives	√	√
Carbohydrates and derivatives	√	√
Biotin and derivatives	√	√
Organosulphur compounds	√	√
Alkaloids and derivatives	√	
Alcohols and polyols	√	
Carbonyl compounds	√	
Quinoline and derivatives	√	√
Beta-hydroxy acids and derivatives	√	
Esters	√	
Hydroxycoumarin		√
Isocoumarans	√	
Benzene and substituted derivatives	√	√
Polycyclic hydrocarbons	√	√
Polyethylene glycols		√

A nitrogenous compound, suggested to be (E)-3-(but-2-enoyl)oxazolidin-2-one by the NIST library, was detected in the last compartment of the Day 96 sample as the bioreactor approached pseudo steady state. A literature search found similar oxazolidine-4-one antibacterial compounds isolated from a novel marine actinomycetes (Gullo et al., 2006), and oxazolidin-2-one compounds to be synthetic antimicrobial molecules (Reck et al., 2005; Seneci et al., 1994).

Indoles and their derivatives are commonly known to be the degradation or transformation products of tryptophan (an amino acid) (KEGG; Lee et al., 2004), which could have been derived from the proteinaceous meat extract and peptone in the synthetic feed, or from metabolism of biological cells i.e. sludge in the bioreactor. The concentration and number of indoles and their substituted derivatives were found to randomly increase and decrease across the ABR, which could be due to the metabolism of the amino acid tryptophan. It was found in the samples collected on Days 34, 56, and 96, that the indoles and their related compounds were detected in the first compartment and none in the last compartment.

4.3.2.2. Alkanes and alkenes

There has been considerable work carried out on the microbial production of alkanes, especially those that can be harvested for biofuels (Choi & Lee, 2013; Yoshino et al., 2015). In our experiments, alkanes and alkenes were observed to have the largest increase in both their concentrations and numbers of such compounds; it was observed that the concentration of alkanes increased across the ABR as the system approached a pseudo-steady state on Days 56, 96, and 158 (Figure 4.3 b, c, f). Similarly, on Day 56 the number of alkanes increased from the 1st to 4th compartment, and from 7th to 8th; 16 out of the 29 alkanes detected were highest in the 4th compartment. The concentration of alkenes detected increased down the reactor, with the largest increase (20%) higher than the concentration found in the first compartment. The alkanes and alkenes accumulated in the last compartment of the Day 96 sample, where 21 out of 23 alkanes showed up to 15 times increase in concentration, and 7 out of 8 alkenes were found to have up to 3.5 times increases. Except for the samples on Day 34 and Day 120, which were collected 24 hours after the increase in influent

concentration, the other samples showed an increase in concentration of alkanes and alkenes across the ABR. The kinetics of alkane and alkene formation and transformation would be an interesting area to research, with an added advantage of extending it to the harvesting of biofuels. In addition, it was found that fatty acids are precursors for alkane biosynthesis by a plant enzyme *Pisum sativum* (Cheesbrough & Kolattukudy, 1984) and cyanobacteria (Schirmer et al., 2010). The authors also found that the carbon chain length of the final alkane or alkene produced depends on the chain length of the intermediate aldehyde. Moreover, a detection of surges in aldehydes in bioreactor systems could also imply an inhibitory process.

4.3.2.3. Esters, acids, aromatic compounds

The number of esters increased across the bioreactor on Day 96, and 8 out of the 11 esters identified showed an increase in concentration by 5 to 6 times. The total concentration decreased initially then increased again, although was not as high as in the 1st compartment (Figure 4.3 c). Previous studies of SMP production in anaerobic systems observed the presence of phthalate esters (Kunacheva et al., 2017c; Trzcinski & Stuckey, 2010), typically plasticizers, but these were not detected in this experiment. This could be due to the longer HRT (24-hour cycle) compared to the previous experiments reported, and hence a longer time for biodegradation, or possibly the rate of removal was higher than its rate of formation. This trend in concentration change was similar for *p*-cresol or its isomers, which reached a peak concentration in the 1st compartment of the ABR and subsequently decreased but was still present in the last compartment (65% decrease) on Day 56. This indicates that such compounds will most likely persist and be present in the post-treatment stage, existing as potential precursors of disinfection by-products. However, from the sample collected on Day 96, phenolic compounds were detected in the 1st compartment but disappeared by the 4th compartment. The acids identified were found in the 1st and 4th compartments of the ABR, but were not detected in the last compartment, except for octanoic and nonanoic acid found in the Day 120 samples. Since esters are more thermodynamically stable compared to their corresponding acids, it is expected that there will be a higher number and concentration of esters detected.

4.3.2.4. Others

Benzophenone, or a benzophenone derivative, was detected in the 4th compartment of the Day 34 sample, but not in the last compartment. This compound was also not detected in the Day 56 and Day 96 samples. For samples collected on Day 158, benzophenone was detected in the influent and decreased in concentration (decreased integrated peak area) across the ABR to 36% of the concentration detected in the influent found in the last compartment. Shock loadings are known to result in the production of certain chemicals, which decreased as the system approaches steady-state (Kunacheva et al., 2017b), but from its detection in the Day 158 samples, it suggested that benzophenone might be a degradation product from the synthetic feed or a microbial product, or from a microbial strain or metabolic pathway which has yet to be identified, since there is a study which found that benzophenone synthase (BPS), a member of the superfamily of type III polyketide synthases, was typical for plant secondary metabolism until it was detected in microorganisms much later (Gross et al., 2006). An epoxide, tetradecyl-oxirane, was detected in the Day 34 sample, but not in the Day 56 and Day 96 samples. This epoxide was found in the headspace by volatile extraction of plants such as the herbs *Pterocarpus marsupium* (Gosetti et al., 2016) and *Viola tianschanica* (Qin et al., 2016), and Eastern Himalayan moss *Cyathophorella adiantum*, and is suggested to be an oxidation product of a C_{16} fatty acid, classified as an oxylipin (Mitra et al., 2013). According to Mitra et al., the fatty acid produced was suspected to be due to cell disruption during sample preparation. In our case where there is minimal mechanical cell disruption in the ABR, it was possibly due to cell degradation (BAP) or other cell activity.

The unknowns possibly include intermediates of the biotransformation of certain compounds, while the number of unknowns were lower in the samples collected as the system approached a pseudo-steady state (Day 96 and 158).

4.3.3. LC-Q-ToF analysis

Although GC−MS is a powerful technique, it is limited to the detection of small (<580 Da), nonpolar, and volatile molecules which are thermally stable, and this method of analysis often requires chemical derivatization of many of the polar

metabolites prior to analysis (Dunn et al., 2008). Liquid chromatography mass spectrometry (LC−MS) had been used for untargeted metabolomics studies such as the analysis of environmental samples (Bowen & Northen, 2010; Dunn et al., 2011), and the method developed by Tipthara et al which utilised LC-Q-ToF was used in this study because of its unbiased nature of analysis. Qualitative analysis of the compounds was carried out using LipidMaps, HMDB and *E. Coli.* metabolite libraries available in the analysis software, and were classified according to their chemical classes shown in Table 2 and Figure 4. Due to the limitation that standards were not available at this stage of analysis, the 'concentrations' in the discussion were related to the integrated peak area. The list of compounds detected from the LC-Q-ToF can be found in the Appendix A1-A3.

The concentration of high MW compounds in the 1st and 4th compartments of the ABR decreased from Day 34 to Day 96 where the system approaches a pseudo-steady state, then increased when the influent concentration was increased on Day 120, then subsequently decreased 38 days later (Day 158). However, in the last compartment, the concentration increased from Day 34 to its peak on Day 120. This could be associated with the accumulation of the higher MW SMPs in the last compartment over time as the concentration decreased again at the second sampling after the increase in influent COD. Across the ABR at the respective sampling times, the total concentration of high MW SMPs decreased. The following section discusses the various classes of compounds that reached their highest concentration in the 4th and 8th compartments (Figure 4.4). From the results obtained, there was no direct relationship observed between the total concentration of the high and low MW SMPs identified in each compartment.

4.3.3.1. Results from 'Highest integrated peak area in compartment 4'

The compounds that showed a maximum concentration in the 4th compartment of the ABR are presented in Figure 4.4 a, and a further break down of the fatty acyls identified are shown in Figure 4.4 c. The highest percentage of methane in the total amount of biogas generated was in the 4th compartment of the ABR, and it is logical that the methanogenic activity is the highest in this compartment. Both the number of compounds and their concentrations, especially lipids, were

highest in the supernatant of the 4th compartment collected on Day 120, which was 24 hours after the increase in influent concentration from 2 g COD/L to 4 g COD/L. 60% of the fatty acyls are comprised of fatty acids and conjugates; fatty alcohols, fatty amides, fatty esters and carnitines made up the remaining in approximately equal quantities. These lipids decreased after the 4th compartment and were found to have the lowest concentration in the last compartment.

The total concentration of the individual amino acids and derivatives in the 4th compartment was highest in the Day 96 sample, followed by the samples collected on Day 158, 34, 120 and 56. Benzene and benzene substituted derivatives were highest in the supernatant collected from the 4th compartment on Day 120, followed by Day 34, 96, 158 and 56 in decreasing concentration. Both Day 34 and Day 120 were 24 hours after the feed strength increase, and the supernatant from the 4th compartment had the highest concentration of organosulphur compounds compared to those collected at other times. This trend was similar for the class of steroids and steroid derivatives detected.

4.3.3.2. Results from 'Highest integrated peak area in compartment 8'

Figure 4.4 b shows the results from LC-Q-ToF analysis for compounds in the last compartment, while a further break down of the fatty acyls identified is presented in Figure 4.4 d. The results showed an increase in the number of glycerolipids and glycerophospholipids 35 days after the increase in influent COD to 2 g COD/L (Day 56), and a doubling over the next 40 days (Day 96), although the COD removals showed that the reactor was approaching a pseudo-steady state at 86% COD removal. A similar trend was observed for amino acids and derivatives, and the other classes of lipids; fatty acyls, sphingolipids, prenol lipids, and polyketides. Following the increase in these classes of compounds during feed CODs of 2 g/L, a further increase in feed COD to 4 g/L saw a repeated trend for these classes of compounds, except for sphingolipids which accumulate in the last compartment of the ABR.

4.3.3.3. The occurrence and changes of higher MW SMPs across the ABR

A possible source of lipids and amino acids detected is the breakdown of bacterial cell walls, which are comprised of peptidoglycan, lipopolysaccharide, proteins and phospholipids (Yoshino et al., 2015). Peptidoglycan is made up of peptides (short chain amino acids) and disaccharides (also known as glycans due to their linkage). This explains the occurrence of a variety of dipeptides and some N-acylated compounds. Natural glycerides also exist as part of the lipid bilayer of the outer cell membrane, although are not as important in terms of their functions compared to that of glycerolipids and phosphoglycerolipids. As such, the long chain fatty acids were probably from the glycerides which broke down after being released from the lipid bilayer, and were present in similar amounts as glycerophospholipids. Another reason for the presence of long chain fatty acids could be from the catabolism of sphingolipids (linked by amide bond to the amino alcohol sphingosine (Figure 5.7b)). In this case, the production of lipids, amino acids and their derivatives can be partly considered as biomass-associated products (BAP). This agrees with a previous study by Barker et al who found sugars and fatty acids in the high MW fractions and deduced the presence of heteropolysaccharides and lipopolysaccharides (Barker et al., 2000).

The amino acids and their derivatives detected were comprised mainly of dipeptides such as L-*cis*-cyclo(aspartylphenylalanyl), glycyl-tyrosine, and alanyl-glutamine. The decrease in the concentration of dipeptides from the 4th to the last compartment might indicate an increase in methanogenic activity in the last four compartments of the ABR (Figure 4.4 a and b). Dipeptides are known to be the short-lived intermediates from incomplete protein digestion or catabolic pathways, of which the cyclic dipeptides are known to possess cell-signaling properties which might be capable of activating or inhibiting AHL-based biosensors in other bacteria (Gu et al., 2013; Holden et al., 1999). The amount of amino acids and their derivatives increased from Day 34 to 96 when the feed concentration was 2 g COD/L, and from Day 120 to 158 when the feed concentration was 4 g COD/L. There was a decrease during the sampling time which was 24 hours after the change in feed concentration to 4 g COD/L (Day

120). This phenomenon can be explained by the secretion of cell-signaling peptides and cyclo-dipeptides (as known as diketopiperazines or DKP) in response to the change in their environment, i.e. a sudden increase in feed load. Another possible reason for the occurrences of amino acids and peptides in the supernatant is the breakdown of cell membrane proteins such as lipoproteins and glycoproteins.

Indoles of higher polarity, including 2-indolecarboxylic acid, 5-hydroxy-L-tryptophan, 5-methoxytryptophan, indoleacrylic acid, cyclobrassinone, tryptamine, 1H-indole-3-carboxaldehyde, alkaloid AQC2, indoleacetic acid, and indole-3-carbinol, were detected using the LC-Q-ToF. The substituted indole derivatives mostly decreased from the first to the fourth, and to the last compartment. Although their concentrations decreased down the ABR, indole-3-carbinol and indoleacetic acid were found in higher quantities compared to the other indole substituted derivatives. In addition to these two compounds, alkaloid AQC2, 5-hydroxy-L-tryptophan, 2-indolecarboxylic acid, 1H-indole-3-carboxyaldehyde and 5-methoxytryptophan had the highest concentrations detected in the last compartment on Day 56 compared to Day 34 and 96. Tryptamine, a known biotransformation product of tryptophan and a common precursor for many hormones and neurotransmitters, was found to increase down the bioreactor, and reached the highest concentration in the last compartment during the initial increase in feed strength (Day 34 and Day 120). These are a handful of the many nitrogen-containing SMPs that were found to increase in response to changes of environment in a bioreactor as the microorganisms adapt to their 'new' surroundings. As such, their potential of becoming DBP might be of importance in designing tertiary treatment process, especially for treatment systems that frequently encounter drastic changes in influent strength. Cyclobrassinone was found to have increased from the 4th to the last compartment for all sampling times and had the highest concentration in the last compartment on Days 56 and 96. This suggested that cyclobrassinone or its isomers could be the end products of tryptophan biotransformation, but there are no studies to prove this yet.

Besides the indole substituted derivatives, hydroxykynurenine, *N*'-formylkynurenine and hydroxyquinoline detected in this experiment are also metabolites of tryptophan but from different pathways (from the indoles) (KEGG). While the formation and accumulation of hydroxykynurenine might increase the possibility of its biotransformation into a neurotoxin, quinolinic acid, or other by-products, this pathway proceeded due to the change in the external environment of the cells which naturally triggers the production of the cell-signaling quinolines that are produced through this metabolic pathway (Bredenbruch et al., 2005).

2'-Hydroxy-4',6'-dimethoxy-3'-methyldihydrochalcone was found to have the highest concentration in the last compartment of the Day 158 samples. Dihydrochalcones are known to be a metabolite from the plant-specific phenylpropanoid pathway, where phenylalanine is converted to coumarin and then dihydrochalcones (Ibdah et al., 2017). Few phenylpropanoids, (Z)-3-Phenyl-2-propenal, hydrocinnamic acid, and 11-Hydroxy-12-methoxydihydrokawain were detected in the Day 158 samples which decrease down the ABR. Their biotransformation pathway is not known, but they could possibly be the intermediates of the pathway that resulted in the accumulation of the dihydrochalcone in the last compartment.

At other sampling points, the total concentration of the accumulated benzene and benzene substituted derivatives was less than half of that detected in Day 158, although in the Day 56 and Day 96 samples a variety of such compounds were found in the last compartment such as synthetic drugs (procarbazine, *N*-acetylprocainamide, tropicamide, olemestran), a natural benzimidazole derivative (5,6-dimethylbenzimidazole, which is a vitamin B_{12} ligand), a plant metabolite (acidissiminol epoxide), and present in more significant amounts, *N*-undecylbenzenesulfonic acid in the Day 56 sample. *N*-undecylbenzenesulfonic acids were also detected in the last compartment on Day 120, but at a lower concentration compared to that detected on Day 56 (highest among all supernatants collected from the last compartment). It was observed that the concentration increased during the initial hike of influent COD load and subsequently decreased, and such benzenesulfonic acids were also found in HRT

shock loads and a SAMBR operating at extreme pH conditions (Kunacheva et al., 2017b). Hence, such compounds will degrade eventually but the time period and extent of degradation remains to be discovered. Such a concentration trend was also observed for dimethylbenzimidazole, the cobalt ligand of vitamin B_{12}.

Previous reports have shown that polysaccharides and polypeptides were the major components of biofoulants. Nevertheless, the methods used for analysing these biofoulants were specific for detection of these two macromolecules and very likely missed identifying other potential biofoulants. A range of lipids were detected in this study using an LC-Q-ToF method developed recently, and this group of compounds might also be responsible for contributing to the fouling processes since they tend to be present even in the last compartment of an ABR operating at an HRT of 24 h.

The metabolism and production of natural products from plants, fungi, algae, and pure strains of microorganisms are well studied, and are still of great interest (Pettit, 2009; Scherlach & Hertweck, 2009). Previous research work involving phylogenetic analysis by Gross et. al. has begun to show the presence of phyto enzymes, such as the super family of type III polyketide synthase, in microorganisms (Gross et al., 2006). As such, there are still undiscovered possibilities of other microorganisms producing such compounds under the stimulation of their varying external environments. This is an area that requires more input and consideration when designing post-treatment processes due to the persistent compounds that remain in the treated water (bioreactor effluent), and in terms of their potential for being precursors to disinfection by-products.

4.4. Conclusions

Chemical characterisation of the supernatants collected down the length of the ABR, representing the various stages of anaerobic treatment, led to the detection of changes in the concentrations of various SMPs. An increase in feed concentration triggered an increase in the production of certain amino acids and their derivatives known to have cell-signalling functions, and the changes in the

production of lipids found in this study had not been noted before in previous work. With a sufficiently long HRT (24 hours), the shift in chemical composition between the sampling dates and down the compartments of the ABR resulted in alkanes and alkenes forming the significantly largest group of SMPs; however, esters, acids, and aromatic compounds decreased as the system approached pseudo-steady state (on Days 96 and 158). Linear alkanes are less reactive compared to their cyclic isomers such as alkenes, carbonyls and aromatic derivatives due to their strong carbon-hydrogen single bond, and lack of reactive sites (such as double bonds, electronegative oxygen and nitrogen atoms that creates a reactive site), hence, they are not expected to further transform in disinfection processes. In fact, linear alkanes of suitable chain lengths are potential sources of biofuel. From the detection of transformation products and intermediates (typically in the 4th compartment of the ABR) over a 24-hour HRT cycle, it shows some of the potential transformation products which can be formed downstream should the HRT becomes shorter. These include : indoles and their derivatives, which are in the metabolic pathway of tryptophans, typically break down over 24 hours (detected in the first but not the last compartment of the ABR); benzophenone (two benzene rings joined by a ketone), a feed degradation product or a phytocompound from secondary metabolism, which remained in the last compartment; epoxides, a reactive hydrocarbon due to the strain in the three-membered cyclic carbon-oxygen-carbon bond hence prone to ring-opening reactions, attributed to the oxidation of unsaturated fatty acids. This study detected the accumulation and disappearance of various chemical compounds, and suggested possible sources and metabolic processes, although there is still much work to be done to understand more about SMP production and catabolism. However, a discussion of the dynamics and transformations of SMPs in anaerobic wastewater treatment systems in this study still lacks any relationship to the microbial communities present in the compartments in which they have been detected.

Chapter 5

Effects of macronutrients on the production of SMPs

5.1. Introduction

Metabolic reactions in biological systems involve cell lysis and regeneration, and the production of enzymes and cofactors for biochemical reactions that enhance cell activity and growth. All these cellular processes require the presence of both macronutrients such as carbon, nitrogen and phosphorus, and trace elements such as cobalt, nickel and iron in their bioavailable form and in the correct proportion to proceed. Research on the bioavailability and uptake of micronutrients in anaerobic processes has been reported extensively (Cao et al., 2018; Wu et al., 2015; Zhang et al., 2015), however, the effects of macronutrients are equally important since they make up the bulk of the nutrients necessary for microbial growth and activity. However, there has been little work carried out on the effect of macronutrients on SMP production, and therefore further studies are required to understand the extent of their influence on bioreactor performance and SMPs.

A study within our group explored the production of SMPs in batch experiments from different macronutrients, and provided an in-depth analysis to find out the proportion of proteins and carbohydrates that were present in the MW fractionated samples (Le et al., 2016; Le & Stuckey, 2016). However, one aspect that was lacking was that batch experiments differ markedly from actual continuously fed reactor systems which are most common in industry. Hence, this led to the aim of this part of the thesis – to provide a more comprehensive analysis of the changes in the chemical composition of SMPs during the anaerobic wastewater treatment of low-strength feeds of different macronutrients, i.e. fructose in place of glucose, and inorganic nitrogen (ammonium chloride) instead of organic nitrogen (meat extract and peptone). This chapter also aims to act as a foundation for understanding more about membrane fouling mechanisms, and hence the experiments are carried out in a membrane bioreactors (MBR). The results from the SMP characterization of the MBR supernatant can be used as a

reference for explaining the membrane fouling characteristics of MBRs, which will be discussed later (Chapter 6).

5.2. Materials and Method

5.2.1. Submerged Anaerobic Membrane Bioreactor (SAMBR)

The SAMBR used in this experiment had a working volume of 3 liters and was made of polymethyl methacrylate (Plexiglas®) (Figure 5.1). A chlorinated polyethylene microfiltration flatsheet membrane module (manufactured by Kubota) with a surface area of 0.116 m^2 and average pore size of 0.2 μm (maximum 0.4 μm) was used. A membrane flux pump (Watsons Marlow) was used to maintain the flux at 15 liters per square meter per hour (LMH). Transmembrane pressure (TMP) was monitored using a digital pressure gauge (Ashcroft). The SAMBR was set to operate at a hydraulic retention time (HRT) of 6 hours controlled using the influent pump. The sludge inoculum was obtained from an anaerobic digester in a wastewater treatment plant (WWTP) in Singapore and cultivated in the batch-fed completely stirred tank reactor described in section 3.2. The initial mixed liquor volatile suspended solids (MLVSS) in the reactor was 6,000 mg/L, and it was operated at a 200-day sludge retention time (SRT). The pH and oxidation-reduction potential (ORP) in the system were monitored using a pH/ORP probe (Mettler Toledo, M300). The pH was maintained in the range of 6.8 and 7.2 using 1 M sodium bicarbonate and 1 M hydrochloric acid; ORP was in the range of -435 ± 33 mV throughout the experiment. The SAMBR was designed with a baffle to direct the liquid flow in an upward direction, past the membrane, and then down the downcomer after gas disengagement (Kunacheva et al., 2017c). The temperature in the reactor was controlled by placing the reactor in a water bath kept at 35±1°C. Biogas was re-circulated at a rate of 6 ± 1 L/min through a stainless steel tube diffuser with four holes which generated coarse bubbles for mixing of the biomass in the reactor and cleaning the surface of the membrane to minimize the rate of membrane fouling. The reactor was continuously fed with the synthetic feed comprised of

glucose, peptone, meat extract, and essential nutrients which had a similar COD to domestic wastewater in Singapore.

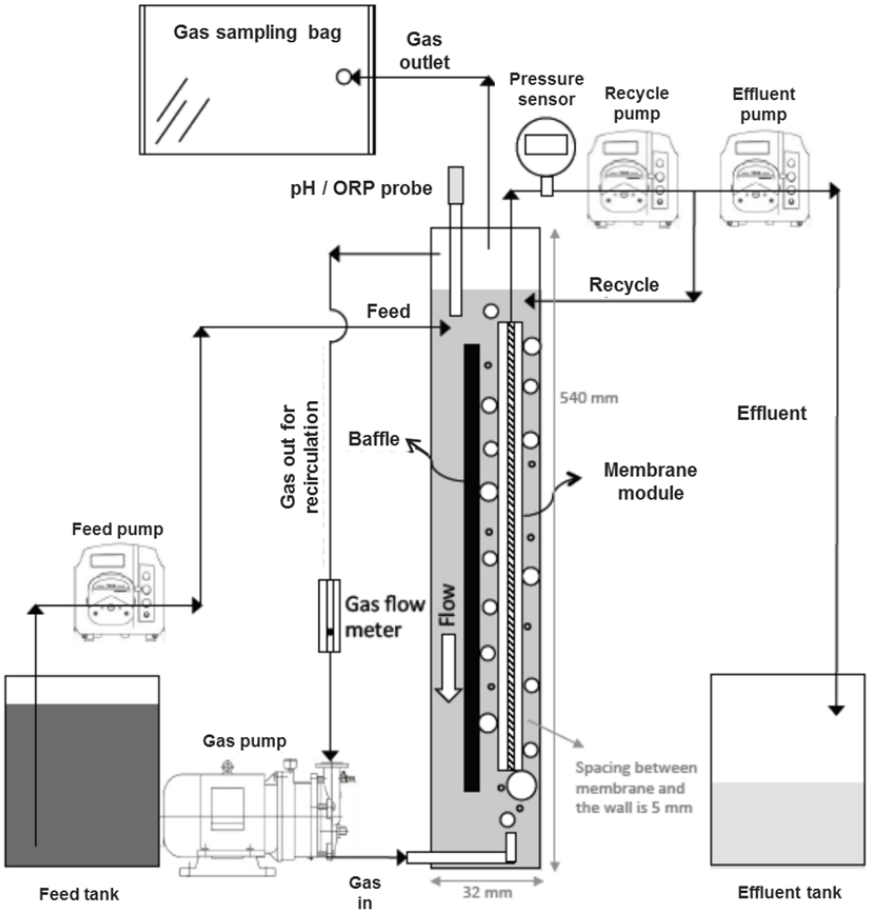


Figure 5.1 Diagram of SAMBR (Kunacheva et al., 2017c)

5.2.2. Feed conditions

The SAMBR was operated under stable conditions (72% – 76% methane produced, COD removal > 90%, no VFAs detected in the effluent) for two weeks, with the continuous feeding of glucose, peptone, meat extract and essential trace elements with a chemical oxygen demand (COD) concentration of 500 ± 20 mgCOD/L (components as per Table 3.1, diluted eighty times to achieve 0.5 gCOD/L) in the initial stage of the experiment. A change in carbon source from glucose to fructose, and nitrogen source from meat extract/peptone to ammonium chloride (Table 5.1) was performed using the same bioreactor, with the influent type switched back to glucose as a carbon source and meat extract/peptone as the nitrogen source and allowed to stabilize for two weeks, between the two sets of experiments. The COD of the inorganic nitrogen influent was 400 ± 20

mgCOD/L as compared to the 500 ± 20 mgCOD/L before the change. This was due to the COD contribution of the organic carbon present in the meat extract and peptone. The decrease in COD was not compensated using glucose or by any other additions since the aim of the experiment was to compare the changes in SMPs due to change from organic to inorganic nitrogen. Any other changes in influent composition might create a different impact.

Table 5.1 SAMBR influent components in the two experiments; change from (top) glucose to fructose, and (bottom) meat extract/peptone to ammonium chloride; highlight rows indicated the (left) initial and (right) changed components.

Component	Concentration for 0.5 gCOD/L influent (mg/L)	Component	Concentration for 0.5 gCOD/L influent (mg/L)
Peptone	102.25	Peptone	102.25
Meat extract	34.25	Meat extract	34.25
Glucose	***341.75***	***Fructose***	***341.75***
$NaHCO_3$	832	$NaHCO_3$	832
K_2HPO_4	10.24	K_2HPO_4	10.24
$CoCl_2.6H_2O$	0.305	$CoCl_2.6H_2O$	0.305
$FeCl_2.4H_2O$	2.01	$FeCl_2.4H_2O$	2.01
$MnCl_2.4H_2O$	0.096	$MnCl_2.4H_2O$	0.096
$Na_2MoO_4.2H_2O$	0.048	$Na_2MoO_4.2H_2O$	0.048
$NiCl_2.6H_2O$	0.058	$NiCl_2.6H_2O$	0.058

Component	Concentration for 0.5 gCOD/L influent (mg/L)	Component	Concentration for 0.5 gCOD/L influent (mg/L)
Peptone	***102.25***	***NH_4Cl***	***15 (TN)****
Meat extract	***34.25***		
Glucose	341.75	Glucose	341.75
$NaHCO_3$	832	$NaHCO_3$	832
K_2HPO_4	10.24	K_2HPO_4	10.24
$CoCl_2.6H_2O$	0.305	$CoCl_2.6H_2O$	0.305
$FeCl_2.4H_2O$	2.01	$FeCl_2.4H_2O$	2.01
$MnCl_2.4H_2O$	0.096	$MnCl_2.4H_2O$	0.096
$Na_2MoO_4.2H_2O$	0.048	$Na_2MoO_4.2H_2O$	0.048
$NiCl_2.6H_2O$	0.058	$NiCl_2.6H_2O$	0.058

*** Total Nitrogen (TN) measured for usual feed containing meat extract and peptone is 15 mg/L, ammonium (NH_4-N) approx. 0.2 mg/L**

The SAMBR was monitored over a period of 24 hours, with sampling for COD, VFA, and SEC analysis before the change in feed type, and 1, 3, 6, 12, and 24 hours after the change. 250 mL was withdrawn from the bioreactor at sampling times 6 (one HRT-cycle) and 24 (four HRT-cycles) hours for SMP analysis. The

"control" of the experiment was internal, i.e. the SMP data was compared to the results obtained before any change.

5.2.3. SAMBR monitoring and analysis of SMPs

The methane gas production, volatile fatty acids (VFAs) and soluble chemical oxygen demand (COD) from the SAMBR were monitored as a measure of reactor performance. Analysis of SMPs were carried out using GC-MS and LC-Q-ToF. The above-mentioned methods of analysis were described in Chapter 3.

Liquid chromatography coupled organic carbon detection and organic nitrogen detection (LC-OCD-OND) was used in this series of experiments. The LC-OCD-OND (DOC-LABOR, Karlsruhe, Germany) is equipped with size exclusion column for separation by molecular size and three detectors, a UV detector (UVD) set at 254 nm, organic carbon detection based on high-sensitivity TOC analysis, and simultaneous organic nitrogen detection, for characterisation of the separated components. The chromatogram data generated by the three detectors are processed using a customized software program (ChromCALC, DOC-Labor, Karlsruhe) to calculate the organic carbon concentrations of biopolymers, humic substances, building blocks, low molecular weight (LMW) acids, and neutrals fractions of NOM based on area integration of the fractional peaks. The detailed method development and specifications of the instrument was reported by Huber et al. (2011) (Huber et al., 2011).

5.3. Results and discussion

5.3.1. COD removal, VFA and methane production, LC-OCD-OND

The pH, COD removal, and methane production when feed type was changed from glucose to fructose did not vary dramatically (Table 5.2). pH of the bioreactor remained in the range of 7.1 - 7.3, the ORP recorded was between -401.1 mV and -467.9 mV, and COD removal was at 86 % - 98 %. This minimal change in COD removal was also observed by Hao and Liao (2015) and Hao et al (2016) when the researchers investigated the effects of change in the

proportion of nitrogen in the feed on sludge properties and membrane fouling of an aerobic MBR (Hao & Liao, 2015; Hao et al., 2016). This shows that both aerobic and anaerobic MBRs can maintain COD removal efficiency with slight changes in their influent nitrogen source.

The minor fluctuations in the parameters monitored were due to disturbances to the system during sample collection when supernatant was drawn out, and then the centrifuged sludge resuspended in buffer solution and returned to the bioreactor. VFAs produced (in supernatant and effluent) comprised of only formic and acetic acid with a total concentration of less than 10 mgCOD/L on the average, and methane composition in the biogas was in the range of 69% - 82%.

SMP (mgCOD/L) = soluble COD of supernatant (mgCOD/L) – VFA (mgCOD/L)

The sample collected six hours after replacing glucose with fructose was found to have the highest COD concentration of SMPs in the supernatant (412.7 mgCOD/L), and (Table 5.2). This was also reflected in the LC-OCD-OND results (Figure 5.2) where the organic carbon detector measuring low MW neutrals and acids was found to be approximately 800 mg-carbon/L (mg-C/L). The ratio increase calculated from total integrated peak area from the GC-MS (Table 3) was 1.14. However, the COD removal remained high at 98%. An increase in VFA concentration in the supernatant was also observed one hour after replacing glucose in the feed with fructose, which continued through the third hour of operation at this feed, and a spike six hours after the change. The methanogenic activity converting VFAs to methane gas resumed at the rate before any change to the system was made, since VFAs were undetected by the twelfth hour.

There is an increase in VFAs in both supernatant and effluent (no VFA removal, VFAs in the range of 2.4 – 3.6 mgCOD/L) three hours after the initial organic nitrogen source was switched to inorganic nitrogen. Effluent VFAs are still detected 24 hours after feeding the SAMBR with ammonium chloride instead of the initial meat extract/peptone. However, there was no change in the other parameters monitored and the LC-OCD-OND results showed no drastic changes. Total biogas volume (collected in a gas bag) measured 24 hours after changing the carbon and nitrogen source type was 1.3 and 0.4 ± 0.1 L, respectively. This

decrease in biogas volume might arguably be due to the decrease in overall influent COD from 500 to 400 ± 20 mgCOD/L, however based on the theoretical conversion of COD to methane (395 mL CH_4/g COD at 35 ^oC, 1 bar) (Kunacheva et al., 2017c), the 100 mgCOD/L difference should only result in a decrease of 39.5 mL of methane gas, whereas from the biogas collected, the difference in the volume of methane gas produced was 666 ± 74 mL. The only other possible reason for this decrease would be the inhibitory action of ammonium chloride.

Biopolymers detected by the size exclusion column in the LC-OCD-OND referred to polysaccharides, proteins and aminosugars larger than 20 kDa (Figure 5.2). In the experimental set where glucose was replaced by fructose, the biopolymers made up 35%-40% of dissolved organic carbon (DOC), except for the sample collected at 6-hours where the biopolymers were only 5% of the DOC, while the bulk was low MW neutrals and acids, and an obvious increase in the concentration of aromatic compounds (detected as 'Building Blocks', referring to oxidation products of humic substances (Huber et al., 2011)). The range of biopolymer (greater than 20 kDa) in terms of concentration in parts per billion of carbon (ppb-C) was 7198-7913 ppb-C. The largest difference between the 6-hour sample and the samples collected from the rest of the time points was the amount of low molecular weight (LMW; molecules below 350 Da) neutrals and acids. After the organic nitrogen in the feed was replaced with ammonium chloride, the total DOC concentration in the range of 12482 – 16725 ppb-C, with 1 hour after the feed change marking the highest concentration and its lowest at 12 hours. Biopolymers made up 35% – 48% of the DOC (6686 – 8197 ppb-C), where the percentage of biopolymers was 48% of the total DOC at all time points except after 3 h (43%) and 12 h (35%).

The robustness of the SAMBR to any change to the system has previously been studied for temperature, HRT and extreme feed conditions, and was generally measured by COD removal, VFA occurence and methane volume/percentage (Chen et al., 2017; Huang et al., 2011; Vyrides & Stuckey, 2009). These previous studies found obvious changes in either one or all the three parameters, and hence decided when the SAMBR was 'stable' and then the reactor was sampled for SMPs.

In this case, the COD removal, VFA and methane production did not obviously increase or decrease i.e. no shock due to changes in feed type. What is interesting is that any changes in the influent composition should be reflected in the system by the theory of mass balances. Previous studies reported the changes in SMPs/EPSs initially by colorimetric methods (such as Lowry's method for 'protein' and phenol-anthrone method for 'polysaccharide' quantification) and then improved to using SEC, FTIR, and EEM-PARAFAC for finding out the shifts in percentage of functional groups in each sample. In this study we report on more comprehensive results using recently developed methods such as GC-MS and LC-Q-ToF to identify SMPs

Table 5.2 SAMBR monitoring (Top: Fructose as carbon source; Bottom: NH_4Cl as nitrogen source).

Fructose as carbon source								
Time (h)	**pH**	**% CH_4**	**ORP (mV)**	**COD removal (%)**	***Sup VFA (mgCOD/L)**	***Eff VFA (mgCOD/L)**	***Sup SMP (mgCOD/L)**	***Eff SMP (mgCOD /L)**
0	7.12	-	-401.1	96	0	0	90.8	17.5
1	7.12	-	-451.0	96	2.5	0	109.6	24.6
3	7.13	-	-450.0	97	3.1	0	113.9	16.9
6	7.18	-	-449.8	98	15.3	1.9	**412.7**	10.0
12	7.17	-	-460.1	97	0	0	82.6	14.0
24	7.15	74	-460.4	95	0	0	82.4	21.4
NH_4Cl as nitrogen source								
Time (h)	**pH**	**% CH_4**	**ORP (mV)**	**COD removal (%)**	***Sup VFA (mgCOD/L)**	***Eff VFA (mgCOD/L)**	***Sup SMP (mgCOD/L)**	***Eff SMP (mgCOD /L)**
0	7.28	-	-467.9	94	0	0	90.9	23.7
1	7.25	-	-432.6	95	0	0	98.2	18.2
3	7.06	-	-447.1	96	2.9	2.5	84.8	13.9
6	7.12	-	-453.5	96	2.7	2.8	137.3	11.4
12	7.18	-	-459.4	96	3.6	3.1	108.0	11.3
24	7.1	74	-453.6	96	2.4	2.5	92.5	14.0

***NOTE: Sup = supernatant; Eff = effluent**

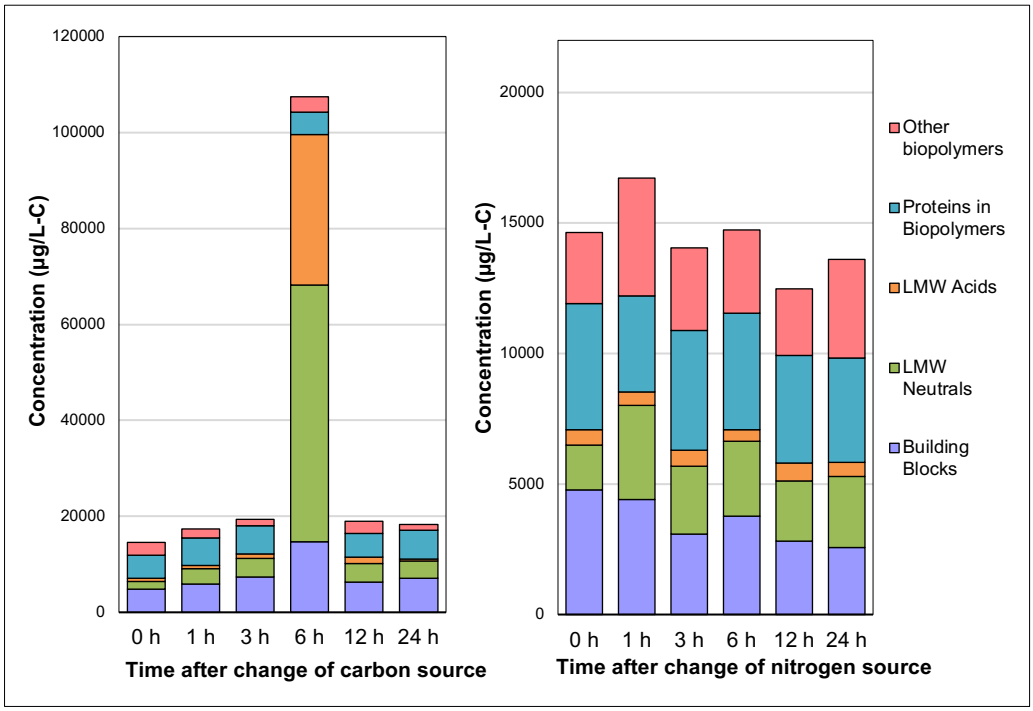


Figure 5.2 Concentration of building blocks (aromatic compounds), low MW neutrals and acids, and biopolymers after the change in carbon source (left) and nitrogen source (right) of the synthetic bioreactor feed.

5.3.2 Changes in SMPs

The COD removal efficiency, pH, and VFA production did not show major fluctuations like those previously reported (Hao & Liao, 2015; Kunacheva et al., 2017b; Kunacheva et al., 2017c; Thanh et al., 2016). From the results of the LC-OCD-OND, the following analysis using GC-MS and LC-Q-ToF revealed the composition of the SMPs and compared the similarities and differences in the compounds detected.

A discussion of the analysis results from GC-MS (section 5.3.2.1) and LC-Q-ToF (section 5.3.2.2) involved samples collected before the change in the macronutrients, and at 6 hours and 24 hours after the change in carbon and nitrogen source type. The abbreviations below are used throughout the discussions in these sections:

F feed – Feed with glucose replaced by fructose

N feed – Feed with meat extract/peptone (organic nitrogen) replaced by ammonium chloride (NH_4Cl, inorganic nitrogen)

Glu – Supernatant collected when operating with glucose feed, 6-hour HRT
F6 – Supernatant collected 6 hours after switching to feed with fructose
F24 – Supernatant collected 24 hours after switching to feed with fructose
N6 – Supernatant collected 6 hours after switching to feed with NH_4Cl
N24 – Supernatant collected 24 hours after switching to feed with NH_4Cl

5.3.2.1 GC-MS analysis

GC-MS analysis of the samples was carried out as described in Chapter 3. The chromatograms generated from the GC-MS were integrated manually and spectrally matched to the NIST11 library for identification, and were only performed for peaks with a signal to noise ratio greater than three. Despite the % COD removal remaining almost constant throughout the experiments, the low MW compounds detected varied between the various samples. A total of 72 – 95 low MW compounds were detected (including unknowns) from the GC-MS; the normalized integrated peak areas of these compounds are presented in Table 5.3 and Figure 5.3, and the number of overlapping and distinct compounds summarised in Figure 5.4. Tables 5.4a-f list the compounds identified from GC-MS analysis and sorted according to their decrease or increase in concentration (integrated peak area) from 6 h to 24 h of the respective feed types, and those compounds which were found only in the supernatant of either of the feed types.

From the normalised integrated peaks areas (Table 5.3, Figure 5.3), the change to different macronutrients was expressed by a surge in the production of different classes of compounds in six hours (one HRT cycle). When glucose in the feed was replaced by fructose, the total concentration of alkenes, esters, acids, aryl compounds, nitrogenous compounds, unknowns and those classified under ‘others’ at least doubled. For the change from meat extract and peptone as a nitrogen source to ammonium chloride with the same total nitrogen content, the concentration of alkanes, acids and unknown compounds doubled, and esters and others increased by more than twice. Out of the total number of compounds detected in all the samples, 62% were found in the samples after the change to fructose or ammonium chloride. Although they occurred in high concentrations in the initial stage, they were undetectable 24 hours later: 21 out of the 37

compounds detected only in the samples collected after the nitrogen source was changed, decreased after 24 hours, of which 17 were undetectable; 21 out of 27 compounds, detected only in the samples collected after the carbon source was changed, decreased after 24 hours, of which 15 were undetectable (Table 5.4c, e). These compounds which became undetectable in the 24-h samples were likely to be the intermediates of metabolic reactions, and included the unknowns which were found after the first HRT cycle after the feed type change. It is known and well-studied that naturally produced fatty acids in the sugar metabolic pathway are even-numbered, typically 16-C and 18-C chain lengths, and the corresponding alkanes in the next steps of the pathway follow the '*n*-1' rule (15-C and 17-C) resulting from the decarboxylation or decarbonylation of the even-numbered fatty acids and fatty aldehydes, respectively (Choi & Lee, 2013; Schirmer et al., 2010). One interesting finding was the changes in alkane composition in our samples where the odd-numbered alkanes (13-C, 15-C, 17-C and 19-C; C refers to carbon) became undetectable 24 hours after the change in feed carbon and nitrogen source. In contrast, the even-numbered 20-C and 22-C alkanes detected only in the samples collected during the fructose feed period (detected in F24), and in the GC-MS results of N-only, the only two alkanes present after 24 hours had carbon chain lengths of between 22-C and 28-C (inferred using retention time of alkane standards). From Figure 5.3, it is obvious that alkanes form a significant proportion of the total concentration of SMPs detected by GC-MS when the organic nitrogen in the feed was first changed to inorganic nitrogen (N6), and then decreased 24 hours later to be around the same concentration as in F24. From Table 5.4f, the alkanes remaining in F24 and N24 are not specific to the metabolic pathways influenced by the changes in the carbon and nitrogen source. In comparison to previous studies conducted by our group, the SMPs in the supernatant of a SAMBR with the same initial feed composition but with different pHs and HRTs (Kunacheva et al., 2017b; Kunacheva et al., 2017c), the SMPs formed from fructose feed are similar (alkanes, and such) while a distinct difference in the SMPs formed from the inorganic nitrogen feed was observed. A number of aldehydes were detected in N24 (Table 5.4e, compounds which showed increment), and from the studies on *E.coli* and cyanobacteria alkane biosynthesis pathways, aldehydes are one of the

metabolic intermediates. This suggests a retardation of the production of alkanes when ammonium chloride is introduced into the system as a nitrogen source.

The spike in supernatant SMP concentration in F6 measured by COD (Table 5.2) was due to the proportional increase in low MW acids and neutrals from the LC-OCD-OND results (Figure 5.2). However, the GC-MS results showed otherwise; the normalised integrated peak area (Figure 5.3) for N6 was higher than F6, and the other peaks areas also did not tally with the COD and LC-OCD-OND results. The most probably reason for this discrepancy would be that this group of compounds are non-volatile/too polar to be detected by GC-MS.

Cyclooctaatomic sulphur (S_8) and cyclohexaatomic sulphur (S_6) were both present in the fructose supernatant (in both samples collected at 6h and 24h). S_6 was present at the same concentration in both F6 and F24, while S_8 in F24 was double the concentration detected in F6. This suggested there is some level of 'shock' due to the switch in feed macronutrient which persisted through four HRT cycles. Previous work investigating the effects of shock-loads on the SAMBR found S_8 in the initial stages of change, but this decreased after the SAMBR returned to its 'steady-state', and elemental sulphur was known to be an intermediate in the biotic or abiotic oxidation of sulphides (Pjevac et al., 2014; Troelsen & Jorgensen, 1982). The accumulation (hence detection) of elemental sulphur in the samples indicated incomplete metabolism; the metabolism was expected to follow the microbial sulphur cycle in which end products are hydrosulphides or sulphate ions, and these forms of sulphur are not detected by the GC-MS analysis developed for this study. The presence of zero-valence sulphur suggested the presence of green and/or purple photosynthetic sulfurobacteria in the system (Fang et al., 2020). A LC-Q-ToF similarity search (section 5.3.2.2) suggested six other sulphur-containing compounds at different concentrations in the SAMBR supernatants and in the feed (Table 5.5). Although these sulphur compounds were not detected in large amounts, the variety of sulphur compounds detected are those available for microorganism utilisation and produce hydrogen sulphide, sulphates and thionates as intermediates or end-products depending on their utilisation (oxidation or reduction),demonstrating the diversity of reactions by the microorganisms.

Table 5.3 Normalised total integrated peak areas of the SMPs using a heat map showing the concentration difference between (a) the chemical classes within each sample; (b) initial and after changing to fructose feed, (c) initial and after changing to NH_4Cl feed.

		Alkane	Alkene	Ester	Acid	*N	Alcohol	Aryl	Other	Unknown
(a)	Glu	156	9	15	11	3	21	38	9	33
	F6	88	22	31	40	9	11	71	24	73
	F24	62	8	16	24	3	4	19	22	15
	N6	292	8	69	22	1	29	14	37	65
	N24	57	8	30	16	4	2	22	30	49
(b)	Glu	156	9	15	11	3	21	38	9	33
	F6	88	22	31	40	9	11	71	24	73
	F24	62	8	16	24	3	4	19	22	15
(c)	Glu	156	9	15	11	3	21	38	9	33
	N6	292	8	69	22	1	29	14	37	65
	N24	57	8	30	16	4	2	22	30	49

*N refers to Nitrogenous compounds

Highest Lowest

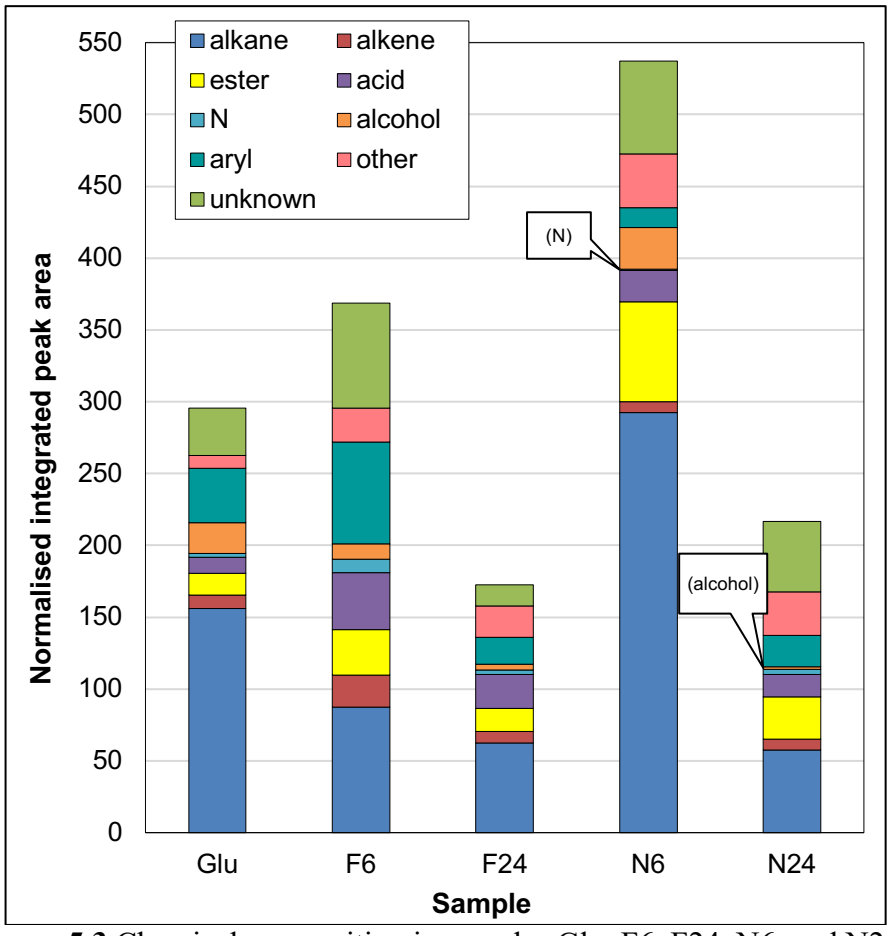


Figure 5.3 Chemical composition in samples Glu, F6, F24, N6, and N24. (corresponding to Table 5.3a)

One striking feature is the case with which thiosulfate and tetrathionate are interconverted and the catalytic versatility of the enzymes associated with their metabolism. Perhaps the metabolism of these compounds involves cyclic mechanisms (metabolic cycle) which enable the cell to generate oxidizing or reducing power depending on cellular needs regarding the regeneration of electron carriers or processing of nutrients such as metal cofactors. The extreme pH changes associated with the metabolism of tetrathionate might also be used to advantage in the manipulation of the proton gradient across the cell membrane (Barrett & Clark, 1987; Sass et al., 1992).

From these two experiments, although fructose has the same atomic composition ($C_6H_{12}O_6$) of glucose, its metabolic route is different due to the difference in their molecular structure (glucose is a hexose, fructose is a pentose). It is expected that if a system had been continuously fed with fructose, the switch to other simple sugars would result in the same effect as observed here. As with the experiment on nutrient availability of organic and inorganic nitrogen, ammonium chloride (inorganic nitrogen) although added in the same concentration measured by total nitrogen, it induced an inhibitory action, retarding the glucose metabolism and hence the detection of intermediate aliphatic aldehydes and the 'disappearance' of alkanes over a period of 24 hours. This was also observed by Hao et al (2016) who studied the effects of COD:N ratios on the sludge properties of an aerobic MBR, where FTIR detected a significant increase in the signal at 1735 cm^{-1} which indicated the presence of an aliphatic aldehyde when the ratio of COD:N was reduced from 100:5 to 100:2.5 (Hao et al., 2016).

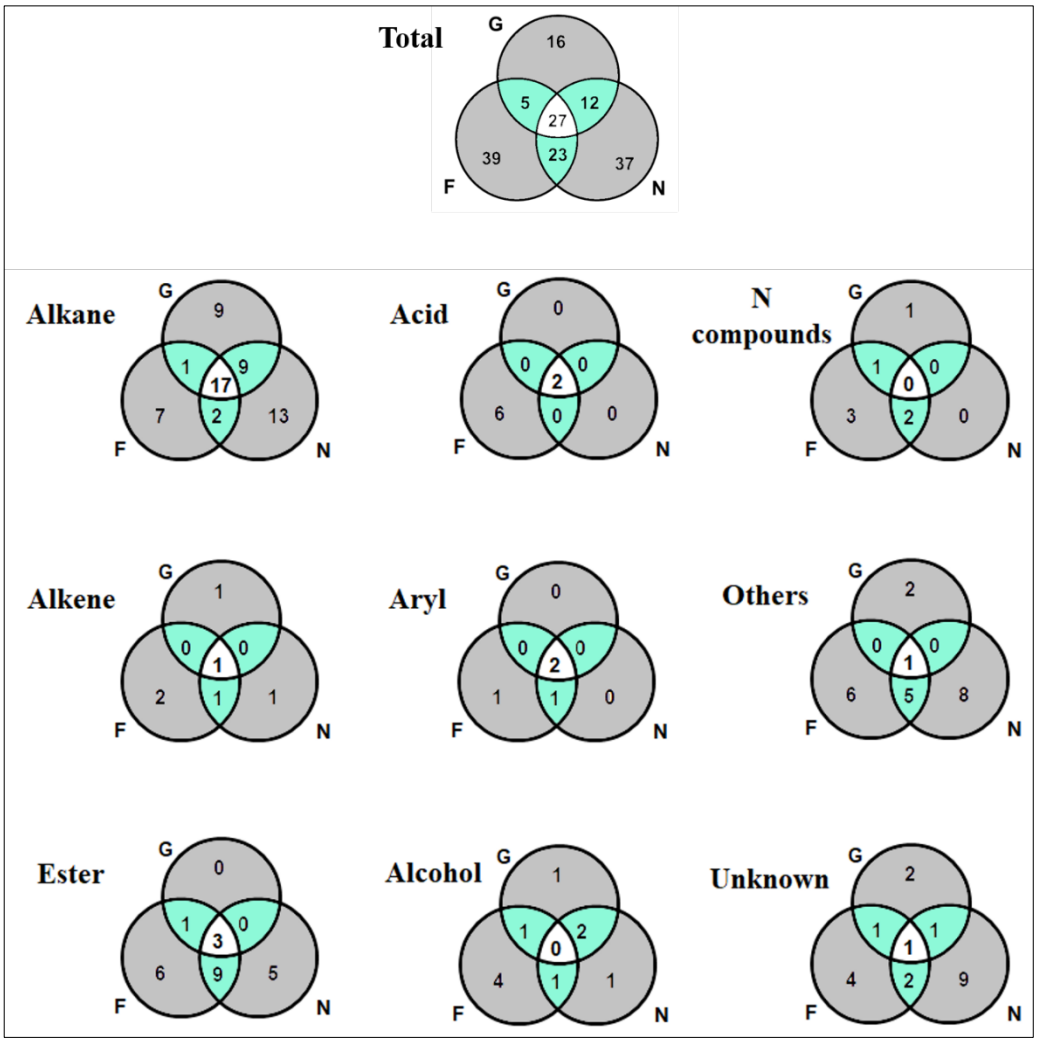


Figure 5.4 Number of overlapping and distinct compounds detected with different SAMBR influents (G = initial glucose-organic nitrogen feed; F = glucose replaced with fructose; N = meat extract/peptone replaced with NH_4Cl.

Table 5.4 Compounds identified (a) before change of feed nutrient, and (b) before and 6 h after changing glucose to fructose; (c) Compounds detected only after changing to fructose; (d) Compounds identified before and after changing organic nitrogen to inorganic nitrogen source; (e) Compounds detected only after changing to inorganic nitrogen feed; (f) Compounds present in all samples except before the changes in macronutrient.
Note: % increase or % decrease †6 hours after, and *from 6 to 24 hours after the change in macronutrient.

a) Glucose only

Chemical class	Name	RT (min)
alkane	alkane	34.452
alkane	5-methyl-undecane	16.988
alkane	2,6,11,15-Tetramethylhexadecane isomer	28.764
alkane	alkane	32.592
alkane	alkane	37.205
amide	cis-11-Eicosenamide	42.228
alkane	2,6,11,15-Tetramethylhexadecane isomer	28.057
alcohol	2-Octyl-1-dodecanol	34.873
others	7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione derivative	33.084
alkane	Squalane	40.183
alkane	8-Hexylpentadecane	32.732
others	Methyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate	31.847
alkane	alkane	39.797
alkene	4-methyl-1-undecene	17.002
unknown	unknown (m/z 43 57 71 85 112)	17.004
unknown	unknown (m/z 57 71 85 99)	21.188

b) Fructose and glucose only

Chemical class	Name	RT (min)	% Increase (% Decrease)†
alcohol	alcohol (m/z 43 59 83 141)	17.921	100 %
alkane	2-methylhexacosane	41.166	(50 %)
ester	Dioctyl hexanedioate	37.840	100 %
N	alkyl amide	35.095	(41 %)
unknown	**unknown (m/z 57 41 165 177 67 205 220)**	**23.931**	**(100 %)**

c) Fructose only

Chemical class	Name	RT (min)	% Increase (% Decrease)*
acid	(9E)-9-Hexadecenoic acid	31.682	10 %
acid	11-(Z)-octadecenoic acid	34.527	100 %
alcohol	2-octyl-1-dodecanol isomer	34.470	100 %
aldehyde	Heptadecanal isomer (RI 1701)	27.699	22 %
alkane	[6-Cyclopentyl-3-(3-cyclopentylpropyl)hexyl] cyclohexane derivative	37.698	100 %
alkane	5-methylundecane	17.005	7 %
alkane	Eicosane	32.487	100 %
alkane	Docosane	35.230	100 %
amide	9-(Z)-Octadecenamide	37.479	51 %
amide	Nonadecanamide/13-(Z)-Docosenamide	42.240	44 %

ester	Hexadecanoic acid, 15-methyl-, methyl ester	31.457	30 %
ester	Methyl 2-hexyl-cyclopropaneoctanoate (RI 1941)/ Methyl 7(Z)-Hexadecenoate (RI 1886)	31.172	47 %
ester	2,2,4-Trimethyl-1,3-pentanediol diisobutyrate	26.244	30 %
ester	Methyl cyclopentanetridecanoate / Methyl stearate	34.314	8 %
ester	Methyl 12-methyl-tetradecanoate	29.478	100 %
other	Cyclic hexaatomic sulfur	24.795	2 %
others	Cyclic octaatomic sulfur	33.819	45 %
unknown	unknown (m/z 64 160 96 224)	29.853	9 %
acid	Pentadecanoic acid	29.990	(2 %)
acid	Tridecanoic acid	26.706	(10 %)
acid	**cis-9-octadecenoic Acid**	**34.470**	**(100 %)**
acid	**Tetradecanoic acid**	**28.842**	**(100 %)**
alcohol	**3-Hexadecanol**	**29.011**	**(100 %)**
alcohol	**2-Hexyl-1-decanol isomer**	**28.760**	**(100 %)**
alcohol/N	6-Nitrohexan-2-ol	17.935	(58 %)
alkane	Dotriacontane	46.126	(12 %)
alkane	**Heptadecane**	**27.860**	**(100 %)**
alkane	**9-octyl-heptadecane**	**38.952**	**(100 %)**
alkene	**1-Octadecene**	**29.374**	**(100 %)**
alkene	**(8E)-8-Methyl-8-heptadecene**	**29.074**	**(100 %)**
aryl	**Benzophenone derivative**	**26.990**	**(100 %)**
ester	**Vinyl stearate derivative**	**49.114**	**(100 %)**
ketone	**2-Hexadecanone**	**28.943**	**(100 %)**
N	**N,N-Diisopropyl-2-propen-1-amine**	**16.007**	**(100 %)**
others	Hexathiane	24.715	(10 %)
others	2,4,7,9-Tetramethyl-5-decyn-4,7-diol	22.788	(41 %)
unknown	**unknown (m/z 55 43 71 143 178 413 430)**	**49.944**	**(100 %)**
unknown	**unknown (m/z 91 43 57 233)**	**30.020**	**(100 %)**
unknown	**unknown (mz 191 57 74)**	**24.685**	**(100 %)**

d) Organic and inorganic nitrogen source only

Chemical class	Name	RT (min)	% Increase (% Decrease) †
alcohol	n-Pentadecanol	29.371	100 %
alcohol	**1-Nonadecanol isomer**	**33.860**	**(100 %)**
alkane	Hexatriacontane	50.380	(77 %)
alkane	alkane	34.997	(85 %)
alkane	alkane	53.460	(77 %)
alkane	**9-Methylnonadecane**	**32.034**	**(100 %)**
alkane	**Nonadecane**	**31.417**	**(100 %)**
alkane	**2-methylhexacosane**	**40.248**	**(100 %)**
alkane	**alkane**	**32.271**	**(100 %)**
alkane	**3-methyltridecane isomer**	**21.824**	**(100 %)**
alkane	**3-methyl-pentadecane/5-propyl-tridecane**	**25.023**	**(100 %)**
unknown	**unknown (m/z 130 117 43 57 101 267 399)**	**41.031**	**(100 %)**

e) Inorganic nitrogen source only

Chemical class	Name	RT (min)	% Increase (% Decrease)*
aldehyde	Hexadecanal (RI 1800)	29.218	40 %

aldehyde	Tetradecanal derivative	26.437	34 %
aldehyde	cis-9-Hexadecenal (RI 1808)	29.524	71 %
aldehyde	Tetradecanal (RI 1601)	25.783	100 %
aldehyde	aldehyde	28.173	100 %
ester	Methyl 10-methylheptadecanoate (RI 2013)/ methyl-cyclopentaneun-decanoate	32.503	34 %
ester	Methyl 14-methyl-pentadecanoate (RI 1814)	30.896	13 %
ester	Methyl pentadecanoate	29.907	100 %
unknown	unknown (m/z 70 43 55 168)	21.044	6 %
unknown	unknown (m/z 43 70 55 168)	20.553	19 %
unknown	unknown (m/z 85 43)	39.092	76 %
unknown	unknown (m/z 85 43)	37.735	79 %
unknown	unknown (m/z 85 43)	38.200	80 %
unknown	alkene/alcohol	33.878	100 %
unknown	unknown (m/z 57 43 71 95 207 191 267)	51.860	100 %
unknown	unknown (m/z 57 43 71 239 267)	49.104	100 %
alcohol	**2-(E)-tridecen-1-ol**	**25.779**	**(100 %)**
alkane	alkane	41.154	(51%)
alkane	alkane	35.089	(67 %)
alkane	**8-Methylheptadecane isomer**	**28.047**	**(100 %)**
alkane	**5-Ethyl-5-methylnonadecane**	**34.541**	**(100 %)**
alkane	**alkane**	**40.169**	**(100 %)**
alkane	**Tetracontane**	**57.614**	**(100 %)**
alkane	**Decane isomer**	**12.634**	**(100 %)**
alkane	**Pentadecane**	**24.269**	**(100 %)**
alkane	**alkane**	**25.096**	**(100 %)**
alkane	**alkane**	**19.900**	**(100 %)**
alkane	**3-methyl-undecane**	**17.344**	**(100 %)**
alkane	**2,6-dimethyl-undecane**	**16.692**	**(100 %)**
alkane (halogenated)	**1-Iodohexadecane**	**34.444**	**(100 %)**
alkene	**7-methyl-3-(E)-undecene**	**17.285**	**(100 %)**
ester	**alkyl propenoate**	**36.507**	**(100 %)**
ester	**methyl ester**	**22.652**	**(100 %)**
others	2,6-Di-tert-butylbenzoquinone isomer	23.919	(36 %)
others	1,2-epoxyhexadecane	27.690	(98 %)
others	**2,6-Ditert-butyl-4-methylphenyl methylcarbamate**	**33.074**	**(100 %)**
unknown	**unknown (m/z 130 117 43 57 101)**	**38.748**	**(100 %)**

f) Compounds identified in F6, F24, N6, and N24 (not present in Glu)

Chemical class	Name	RT (min)	F6, F24 % Increase (% Decrease)*	N6, N24 % Increase (% Decrease)*
alcohol	2-octyl-1-dodecanol isomer	34.470	100 %	100 %
aldehyde	**Dodecanal**	**22.661**	**(100 %)**	**51 %**
aldehyde	**1-Pentadecanal isomer**	**27.681**	**(100 %)**	**100 %**
aldehyde	Heptadecanal isomer (RI 1701)	27.699	22 %	71 %

alkane	5-methylundecane/3-ethyl-5-methylheptane	17.005	7 %	(91 %)
alkane	2-methyl-nonadecane	32.510	(50 %)	12 %
alkene	trans-Squalene isomer	42.669	(43 %)	(51 %)
amide	Nonadecanamide/13-(Z)-Docosenamide	42.240	44 %	100 %
aryl	**(1,3,3-Trimethylnonyl) benzene**	**28.053**	**(100 %)**	**100 %**
ester	2,2,4-Trimethyl-1,3-pentanediol diisobutyrate	26.244	30 %	(1 %)
ester	Methyl-tetradecanoate isomer (RI 1680)	28.313	(51 %)	26 %
ester	Methyl-pentadecanoate	29.339	(32 %)	38 %
ester	Methyl-12-methyl-tetradecanoate	29.478	100 %	71 %
ester	Methyl-7(Z)-Hexadecenoate isomer	31.172	47 %	45 %
ester	Methyl-15-methyl-hexadecanoate isomer	31.436	(38 %)	100 %
ester	Methyl-15-methyl-hexadecanoate isomer	31.457	30 %	44 %
ester	Methyl-9(Z)-Octadecenoate (RI 2085)	34.067	(39 %)	41 %
ester	Methyl-cyclopentane-tridecanoate isomer	34.314	8 %	10 0%
ketone	**16-Hentriacontanone**	**46.984**	**(100 %)**	**100 %**
N	**2-Pyrrolidinone derivative**	**14.635**	**(100 %)**	**49 %**
others	Cyclic octaatomic sulfur	33.819	45 %	25 %
unknown	Pentadecanal isomer/E-2-Tetradecen-1-ol	27.550	(43 %)	42 %
unknown	**unknown (m/z 236 57 162 251)**	**27.888**	**(100 %)**	**100 %**

5.3.2.2. LC-Q-ToF analysis

The LC-Q-ToF method used was as described in Chapter 3. This method covered compounds with an m/z from 50 up to 1200 (polar metabolites) and 2000 (lipids), and identification with reference to the Human Metabolome Database (HMDB), LipidMaps, *E. coli* metabolites library and ChEBI. The compounds suggested had the highest overall score calculated using the Progenesis software based on isotope similarity and mass error. In this experiment, the chromatographic peaks of the top 200 abundant peaks from the LC-Q-ToF runs of lipids and polar metabolites in both positive and negative ionisation mode were identified (Appendix Table A3).

As with the findings from the LC-Q-ToF results of the ABR samples (Chapter 4), lipids form a significant portion of the top 200 compounds identified. The plots of principal component analysis (PCA) (Figure 5.5) showed the similarities/differences in the analytes detected by the LC-Q-ToF metabolites and lipids extracts of all the samples. The components of the metabolite fractions in the supernatant samples (N6, N24, F6, F24, Glu) were distinctively different from the feed, but were similar between the supernatant samples. A significant difference between the samples collected during the glucose-fructose experiment and the organic-inorganic nitrogen experiment was observed in the lipid extracts; N6 and N24 were still in close proximity in the PCA plots of lipid analysis in both positive and negative modes, while F6, F24 and, Glucose (Glu) varied significantly. In comparison with the ABR samples (operating at 24-h HRT instead of 6-h HRT in this set of experiments), fatty acyls (with fatty acids and conjugates as the major composition) are the biggest group in these samples, whereas sphingolipids, glycerophospholipids, purines and derivatives, and amino acids and their analogues form the majority in the N6 and N24 samples (Figure 4.4, Figure 5.6). The production of dipeptides decreased 6 hours after the change in carbon and nitrogen sources in the two experimental sets. Cyclic dipeptides are known to be cell-signalling molecules, but the dipeptides detected in this study are linear and hence are most likely metabolic intermediates and cell wall components.

Glycerolipids, glycerophospholipids, and sphingolipids were present in the SAMBR supernatant at the start of the experiments, but not detected in F6 and F24; however, their concentrations increased when the organic nitrogen source was replaced with ammonium chloride (N6, N24 samples). The lipid raft model, which is a newer perception of cell membrane structure from Singer-Nicholson's fluid mosaic model, postulates that the membrane is a random sea of lipids with protein structures in various positions. This model proposes embedded structures of sphingolipids and cholesterol in the lipid bilayer, with organised proteins which function as signalling molecules and signal transducers, which change in size and composition in response to intracellular or environmental stimuli (Pike, 2003; Simons & Toomre, 2000). Sphingolipids and glycerophospholipids (classification of sphingolipids shown in Figure 5.7a) are found in high

concentrations in the samples collected when the SAMBR was operating with an inorganic nitrogen feed (Figure 5.6), even though approximately 85% of the total number of sphingolipids decreased from N6 to N24. There are different types of mechanisms of lipid rafts that can be present in the cellular lipid bilayer, "Hedgehog" being one of the mechanisms. This mechanism assumes that the membrane structure (in the form of the lipid raft model) mutates and releases a signal to several cell layers away from its original cell (Simons & Toomre, 2000). The phenomenon observed in this experiment can then be explained: a spike in the number of sphingolipids and glycerophospholipids and their concentrations is due to the release of the lipid rafts during the change in feed (affecting cell environment), and their concentration decreased by N24 demonstrating its adaptability to a 'new' cell environment. Of those sphingolipids which remained in the N24 samples, approximately 80% were ceramides which are hydrolysis by-products of sphingomyelin (an additional phospho-ethanolamine group on the 1-hydroxy of the backbone structure). These ceramides can be synthesized *de novo* from serine and palmitate, participate in the biosynthesis of glycosphingolipids and gangliosides (ceramide with oligosaccharide residue on 1-hydroxy position), and holds key functions in cellular signals for inducing apoptosis (cell death) (The Human Metabolome Database). The presence and the decreasing trend of ceramides, also known as N-acylsphinganines (Figure 5.6), in N6 and N24 samples might explain the detection of aldehydes in N24 sample besides incomplete metabolism to alkane formation and the elevated elemental sulphur concentration in the F6 sample (section 5.3.2.1 GC-MS analysis).

Goyaglycoside c was identified in the F24 sample, as reflected in the high concentration of 'steroids and derivatives' in Figure 5.6. This compound is a cucurbitacin glycoside which is part of the steroids and steroid derivatives family; however the reason for their occurrence in anaerobic systems remained unknown.

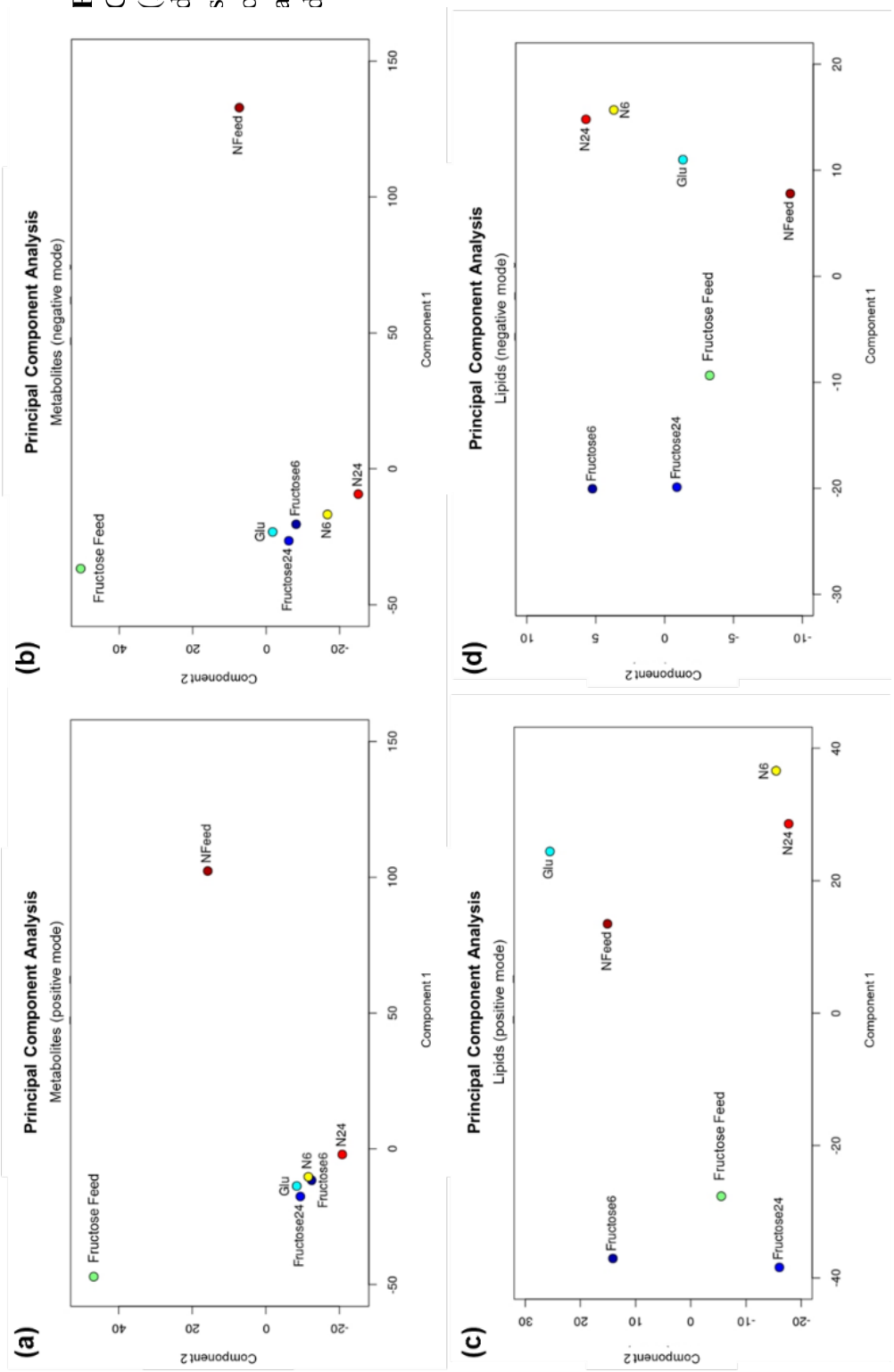


Figure 5.5 Principal Component Analysis (PCA) of the SMPs detected using LC-Q-ToF showing the similarities or differences in the analytes detected in the different samples.

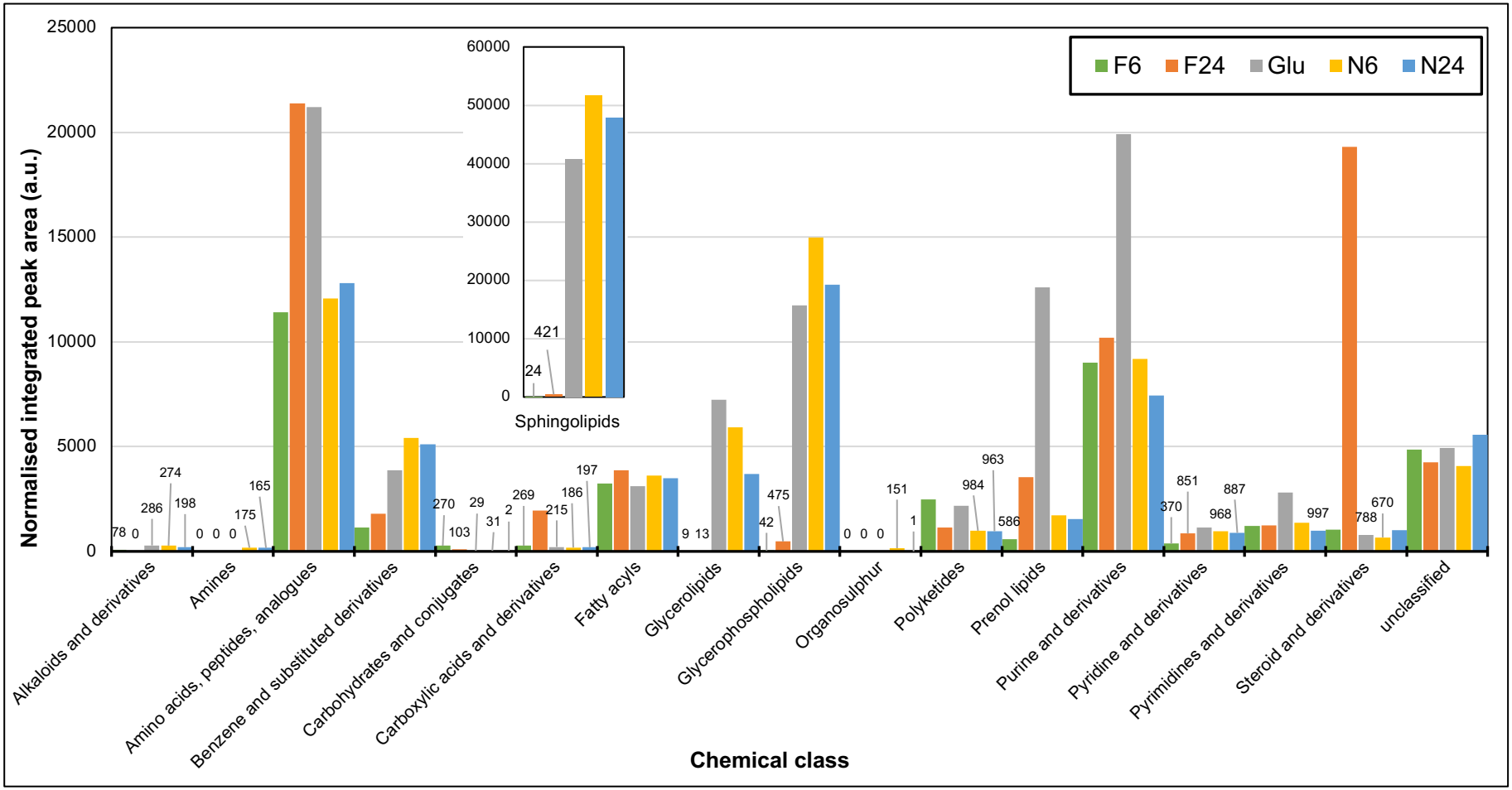
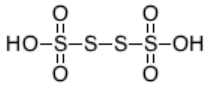
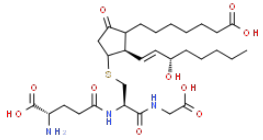
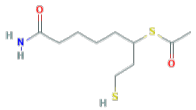
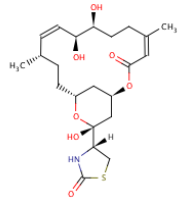


Figure 5.6 Integrated peak areas of each chemical class in the samples

Table 5.5 Sulphur compounds detected in the LC-Q-ToF

Compound	Chemical formula	Structure	Chemical class	Normalised integrated peak area						
				Glu	Fructose feed	F6	F24	Inorganic N feed	N6	N24
tetrathionic acid	$H_2O_6S_4$		Sulphur oxoacid	35	48	2.2	8.9	1.4	459	4.5
S-(PGA1)-glutathione	$C_{30}H_{49}N_3O_{10}S$		Amino acids, peptides, analogues	90	4656	116	186	not detected	125	136
S-Acetyldihydro-lipoamide	$C_{10}H_{19}NO_2S_2$		Fatty acyls - fatty amides (primary amides)	1421	538	1213	1023	4736	1339	1599
latrunculol A	$C_{22}H_{33}NO_7S$		Macrolide - thiazolidines	350	12024	319	388	1.0	396	402

Amoxicilloyl-butylamine	$C_{20}H_{30}N_4O_5S$		Thiazolidinemono-carboxylic acid	782	2166	1861	2713	1064	662	991
Cephalexin(1^-)	$C_{16}H_{16}N_3O_4S^-$		beta-lactam	113	42	100	85	2722	37	29

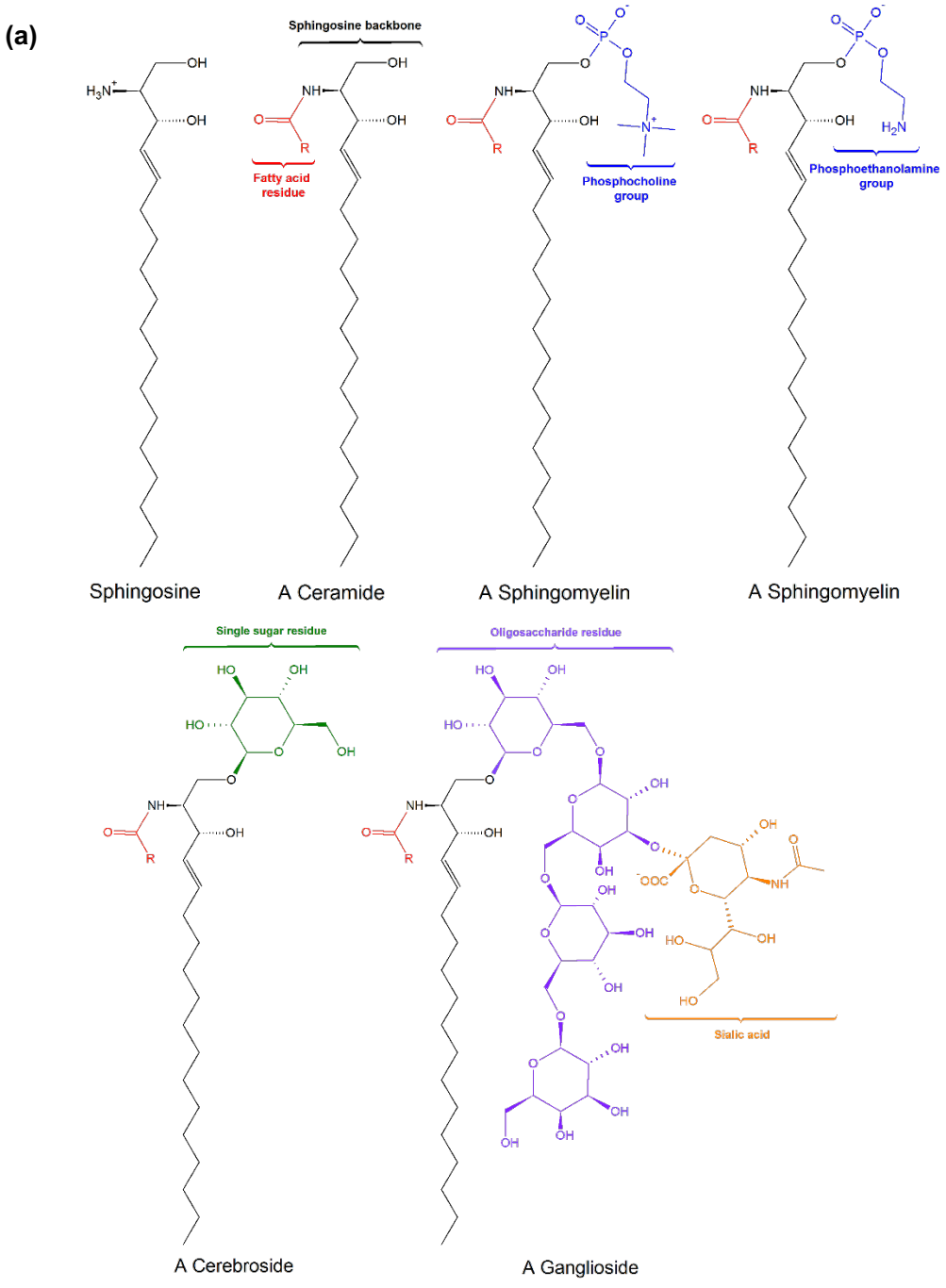


Figure 5.7 (a) Structures of sphingolipids (reference: https://en.wikipedia.org/wiki/Sphingolipid#/media/File:Sphingolipids_general_structures.png), (b) proposed degradation of amino alcohol moiety (Lisovskaya et al., 2012).

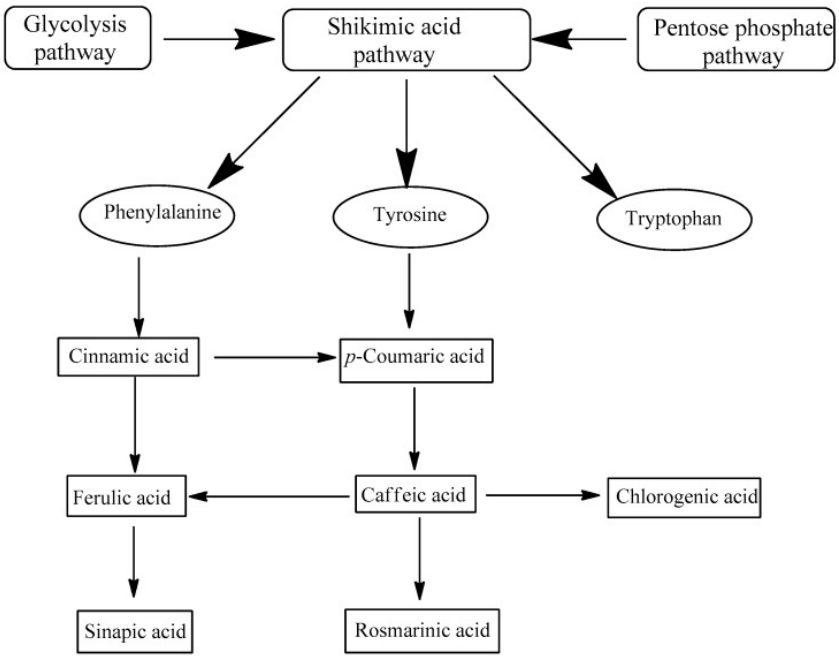


Figure 5.8 Biosyntheic pathway of cinnamic acid and hydroxy-cinnamic acid in a cell (Taofiq et al., 2017)

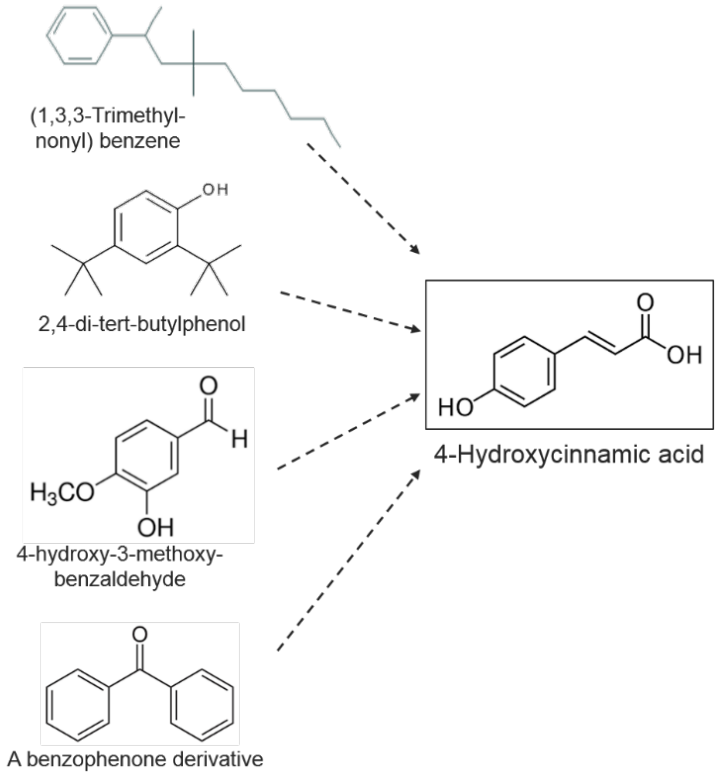


Figure 5.9 Proposed transformation of four aryl compounds to 4-hydroxy-cinnamic acid

4-Hydroxycinnamic acid was at the highest concentration in the F24 sample. Hydroxycinnamic acid is a well-studied phenylpropanoid for its biosynthesis of lignins and other cell wall components of plants, as well as for bioengineering of microbes for its production since it has pharmaceutical properties and a precursor industrial chemical (Mäkelä et al., 2015; Taofiq et al., 2017; Vargas-Tah & Gosset, 2015). The metabolic pathway proposed its biosynthesis from L-phenylalanine and L-tyrosine. The common aromatic pathway from glucose through phosphoenolpyruvate, and then further enzymatic reactions to biosynthesize L-phenylalanine and L-tyrosine, and finally cinnamic acid and its hydroxylated derivative was proposed for bioengineering of bacteria to produce the phenylpropanoids (Figure 5.8). In the conversion of glucose to phosphoenolpyruvate, fructose-6-phosphate was a metabolic intermediate. From our experiment where glucose had been replaced by fructose, the switch in the carbon source possibly triggered the metabolic pathway, and hence the surge in production and release of the hydroxycinnamic acid into the cell environment.

Further with reference to the GC-MS data, F6 was found to have the highest concentration of aryl compounds consisting of 4-hydroxy-3-methoxy-benzaldehyde, 2,4-di-tert-butylphenol, a benzophenone derivative, and (1,3,3-trimethylnonyl) benzene. From these compounds detected, the occurrence of 4-hydroxycinnamic acid in F24 might have been a transformation product of the four aryl compounds (Figure 5.9) which dropped significantly in concentration from F6 to F24 (Table 5.3).

5.4. Conclusions

In this study, the composition of SMPs was examined for changes in the type of carbon and nitrogen source in an anaerobic bioreactor treating low-strength synthetic wastewater. The findings in this series of experiments highlighted the fact that although the usual bioreactor performance monitoring parameters, effluent COD and VFA, did not reflect major fluctuations in the system when the nitrogen source was changed from organic to inorganic, underlying changes in biochemical reactions resulted in changes in the chemical characteristics of

supernatant SMPs. On the other hand, the change in the feed carbon source from a hexose to a pentose monosaccharide did trigger a surge in the supernatant COD and SMP concentrations due to the difference in the metabolic pathways of the two types of monosaccharides; however, the system recovered within 24 hours (decrease in supernatant COD). The compounds with increments from 6 hours to 24 hours after the change in macronutrient were generated by microorganisms in response to these changes, and different metabolic pathways were affected as shown from the SMPs detected in the two sets of experiments.

Cyclooctaatomic sulphur was detect when the carbon source was initially changed. This indicated the disruption of the stability of the system, although this appeared to be the only major change when switching from a hexose to a pentose sugar. In contrast, the switch from an organic to an inorganic nitrogen source did not affect the metabolic pathway of the oxidation of sulphides. A sudden increase in the concentration of hydroxycinnamic acids was explained by an increase in the production of this metabolic intermediate due to the change in the usual biosynthetic pathway of L-phenylalanine and L-tyrosine. Another possibility was the biotransformation from aryl compounds accumulated during the initial change in carbon source type.

Finally, a distinctive appearance of aldehydes in the sample collected 6 hours after the organic nitrogen source was changed to ammonium chloride reflected the retardation of glucose metabolism (aliphatic aldehydes were metabolic intermediates in this pathway). A further decrease in alkane concentration of the sample collected 24 hours later enhanced this phenomenon.

The robustness of the SAMBR allowed the system to recover quickly from changes in process conditions. In order to further investigate the process of change in SMPs, it would be better to increase the HRT or to run the experiment in an ABR, which allows for the segregation of the stages of the anaerobic treatment process.

Chapter 6

Effects of changes in influent macronutrient on membrane fouling and chemical characteristics of foulant

6.1 Introduction

Membrane bioreactors were introduced in the 1960s and the development of membrane technology flourished over the next decade due to its significant advantage of high-quality effluents and small footprint (smaller reactor volume for the same loading rate) compared with "normal" treatment reactors. Unfortunately, membrane fouling is inevitable due to the deposition of colloids and soluble materials from the sludge and wastewater, and hence the fouling potential has always been a consideration in the design of wastewater treatment bioprocess and the fabrication of membrane modules suitable for biological treatment of wastewater (Le-Clech et al., 2006). To determine the effect of colloids produced during the pH shock on membrane fouling, our group carried out membrane fractionation of the bulk supernatant collected when the pH of a SAMBR influent was changed. A membrane fouling test was then carried out using the fractionated supernatant as the influent and the transmembrane pressure was measured over 24 hours to determine the fouling rate (Kunacheva et al., 2017b); however, the fouling layer was not characterized. Lyko et al characterized the soluble extracellular polymeric substances in a full-scale municipal membrane bioreactor using Dubois and Lowry methods for the photometric analysis of carbohydrates and proteins, respectively, dissolved organic carbon (DOC), and size-exclusion chromatography (SEC). The chemical properties deduced from these methods were correlated with the filtration performance as a method of characterization of foulants in the liquid phase, but was still insufficient as a characterization method of membrane foulants (Lyko et al., 2008). Studies later on used more advance methods such as EEM for chemical

characterization, as described in Chapter 2, but this method only considered the analytes with light absorbing moieties.

The characterization of membrane foulants might not be a direct solution for membrane fouling in MBRs, but nonetheless provides insights into the substances (foulants) to be dealt with. In this study, the membrane foulants were characterized in more detail using LC-Q-ToF to determine their compositions.

6.2 Materials and methods

6.2.1 Sample preparation – membrane filtration

The samples used for the membrane fouling tests were collected from the feed-change experiments described in Chapter 5. Supernatants collected from both experimental sets (change from glucose to fructose; change from organic nitrogen to inorganic nitrogen) were filtered through 5µm, 1µm, 0.45µm, 0.1µm, and 100 kDa mixed cellulose ester membrane filters (Advantec, Toyo Roshi Kaisha Ltd., Japan).

6.2.2 Fouling test set-up

A cross-flow set-up (50 mL working volume) was designed with a similar configuration to the SAMBR, with gas sparging underneath the membrane section (4 × 2 cm) to control membrane fouling (Figure 6.1). The flowrates of the influent and effluent were set such that the set-up was operating at a 6-hour HRT and a critical flux of 24 LMH, which was the same operating condition as the SAMBR. Fractionated samples (5µm, 1µm, 0.45µm, 0.1µm, and 100 kDa) were used as a feed for this reactor to evaluate which colloid size had the most effect on membrane fouling; in this case 5µm represented the colloids smaller than 5µm. A virgin piece of identical membrane to that used in the SAMBR was used in every test, and the TMP was recorded using a sensitive pressure sensor and a datalogger (Graphtec Midi Logger GL 220, Ohio, USA) on the permeate side. Each fouling test was run from a TMP of -2 kPa to -20 kPa; ultrapure water was used as the influent for the first 24 hours to measure membrane resistance before

each set of tests. If fouling did not occur after 15 days, the gas recycle line (Figure 6.1 (D) gas inlets and (E) gas outlet) were turned off to speed up the process of fouling. A parallel run was set-up to check the repeatability, and the different increases in TMP between the identical set-ups were within ±0.74 kPa. Since the repeatability was high between the two parallel runs, the fouling test for each sample was not repeated.

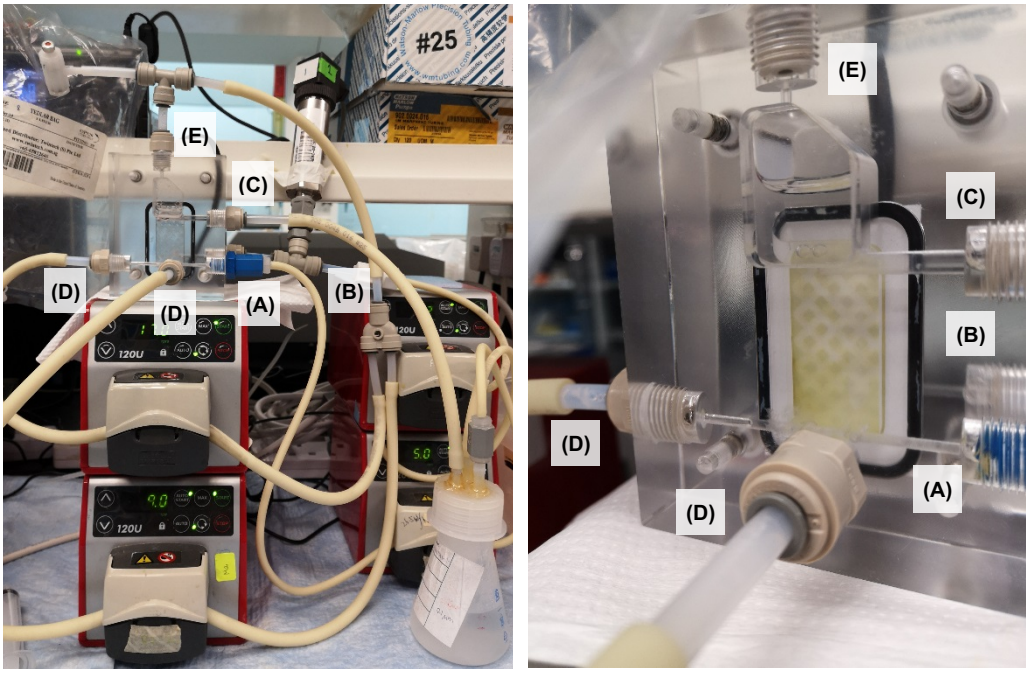


Figure 6.1 Fouling test set-up (left) and a close-up view of the set-up (right); labelled (A) Influent, (B) Effluent, (C) Recycle, (D) Gas inlets, (E) Gas outlet.

6.2.3 Chemical characterization of foulant

This experiment focused on the chemical characterization of the foulant. When the TMP recorded reached -20 kPa, the run was stopped and the membrane removed. The fouling layer on the membrane surface was washed and gently brushed off using a toothbrush, into a clean tube using 15 mL of ultrapure water. 10 mL of the foulant washed from the membrane surface was freeze-dried and analysed using LC-Q-ToF (method as described in Chapter 3).

6.3 Results and discussion

The LC-OCD-OND analysis was comprised of organic carbon and organic nitrogen detection after size-exclusion chromatography. The method identifies biopolymers with a MW greater than 20 kDa (sum of 'Other biopolymers' and 'Proteins in biopolymers'), compounds with aromatic structures ('Building blocks') in the MW range of 300 to 1000 Da, and low MW (LMW) acids and uncharged compounds from 300 to 500 Da (Figure 6.2). From the LC-OCD-OND results, the total dissolved organic carbon in fractions larger than 0.45μm were higher in the sample collected when organic nitrogen (meat extract and peptone) was replaced by inorganic nitrogen (ammonium chloride). Comparing the rate of fouling (Figure 6.3) for the larger size fractions (0.45 - 1 μm, 1 - 5 μm, and > 5 μm), the fractions collected from both fructose and ammonium chloride feed experimental sets fouled at almost the same time when the ultrapure water (for measuring membrane resistance) was changed to the sample fractions. A slight delay in the fouling rate was observed for the 1 - 5 μm fraction from the fructose feed experiment. The obvious difference in the general composition of these two 1- 5 μm fractions was the higher percentage of low MW neutrals and biopolymers other than proteins in the sample from the ammonium chloride feed experiment. The fouling rates of the 100 kDa – 0.1 μm and 0.1 – 0.45 μm fractions were different for the samples collected from the two sets of feed change experiments. The 100 kDa – 0.1 μm fraction from the ammonium chloride feed experiment increased at a much slower rate compared to that from the fructose feed experiment. Their difference in the LC-OCD-OND results was the higher concentration of low MW neutrals in the fructose feed experiment sample. The fouling rates were directly opposite for the 0.1 – 0.45 μm fraction. The difference observed from the LC-OCD-OND results was similar: higher concentration of low MW neutrals in the ammonium chloride feed experiment sample. From these results, it suggested that the low MW neutrals (300 – 500 Da) might played a significant role in the rate of fouling.

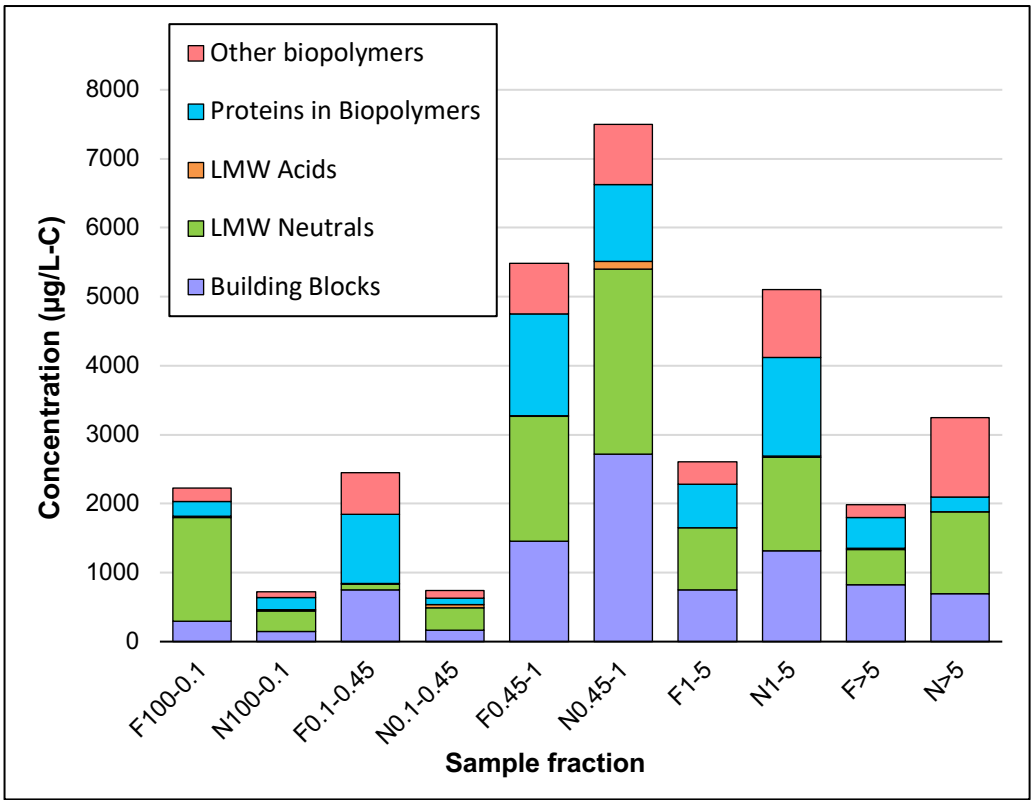


Figure 6.2 LC-OCD-OND results of the sample fractions used for fouling tests.

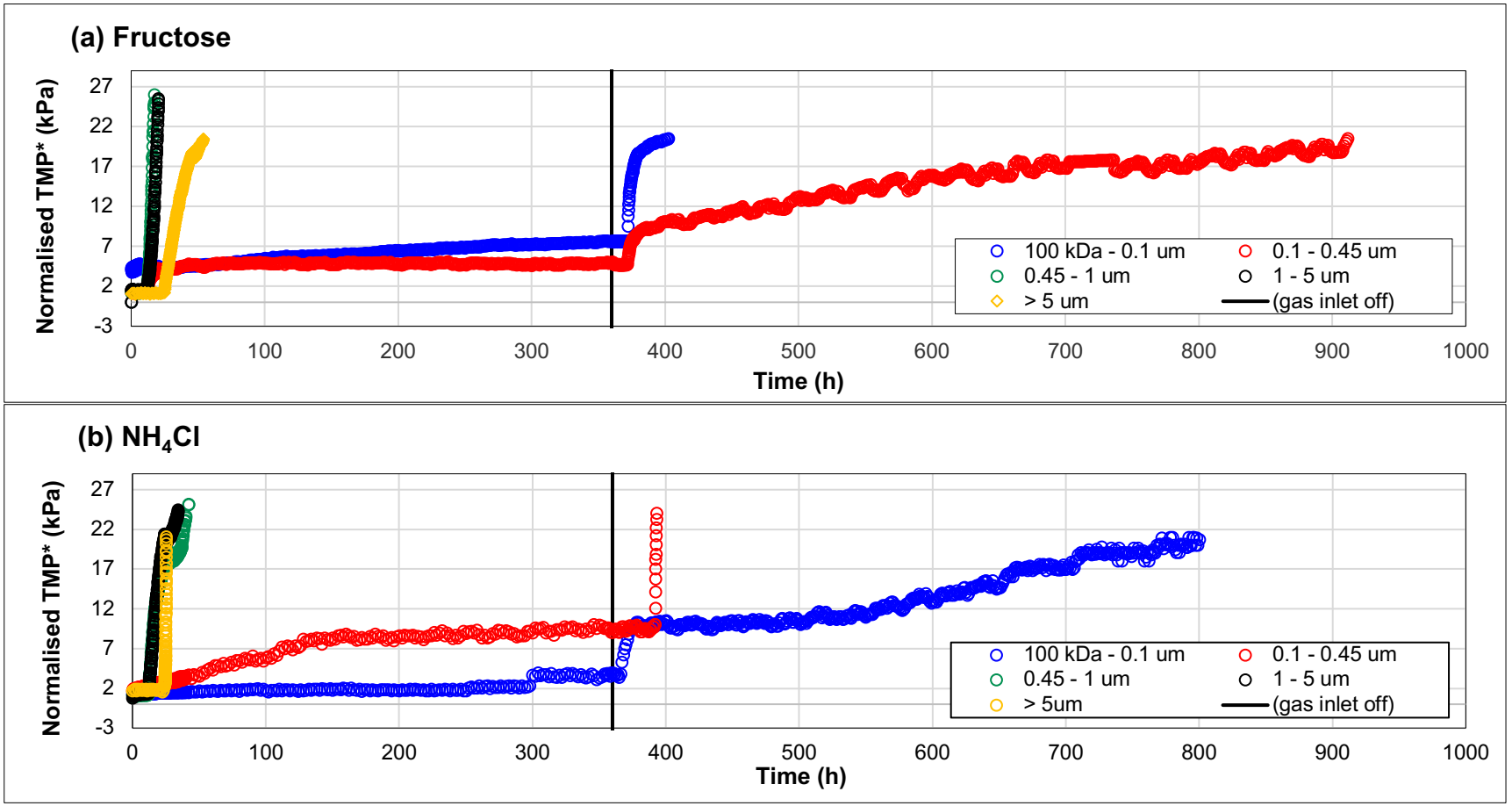


Figure 6.3 Fouling rates of sample fractions from supernatants collected when SAMBR was operating with (a) fructose and (b) ammonium chloride feed; 'gas inlet off' refer to turning off of the gas recycle line on Day 15; *TMP – transmembrane pressure.

6.3.1 Chemical characterisation by LC-Q-ToF

The LC-Q-ToF analysis in Chapter 5 detected the SMPs in the bulk supernatant collected during the process of change in macronutrient type in the SAMBR influent. The bulk supernatant was further fractionated by its MW as described in Section 6.2, using filters of various pore sizes. These fractions were then used as the influent in a small membrane set-up which mimicked the operation of the 3-L lab scale SAMBR, in the absence of sludge, to measure their fouling potential (Figure 6.1). The concentration inferred from the integrated peak area may not tally with the low MW acids and neutrals from the LC-OCD-OND results (Figure 6.2) due to the MW of the compounds detected; the low MW from the LC-OCD-OND covered the range of 300 – 500 Da, whereas for the LC-Q-ToF it included compounds from 50 to 2000 Da.

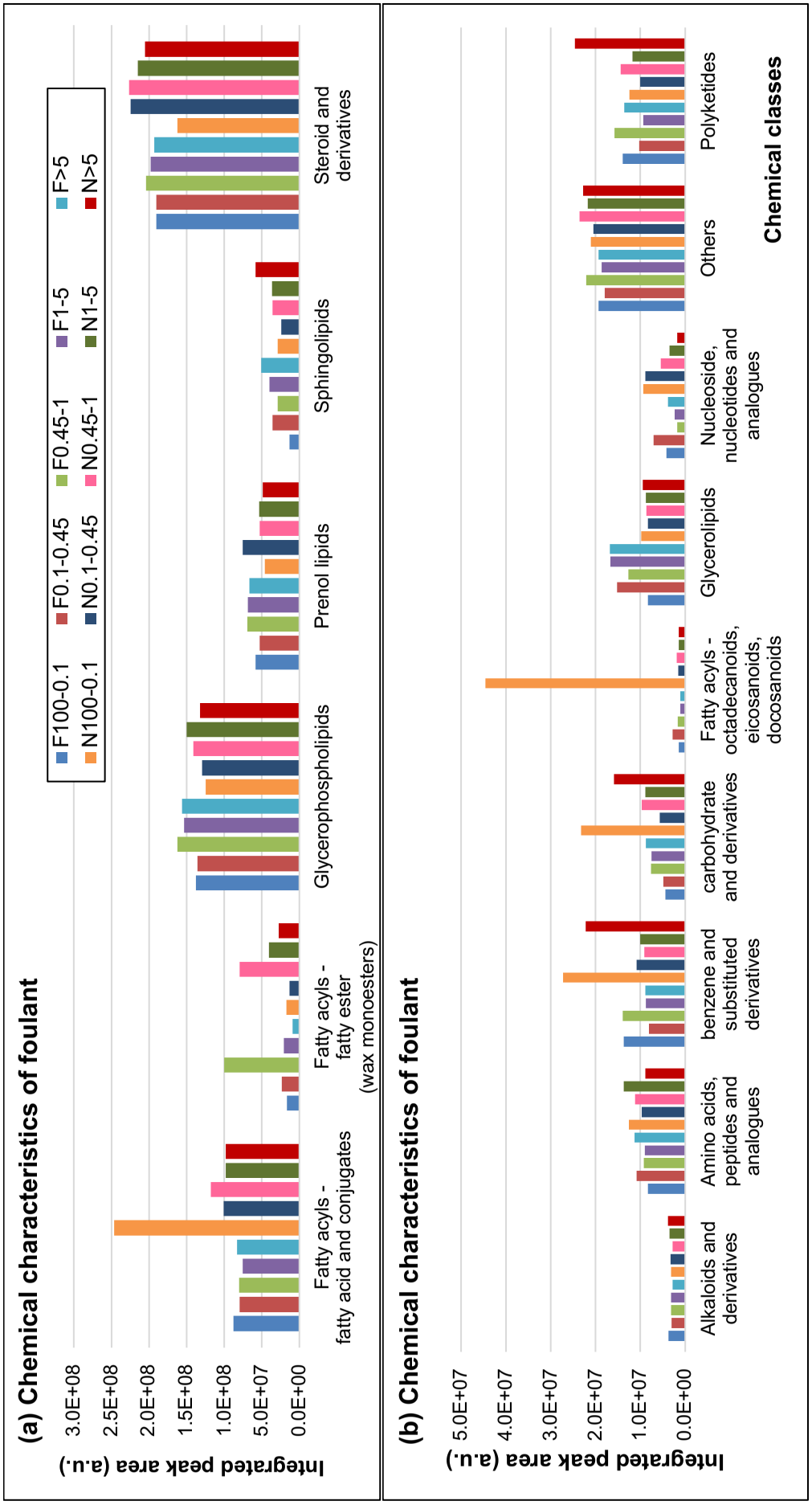
LC-Q-ToF of the fouling layer revealed the composition and the different chemical classes of compounds present (Appendix A4) – past research tends to only mention 'polysaccharides', 'proteins', and their MW distribution, due to limitations in the extraction and characterization methods available. Some research groups used EEM, but this method only show the functional groups with absorbance properties. Figure 6.4 (a-d) presented the abundance of each chemical class detected in the fouling layer washed from the membrane surface after the TMP reached -20 kPa. From normalised TMP plots in Figure 6.3, the rates of fouling, where the influent were the fractions larger than 0.45 µm, were not affected by the scouring effect from the gas recycle stream and fouled (TMP reached -20 kPa) within 48 hours. 0.1 – 0.45 µm and 100 kDa – 0.1 µm were the two smallest size fractions, and the normalized TMP remained below 10 kPa after 15 days of the run. These membranes fouled only after the gas recycle line was turned off (removed the scouring effects from the gas bubbles from the gas inlets). The fraction F 0.1 -0.45 µm and N 100 kDa – 0.1 µm fouled within 48 hours after the gas recycle line was turned off; F 0.1 – 0.45 µm took 4 days more to reach -20 kPa compared to N 100 kDa – 0.1 µm. We try to explain the contrast in the two smallest fractions which fouled the membranes last, but there was no significantly higher or lower abundance in any class of compounds detected in the foulants except from the N 100 kDa – 0.1 µm fraction (Figure 6.4 a-d and

Table 6.2). The fatty acids and their conjugates, and eicosanoids, octadecanoids and dodecanoids were found to be in the MW range of 200 – 299 Da; its benzene and substitutes, and carbohydrates and derivatives were detected highest in MW 300 – 399 Da. In comparison to the findings on the MW range 500 – 599 Da, prenol lipids might be a potential foulant but were in the lower MW range as detected in the foulants from F 100 kDa – 0.1 µm and N 0.1 – 0.45 µm hence the delayed fouling effects (fouling started after the gas recycle line was turned off). These compounds, although in high concentrations, were at the lower end of the MW distribution, hence they had minimal effects on membrane fouling, as shown in Figure 6.3, where the accumulation of the foulants in the absence of scouring effects from the gas recycle line took approximately 10 days.

The further breakdown of the LC-Q-ToF results into various MW ranges (Table 6.1 and 6.2) found that the MW range of the compounds identified in the foulants were highly concentrated in the range of 200 – 799 Da. For the 100 kDa – 0.1 µm fractions which do not foul the membrane under normal conditions, there was a comparatively higher concentration of compounds in the 200-299 Da and 300-399 Da range. In the 300-399 Da range, the compounds with significantly higher concentrations were C_{24} to C_{26} Mycosanoic acid (fatty acid with total 24 to 26 carbon atoms), 3-hydroxy-*cis*-5-octenoylcarnitine (fatty acyl carnitines), Piperochromenoic acid (monoterpenoid); In the 200-299 Da range, the compounds with significantly higher concentrations were Sulfamethazine and [4-(3-oxopentyl)-phenyl]-oxidanesulfonic acid (benzene and substituted derivatives), Myristic acid and 11-amino-undecanoic acid (fatty acids and conjugates). A majority of the high abundance compounds identified in the 200 – 299 Da range were fatty acids and conjugates.

Of the fractions which fouled the membrane within 48 hours, the 0.45 – 1 µm fraction from both the supernatants collected from the SAMBR operating with different carbon and nitrogen source showed the highest concentration in the MW range of 400 – 499 Da (Table 6.2).

The significantly high concentration of fatty acyl glycosides in F 0.45 – 1 µm membrane foulants (Figure 6.4c) were found to be in the MW range 300 – 399 Da only (Table 6.2); Indoles and derivatives in the F > 5 µm and N 1 – 5 µm


(a) Chemical characteristics of foulant
Integrated peak area (a.u.)
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
F100-0.1
F0.1-0.45
F0.45-1
F1-5
F>5
N100-0.1
N0.1-0.45
N0.45-1
N1-5
N>5
Fatty acyls - fatty acid and conjugates
Fatty acyls - fatty ester (wax monoesters)
Glycerophospholipids
Prenol lipids
Sphingolipids
Steroid and derivatives
(b) Chemical characteristics of foulant
Integrated peak area (a.u.)
5.0E+07
4.0E+07
3.0E+07
2.0E+07
1.0E+07
0.0E+00
Alkaloids and derivatives
Amino acids, peptides and analogues
benzene and substituted derivatives
carbohydrate and derivatives
Fatty acyls - octadecanoids, eicosanoids, docosanoids
Glycerolipids
Nucleoside, nucleotides and analogues
Others
Polyketides
Chemical classes

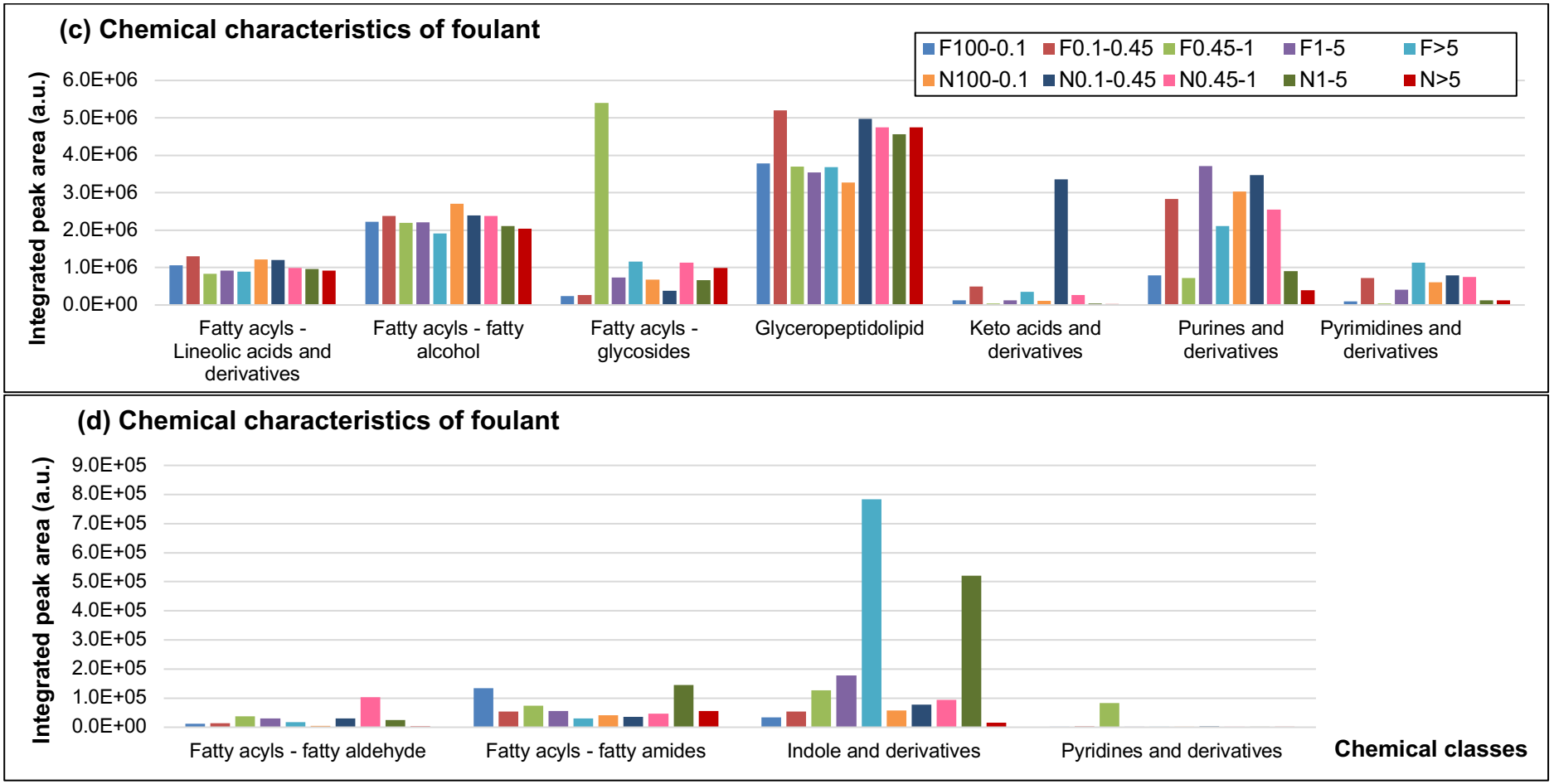


Figure 6.4 (a-d) Results from LC-Q-ToF analysis of foulants (first 200 analytes with the highest integrated peak area).

Table 6.1 Normalised integrated peak area of the compounds (of different MW) detected in the foulants.

	Compounds detected by LC-Q-ToF (classified by MW range)										
	< 100 Da	**100 – 199 Da**	**200 – 299 Da**	**300 – 399 Da**	**400 – 499 Da**	**500 – 599 Da**	**600 – 699 Da**	**700 – 799 Da**	**800 – 899 Da**	**900 – 999 Da**	**> 1000 Da**
F 100 kDa- 0.1 µm	3	294	2834	1799	2800	887	5627	5248	97	22	144
F 0.1 - 0.45 µm	5	482	2605	1171	2782	1478	5669	5340	147	89	736
F 0.45 – 1 µm	7	278	2648	1655	5729	2005	5945	6476	133	23	137
F 1 – 5 µm	4	411	2346	1156	2808	2560	5788	6131	219	46	144
F > 5 µm	7	455	2560	1197	2744	2449	5934	6387	175	31	135
N 100 kDa - 0.1 µm	1	546	9456	2378	2746	1410	4920	5088	109	60	157
N 0.1 - 0.45 µm	5	588	3099	2245	2971	1528	6398	4893	132	21	372
N 0.45 – 1 µm	12	403	3587	1425	5496	1558	6793	5743	67	31	171
N 1 – 5 µm	4	386	2983	1372	4022	1326	6562	6140	64	29	165
N > 5 µm	26	201	3513	1769	3468	1674	6504	5685	82	49	173

NOTE: 'F' – samples collected from fructose-fed SAMBR, and 'N' – samples collected from ammonium chloride- fed SAMBR in Chapter 5

Table 6.2 Summary of compounds detected in the foulants from the membrane fouling tests conducted using different sample fractions. The compounds categorised into the different chemical classes were further charaterised by MW range as presented below.

MW range of suggested compounds	**Compounds detected**
> 1000 Da	▪ Sphingolipids detected in elevated concentrations in the foulants from F 0.1 – 0.45 µm and N 0.1 – 0.45 µm fractions; ▪ Approximately the same concentration of glyceropeptidolipids in foulants from all fractions. This could be where the detection of high 'protein' concentration comes from, in this case the high signal intensity from the colorimetric 'protein' quantification was likely from the peptide groups attached to the glyceropeptidolipids.
900 – 999 Da	▪ High concentrations of : 1. glycerophospholipids and glycerolipids in N 100 kDa – 0.1 µm foulant; 2. glycerophospholipids in N > 5 µm and F 0.1 – 0.45 µm foulants; ▪ Sphingolipids and steroids and steroid derivatives are almost equal in concentration for all foulant samples.
800 – 899 Da	▪ Glycerolipids higher in abundance in the foulants from smaller fractions, and ▪ Glycerophospholipids higher from foulants of fractions larger than F 0.45 µm and fractions smaller than N 0.45 µm.
700 – 799 Da	▪ High concentration of glycerophospholipids in all foulants sampled; ▪ Concentration of prenol lipids approximately equal in all foulants sampled.
600 – 699 Da	▪ Steroids and derivatives detected in dominantly high concentration in all foulant samples.
500 -599 Da	▪ Highest concentration of : 1. sphingolipids in the foulant from N >5 µm; 2. steroids and derivatives in the foulant from N 0.1–0.45 µm; ▪ Prenol lipids, sphingolipids and steroids and derivatives were found in relatively higher concentrations in the foulants from the F > 0.45 µm fractions.

400 499 Da	▪ Highest concentration of fatty esters detected in foulants from F 0.45 – 1 μm and N 0.45 – 1 μm; ▪ Glycerophospholipids, fatty acids and conjugates, and steroids and derivatives about equal in all foulants sampled.
300 – 399 Da	▪ Highest concentrations of : 1. benzene and substituted derivatives, carbohydrates and derivatives, fatty acids and conjugates, and eicosanoids, octadecanoids and dodecanoids in foulants from N 100 – 0.1 μm; 2. fatty esters in foulants from F 100 kDa – 0.1 μm and N > 5 μm; 3. polyketides in foulant from N > 5 μm; 4. prenol lipids in foulants from F 100 kDa – 0.1 μm and N0.1 – 0.45 μm (highest across all samples); 5. fatty acyl glycosides in foulant from F 0.45 – 1 μm.
200 – 299 Da	Fatty acids and conjugates in approximately equal concentrations in all foulants from the fractionated supernatant collected from the SAMBR operating in fructose feed; concentration was highest in N 100 kDa – 0.1 μm while approximately the same for the other foulants, its concentration was 10 times higher than that detected in the 300 – 399 Da range.
100 – 199 Da	▪ Highest concentrations of : 1. amino acids, peptides and analogues in foulants from F0.1 – 0.45 μm and N 1 – 5 μm; 2. benzene and substituted derivatives in foulants from F 100 kDa – 0.1 μm and N 1 – 5 μm; 3. keto acids and derivatives in foulant from N0.1 – 0.45 μm; 4. nucleosides, nucleotides, and derivatives in foulants from F0.1 – 0.45 μm and N 100 kDa – 0.45 μm fractions; 5. purines and derivatives in foulant from F 1 – 5 μm, F 0.1 – 0.45 μm, F > 5 μm, and N 100 kDa – 0.45 μm fractions.

Table 6.3 Compounds of high abundance in F 0.45 - 1 μm and N 0.45 - 1 μm membrane foulants.

Suggested compounds (MW 400 - 499 Da)	Chemical formula	Chemical class
2-Methylacetophenone	$C_{20}H_{38}O_7S$	Fatty acyls - Fatty acid esters
PA(21:4(6Z,9Z,12Z,15Z)/0:0)	$C_{24}H_{41}O_7P$	Glycerophospholipids
Pentacosanoylglycine	$C_{27}H_{53}NO_3$	Amino acids, peptides and analogues
Chamuvaritin	$C_{29}H_{24}O_5$	Polyketides
5,7-dihydroxy-3-[3-hydroxy-4-methoxy-5-(3-methylbut-2-en-1-yl)-phenyl]-8-(3-methylbut-2-en-1-yl)-4H-chromen-4-one	$C_{26}H_{28}O_6$	Polyketides
Melagatran	$C_{22}H_{31}N_5O_4$	Others - azetidine (C3N ring)
17-O-deacetylvindolinium	$C_{23}H_{31}N_2O_5^+$	Alkaloids and derivatives
Sodium deoxycholate	$C_{24}H_{39}NaO_4$	Steroids and derivatives
Eplerenone	$C_{24}H_{30}O_6$	Steroids and derivatives
1-Hydroxyprevitamin D3 diacetate	$C_{31}H_{48}O_4$	Steroids and derivatives
Calicoferol D	$C_{28}H_{42}O_2$	Steroids and derivatives
Cholesterol sulfate	$C_{27}H_{46}O_4S$	Steroids and derivatives

foulants (Figure 6.4d) span over 100 – 299 Da. Due to the smaller MW range of these compounds, they might be neglected as the cause of membrane fouling. In this series of membrane fouling tests and chemical analysis of the fouling layer, these lower MW analytes were found to be at a relative high concentration in the sample fractions between 0.45 µm to 5 µm. More importantly, these fractions resulted in membrane fouling within 48 hours.

6.3.2 Anti-fouling natural products?

Two set-ups running in parallel (using the sample fraction N > 5 µm as influent) had the transmembrane pressure increasing at the same rate for the first 76 hours. Subsequently, the TMP started to increase in Set-up 1 (TMP last recorded was -24 kPa) faster than in Set-up 2 (TMP remained at 10 kPa) until the data-logging was stopped at 100-hours. Set-up 2, which did not show signs of fouling from the TMP recorded, had a layer of algae on the membrane surface, and this suggested the possibility that the algae may have had anti-fouling properties. The fouling layers on the membrane surface were washed down with ultrapure water for LC-Q-ToF analysis (sample preparation and method analysis is the same as for the other analyses in this Chapter), to check for the differences in the chemical properties of the foulant. In the following discussion, the foulant on the membrane from Set-up 1 and 2 are referred to as Foulant 1 and Foulant 2, respectively.

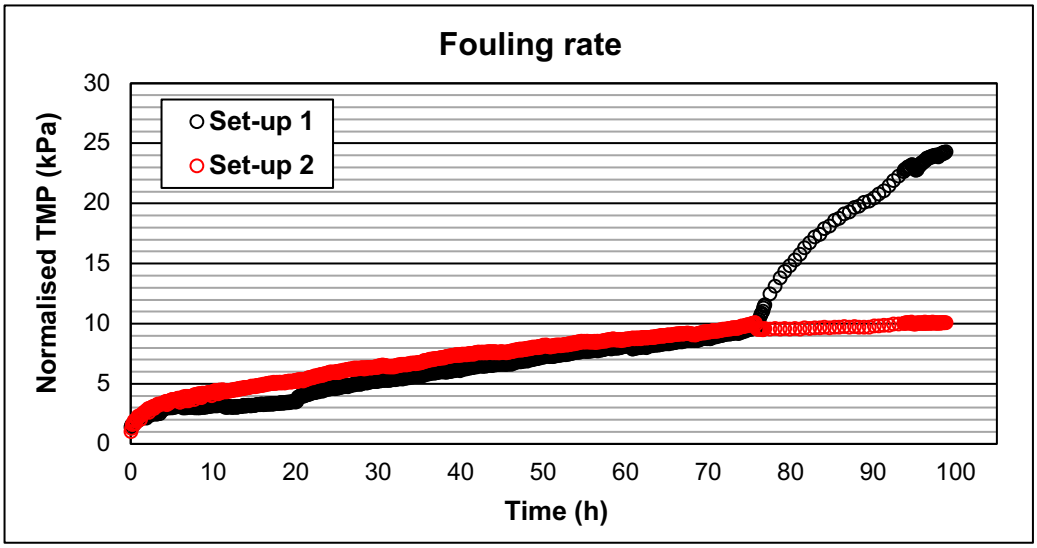


Figure 6.5 Difference in fouling rates due to algal growth on membrane surface

A total of 183 compounds (from the top 200 highest peak abundance in the four analysis modes) picked up from lipids and metabolites analyses in both positive and negative ionisation modes in the foulants collected from the membranes of both set-ups. From the comparison of the integrated peak areas of the compounds detected in both set-ups, 64 out of the total number of compounds was more than 20% higher in peak area in Foulant 1 than that in Foulant 2 (Table 6.4a); 58 compounds were within ±20% difference in peak areas; the balance number of compounds had higher peak areas in Foulant 2 (Table 6.4b), of which three were not detected in Foulant 1 (Table 6.4c). A comparison of the chemical compositions in the foulants are presented in Figure 6.5.

As shown in Table 6.3 and Figure 6.4 b, the concentration of steroids and derivatives in the foulant from sample fractions larger than 0.1 µm are comparatively higher (in Figure 6.4 b, more obvious in the sample fractions collected when the SAMBR was operating on ammonium chloride feed), which was compared with the findings in Figure 6.5. For fatty acids and their conjugates, the results did not relate directly to those in Section 6.3.1.

The three fatty acyls detected only in Foulant 2 are oxygenation products of poly-unsaturated fatty acids in plants (octadecanoids) and their secondary product during the oxidation process (jasmonate derivative) (Bouarab et al., 2004). The oxygenation process in marine red algae is known to be initiated as a natural defence mechanism in the presence of pathogens. 5,8,12-trihydroxy-9-octadecenoic acid was also detected in the foulants from F 0.1 – 0.45 µm and N 100 kDa – 0.1 µm fractions, in higher concentration compared to that in the foulants from other fractions (Appendix Table A4). The octadecanoids produced in the jasmonate pathway in plants were studied and found to function as cellular signals to induce proteinase inhibitors, volatile compounds and secondary metabolites (Fliegmann et al., 2003; Kramell et al., 2000). It is possible that in the same way it could generate other microbial products and protein inhibitor molecules which reduced the chances of the formation of a fouling layer, although this hypothesis has not been proven anywhere.

6.4 Conclusions

As expected, the fractions larger than 0.45 μm fouled the membrane within 48 hours, even with the gas recycle line. The initial LC-OCD-OND analysis of the fractions before the start of the fouling tests suggested that the fouling was a result of low MW neutral compounds (uncharged species). Detailed chemical characterization of the foulants after the fouling test using LC-Q-ToF revealed that the foulant was comprised of compounds in the MW range of 200 – 799 Da, other than colloids and larger sized particles. Fatty acids and conjugates, and steroids and their derivatives formed the major composition of SMPs detected. Steroids and derivatives were detected to be in the MW range of 400 – 699 Da; fatty acids and conjugates mainly in the range of 200 – 499 Da. The membrane fouling rates due to the fractions of 100 kDa – 0.1 μm and 0.1 – 0.45 μm collected from the SAMBR fed with fructose as the carbon source found that the 100 kDa – 0.1 μm fraction caused fouling much faster than the 0.1 – 0.45 μm fraction. A further analysis of foulants from the comparison of a parallel run, but different fouling rates due to algal growth on the membrane surface on one of the set-ups suggested that the production of octadecanoids from the jasmonate pathway triggered by cell stress might have contributed to a delay in membrane fouling. This study on the effects of fouling was carried out using filtered supernatants, i.e. without microorganisms, and hence there would be variations in foulant components compared to a full-scale MBR. Examining membrane fouling characteristics would have been more complete if we had included a study of the morphology of the membrane surface and the membrane cross-sections.

Table 6.4 Number of compounds which the integrated peak area was more than 20% higher (a) in Foulant 1 and (b) in Foulant 2 than the other; (c) the three compounds which were detected in Foulant 2 only**.**

(a)	**Chemical class**	**Number of compounds**
	Amino acids, peptides and analogues	15
	Benzene and substituted derivatives	3
	Carbohydrates and derivatives	2
	Fatty Acyls - Fatty Acids and Conjugates	6
	Fatty acyls - Fatty Esters	1

Glycerophospholipids	5
Glycopeptidolipid	1
Indoles and derivatives	1
Keto acids and derivatives	2
Others	3
Polyketides	7
Prenol lipids	4
Purine and derivatives	2
Nucleosides, nucleotides and analogues	8
Steroids and derivatives	4

(b)

Chemical class	**Number of compounds**
Alkaloids	1
Amino acids, peptides and analogues	8
Benzene and substituted derivatives	2
Carbohydrates and derivatives	6
Fatty acyls - Fatty Acids and Conjugates	6
Fatty acyls - Fatty Alcohol	1
Fatty Acyls - Octadecanoids	2
Glycerolipids	1
Glycerophospholipids	3
Others	3
Polyketides	4
Prenol lipids	3
Purine and derivatives	1
Pyrimidine derivatives	1
Nucleosides, nucleotides and analogues	2

(c)

RT (min)	**Chemical class**	**Suggested compound**	**Formula**
6.352	Fatty Acyls - Lineolic acids and derivatives	Methyl dihydrojasmonate	$C_{13}H_{22}O_3$
7.530	Fatty Acyls - Octadecanoids	(1S,2S)-3-oxo-2-pentyl-cyclopentanebutanoic acid	$C_{14}H_{24}O_3$
8.014	Fatty Acyls - Octadecanoids	5,8,12-trihydroxy-9-octadecenoic acid	$C_{18}H_{34}O_5$

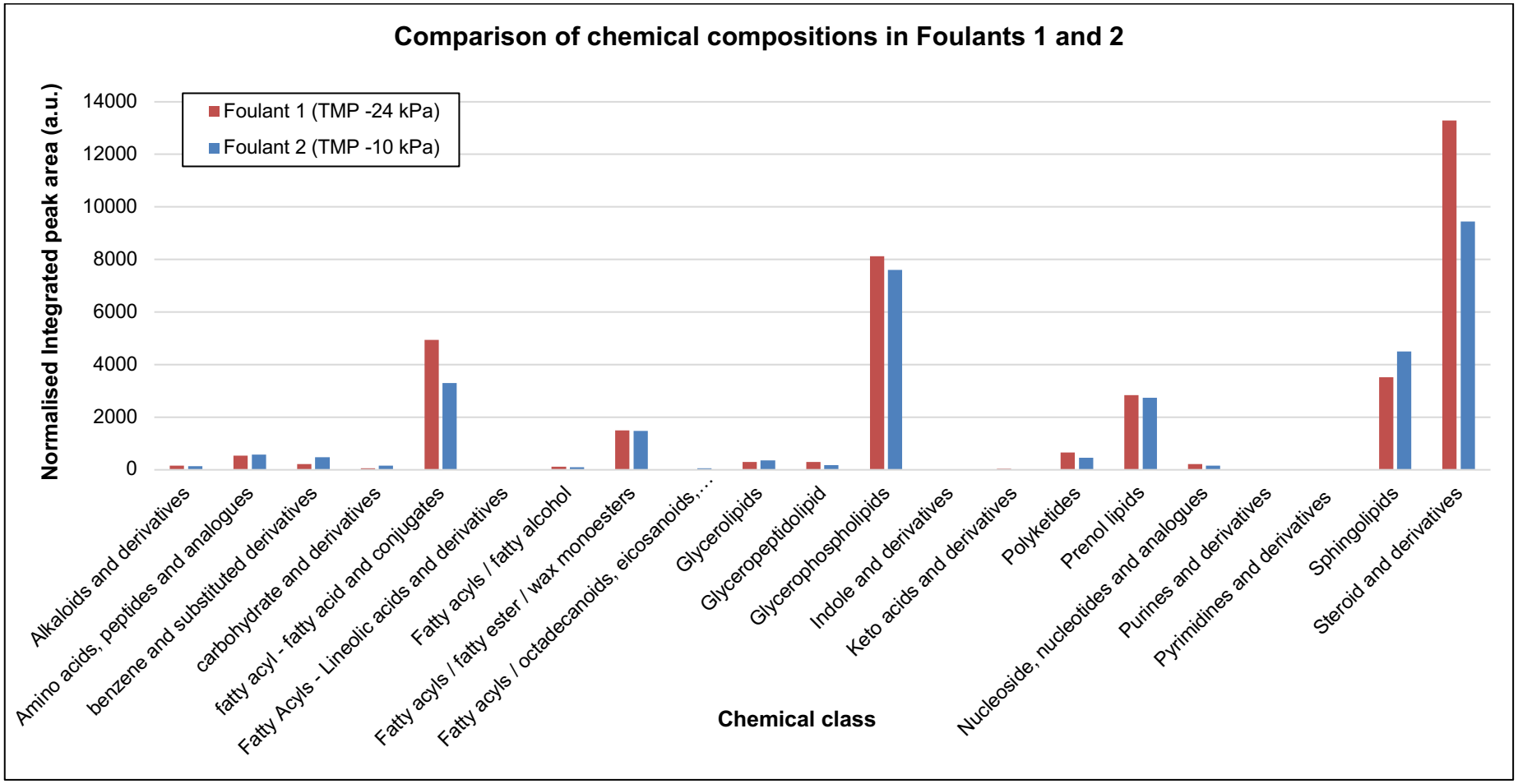


Figure 6.6 Comparison of chemical compositions of Foulant 1 and 2.

Chapter 7

Evaluation of the production of SMPs in full-scale industrial wastewater treatment system

7.1 Introduction

Effluents from biological wastewater treatment systems contain a variety of organic compounds, including end products from the degradation of influent substrates, non-biodegradable feed compounds, and soluble microbial products (SMPs) produced by microbial metabolism and cell lysis. It is important to identify the major components of these SMPs in order to understand what is in wastewater effluents during different periods of operation, and the effect different feed compositions have on SMP production and reactor performance.

Zhou et al conducted an analysis of SMPs from a low organic loaded full-scale upflow anaerobic sludge blanket (UASB) (Zhou et al., 2009). They found that the SMPs, mainly long chain esters (using GC-MS) and carbohydrates (using acid-anthrone spectroscopic analysis), made up 55-65% of the effluent COD. However, as is now well known, the drawback of the acid-anthrone method is the inaccuracy of the method itself, and the presence of interfering factors which potentially give false positive or negative results (Le & Stuckey, 2016). Hence this data may not be very robust in terms of its insights.

In the recent past there has been an increasing number of studies focussed on the detection of SMPs treating synthetic wastewater using different types of bioreactors such as activated sludge chemostats (Ni et al., 2009; Wang & Zhang, 2010), UASBs (Wu & Zhou, 2010), anaerobic membrane bioreactors (AnMBR) (Kunacheva et al., 2017a; Shen et al., 2015; Wang et al., 2007), and sequencing batch reactors seeded with activated sludge (Jarusutthirak & Amy, 2007), at varying scales and organic strengths to evaluate their operational efficiencies, however, studies on SMP production and identification from full-scale wastewater treatment systems is still limited. Hence the objective of this Chapter were twofold: to extend the identification of SMPs to a wider MW range of 30 to

2000 Daltons (Da) produced from the two stages of a full scale biological treatment process (UASB and aerobic membrane bioreactor (MBR)) treating an industrial wastewater, and; secondly, to compare the SMPs produced from industrial wastewaters to those produced using a synthetic feed in a laboratory AnMBR. From this it may be possible to deduce whether there are some generic compounds in the SMPs produced that are independent of the feed used. This in turn will enable insights to be drawn from laboratory studies using synthetic feeds about the performance of industrial plants.

7.2 Material and Methods

7.2.1 Reagents and chemicals

GC-MS or LC-MS grade chemicals purchased from Sigma-Aldrich were used for sample preparation, chemical extraction and analysis using GC-MS and LC-Q-ToF. A Merck Millipore Advantage A10 Milli-Q water system was used to obtain ultrapure water for sample dilution and preparation of HPLC mobile phases, where needed. Analytical grade volatile fatty acids (VFAs) standard solutions (formic, acetic, propionic, iso-butyric, butyric, iso-valeric and valeric acid) were purchased from Sigma-Aldrich Co., USA. An alkane standard mixture (C10 - C40, all even, 50 mg/L each in hexane, Restek©) was used for the calibration of the GC-MS. All the glassware used for sample preparation were rinsed with LC-MS grade methanol prior to use.

7.2.2 General parameters

All samples were filtered through 0.45µm glass fibre filters to separate any residual biomass, and then analysed in duplicate for glucose, VFAs and soluble chemical oxygen demand (SCOD). The amount of SMPs is typically estimated by subtracting the COD due to intermediate VFAs and residual substrate, from the soluble effluent COD (not including methane in the dissolved phase) using the following equation (Aquino et al., 2009).

SMPs (as COD) = soluble effluent COD – [volatile fatty acids (as COD)

+ residual substrate (as COD)]

The methods for VFA and COD analysis are described in detail in Chapter 3.

7.2.3 Sampling

Samples were collected from a central industrial wastewater treatment plant (68,000 m^3/day) in Singapore which received various types of wastewater from the chemical industry, refineries, textile industry, etc. Three samples were collected, and Figure 7.1 shows the sampling points. The industrial wastewater samples were from the influent and effluent of the upflow anaerobic sludge blanket (UASB), and effluent of the aerobic membrane bioreactor (MBR).

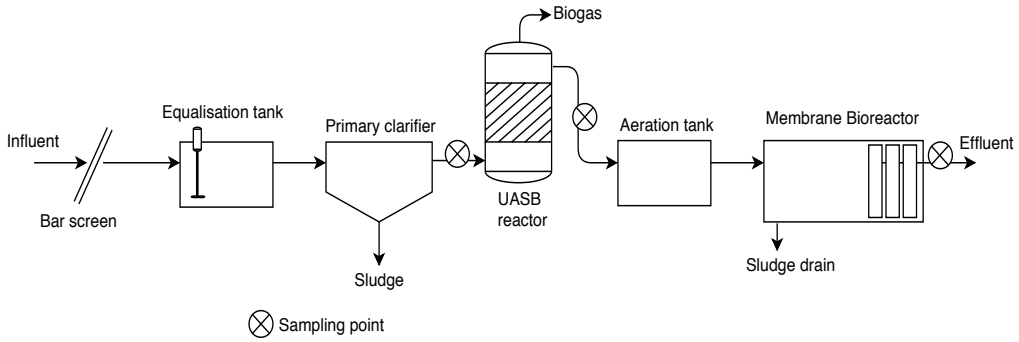


Figure 7.1 Sampling points in an industrial wastewater treatment process.

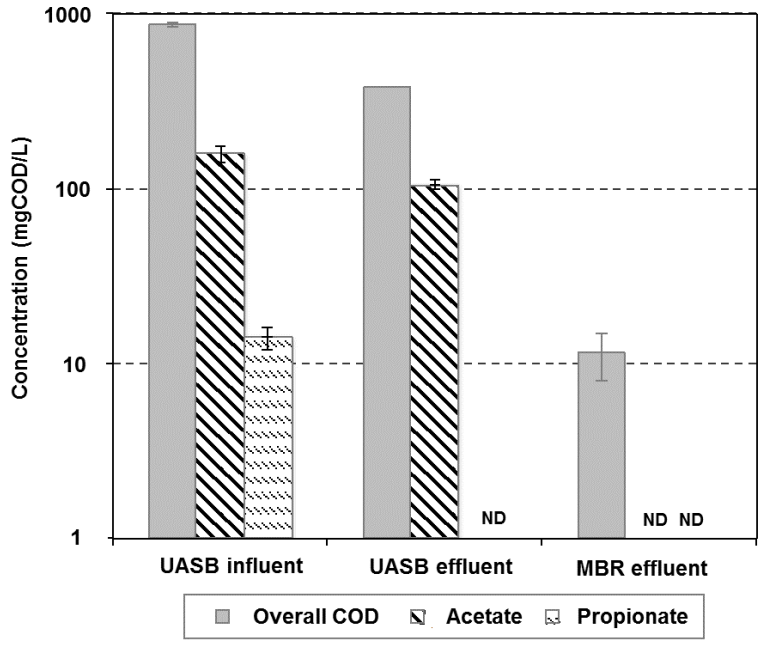
7.2.4 GC-MS and LC-Q-ToF for SMP analysis

Samples collected were filtered (0.45 μm, Advantec Grade GC50 glass fibre filters) before proceeding with the analysis using the analytical methods developed for SMP identification for comparison of the compounds produced by the different processes. The GC-MS and LC-Q-ToF analysis methods were described in detail in Chapter 3.

7.3 Results and Discussion

7.3.1 COD and VFA results

The three samples collected (UASB influent, UASB effluent and MBR effluent) were analysed for COD and VFAs (Figure 7.2). The COD of the samples coming into the central wastewater treatment plant varied over time, but at the time of sampling the UASB influent COD was 876±27 mgCOD/L before going into the UASB reactor. Acetate and propionate were found in the UASB influent with a concentration of 158±17 and 14±2 mgCOD/L, respectively, indicated that there was anaerobic degradation in the pipeline and in the equalisation tank. The UASB was only able to remove ~55% of the COD, and acetate was still found in the effluent sample (105±7 mgCOD/L). However, the final stage MBR effectively removed the COD down to 12±4 mgCOD/L in the effluent, and no VFAs were detected in the sample.



Note: UASB = Upflow anaerobic sludge blanket; MBR = membrane bioreactor; ND = Not detected.

Figure 7.2 Overall COD and COD equivalent of VFAs in samples.

7.3.2 Analysis of SMPs from industrial WW samples, and comparison with SMPs from synthetic WW treatment

Both the methods for low and high MW SMP analysis allowed partial identification of the compounds present using the available libraries, NIST 11, Human Metabolome Database (HMDB), ChEBI, LipidMaps, and *E. coli*. The low MW SMP analysis method detected compounds in the range of the mass-to-charge ratio (m/z) of 30 to 580, and for the high MW SMP analysis scanning was up to m/z 2000; most of the compound ions detected bore a ± 1 charge, and hence the molecular weight range was 30 – 2000 Da. The results from the aerobic MBR effluent of the industrial WW treatment process was compared with the SMPs detected in a submerged anaerobic membrane bioreactor (SAMBR; 3-L working volume, 6-h HRT) treating synthetic WW of 500 mgCOD/L (Zhou et al., 2016).

7.3.2.1 GC-MS analysis

The low MW SMPs were captured by solid phase extraction (SPE) and liquid-liquid extraction (LLE), and then detected using a GC-MS equipped with the NIST11 library of compounds. These do not include those detected in the synthetic field blank, and were classified into alkane, alkene, alcohol, aryl compounds (contains an aromatic substituent such as phenyl and naphthyl), nitrogenous compounds (denoted 'N'), esters, acids, others (the other classes of compounds which does not fall into any of those mentioned earlier), and unidentified, as presented in Table 7.1 and Figure 7.4a. The integrated peak area of the GC chromatogram represented the amount/concentration of the compound present in the sample. Alkanes were produced from the aerobic MBR, which was also found to be the case for other studies carried out on anaerobic processes (Trzcinski & Stuckey, 2009a; Wu & Zhou, 2010). The list of aryl, nitrogenous, unidentified, and compounds classified under 'others' can be found in the Appendix (Table A5). In this study it was found from the GC-MS analysis (detection of compounds from 30 Da to 580 Da) that the UASB produced a higher concentration of low MW SMPs when compared to the effluents of the UASB and aerobic MBR (Table 7.1b).

A total of 119, 124 and 65 compounds were identified in the UASB influent, UASB effluent (MBR influent), and MBR effluent, respectively. There was a 90% increase in the total integrated peak area after the UASB, and an 85% reduction after the aerobic MBR (Figure 7.4a). The total integrated peak area of the MBR effluent was 1.5 times that of the UASB influent, and this implies that microbial metabolism during WW treatment resulted in the release of more organic compounds than those present in the industrial WW feed. From the composition of the chemical classes of SMPs detected, the unidentified was almost 60% that of the total amount of SMPs. Half of the unidentified SMPs in the MBR effluent were late eluents (GC elution after 30 minutes of the run) (Table A5), which means they have a volatility equivalent to or lower than n-octadecane (linear $C_{18}H_{38}$, boiling point 317°C, flash point 165°C). The composition of low MW SMPs detected changed as shown in Figure 4a, and a significant reduction in aryl compounds occurred, as presented in Table S1. An increase after the aerobic MBR was observed for the compound benzethonium chloride. Notable compounds from the analysis for low MW (30-580 Da) SMPs were (iodomethyl)benzene, 2,6-ditertbutylphenol, benzophenone, and a 3,5-ditertbutyl-1,2-benzenediol derivative. These are the compounds which were not detected in the UASB influent and effluent, but were found in the MBR effluent.

A large peak detected in the GC chromatogram of the UASB effluent was identified as cyclooctasulfur (S_8) (Figure 7.3). The amount (represented by the integrated peak area) of S_8 present contributed to 96% of the total amount of compounds categorised as 'others' in the UASB effluent; S_8 was not detected in the UASB influent or the MBR effluent. From a literature search, S_8 is a central intermediate in the biotic or abiotic oxidation of sulfides (Troelsen & Jorgensen, 1982). The cyclooctasulphur disappeared after the MBR process, and this could be due to the activity of deltaproteobacteria (Pjevac et al., 2014). The occurrence of S_8 can be an indicator of the reactor performance: the metabolism in the UASB is not keeping up with the hydraulic retention time (HRT, measured in volume per unit time), as in an earlier study of the same phenomenon of an increase in S_8 concentration during an organic shock load due to a decrease in HRT (Kunacheva et al., 2017c). A reasonable explanation for the disappearance of elemental sulphur after the MBR process, but with no sulphur compounds being detected

using both GC- and LC-MS, would be bacteria utilising sulphur as electron donor/acceptor for the formation/transformation of SMPs. This indicator of microorganism activity was shown by the disappearance of aryl compounds and the appearance of a pool of unidentified low MW compounds in the MBR effluent. One of the unidentified compounds with a significant m/z 205 in its mass spectra could be 2-methylhopane or its derivatives. This group of compounds are biomarkers indicating the presence of cyanobacteria and green sulphur bacteria (Huang et al., 2007). This is yet an added advantage of using mass spectrometry coupled analytical instruments for chemical characterisation; chromatographic separation without mass detection will not be able to reveal the identity of the compound (each peak in the chromatogram is a chemical compound, if no co-elution), let alone spectroscopic methods such as UV and EEM (Ni et al., 2009).

Several aryl compounds (in the total integrated peak area of aryl compounds identified) were detected in the aerobic MBR effluent, but not in the anaerobic UASB influent and effluent: benzophenone (27%), 3,5-di-tert-butyl-1,2-benzenediol derivative (1.6%), 2,6-di-tert-butylphenol (17%), and iodomethyl-benzene (5.3%). Aryl compounds detected, other than the above mentioned, increased after the UASB process (Table A5). The same compounds were not found in the MBR effluent indicating their degradation (into other compounds) during the aerobic process, or being removed by the membrane (adsorption onto membrane/biofilm on membrane). A further analysis of the membrane fouling layer would be a good way to find out how these aryl compounds, which are potentially toxic to the environment/human and as disinfection by-product (DBP) precursors, are being effectively removed by the aerobic MBR process.

7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione was detected in the MBR effluent (Table 7.5), making up 70% of the compounds classified under ‘Others’. It was found to be a degradation product of commercial antioxidants used in the production of polypropylene films due to the microbial decontamination process during production of the film (Biedermann et al., 2014). The occurrence of such degradation products would not be uncommon since the wastewater treated in this study was from these industries, however, it was

concentrated in the MBR effluent (undetected in the UASB influent and effluent) suggesting its formation in the MBR and its refractory nature, since it is not removed by retention using the membrane in the MBR (despite the 85% decrease in total low MW SMPs after the MBR process). This compound was also detected in the lab-scale SAMBR treating low strength synthetic WW, but was approximately 50 times lower in concentration. Ruling out the difference in the load and composition of the influents that caused the large difference in the concentration of this compound in its effluent, it could be a microbial product.

From the GC-MS results of the aerobic MBR treating industrial WW and the SAMBR treating synthetic WW, there was a 13% similarity (28 out of 218 compounds) in the identified compounds (Table 7.2). Of these common compounds, decane ($C_{10}H_{22}$) had the smallest MW, while the other 27 compounds had a retention time of between 21.6 min to 50.9 min (volatility comparable to linear-C_{13} alkane and above). Most of the compounds which were identified after the MBR process were concentrated within this retention time frame as well. This suggested that the formation of compounds with higher molecular weights still maintain a certain extent of volatility, and tend to form during this part of the treatment process. Two phthalate esters, diisobutyl phthalate and di-(6-methyl-2-heptyl) phthalate, di-tertbutyl phenol, and benzophenone were detected in the MBR effluents but not in their respective influents. These compounds are likely to be discharged as it is or undergo possible transformations downstream, potentially during the disinfection process.

Figure 7.5 shows the comparison of the distribution of the different classes of compounds detected in the effluents of the aerobic MBR and the SAMBR, detected using GC-MS (lower MW, higher volatility SMPs) and LC-Q-ToF (higher MW, more polar, lower volatility). From the GC-MS results, the nature of the aerobic processes in the MBR could be more volatile compared to anaerobic process in the SAMBR, resulting in the formation of a high percentage (more than 50% of the total amount of SMPs detected by GC-MS) of unidentified compounds. Otherwise, from the SMP composition of the aerobic MBR treating a high COD concentration influent (which is the UASB effluent (Figure 7.4a) comprising of approximately 80% of elemental sulphur (Figure 7.3)), the MBR

may not be operating at its optimum conditions at the time of sampling. From the monitoring of SAMBR performance (no VFAs detected in effluent, effluent COD below 15 mgCOD/L), sampling time since initial start-up (more than four weeks), and the SMP composition (difference in SMPs during shockloads, and "steady-state" had been investigated (Kunacheva et al., 2017b; Kunacheva et al., 2017c)), the SAMBR was operating in "steady-state".

7.3.2.2 LC-Q-ToF analysis

Untargeted analysis using LC-Q-ToF gave insight into the polar metabolites and lipids that are present in the samples collected (Appendix Table A6). Partial identification (without chemical standards for exact identification) and classification of the peaks with abundance greater than 5000 (arbitrary units) is presented in Figures 7.4b and c. Amino acids and their derivatives, glycerolipids, glycerophospholipids, alkaloids and derivatives, alcohols and polyols, prenol lipids, steroids and derivatives and sterol lipids were being removed (70% - 90% removal) in the aerobic MBR by biological catabolism or retention by the membrane/biofouling layer.

Eicosanoids were at the highest concentration in the MBR effluent (Figure 7.5b); the eicosanoids detected were Ent-8-D2c-IsoP, 15R-hydroxy-5E,8Z,11Z,13Z-eicosatetraenoic acid, and 5-J2-IsoP. The biology of eicosanoids is a broad topic in lipidomics; 15R-hydroxy-5E,8Z,11Z,13Z-eicosatetraenoic acid detected belongs to a sub-class of hydroxy/ hydroperoxyl-eicosatetraenoic acids, which are intermediates in the formation of leukotrienes from arachidonic acids (The Human Metabolome Database). Its concentration (by integrated peak area) increased after the UASB (32 times compared to the influent), and a further 1.6 times increase after the MBR. Ent-8-D2c-IsoP and 5-J2-IsoP belong to the sub-class of isoprostanes, which are a biomarker for oxidative stress (Montuschi et al., 2004). However, only 5-J2-IsoP increased throughout the treatment process to its highest concentration in the MBR effluent (detected in the UASB effluent and from there increased by 1.4 times after the MBR process). The reason for this increase is not known yet.

The differences in the SMPs detected using the LC-Q-ToF showed significantly higher percentage of carboxylic acids and derivatives (20.5%), and eicosanoids and octadecanoids (20.2%) in the aerobic MBR effluent; the SAMBR effluent had a higher percentage of sphingolipids (23.3%), steroids and steroid derivatives (19.9%) and amino acids and analogues (11.8%). The data was plotted based on the percentage of each chemical class to the total concentration (integrated peak area) of the top 200 most abundant compounds detected. Sphingolipids (highest percentage in SAMBR effluent) and eicosanoids (second highest percentage in aerobic MBR effluent) are involved in metabolic pathways which produces bioactive lipids, essentially for cell-signalling (Dennis & Norris, 2015). Although eicosanoids are detected in both effluents, those in the MBR effluent belong to the class of isoprostanes as described above and formed a significant percentage of the top 200 abundant compounds, those in the SAMBR effluent belonged to the class of leukotrienes (12-oxo-c-LTB3 and 20-oxo-leukotriene E4) and made up less than 0.1% of the more abundant compounds detected. Their compositions present in the respective samples was probably indicative of the preference of cell-signalling compounds that microorganisms in the different systems (anaerobic and aerobic) might produce. The amino acids, peptides and analogues are present in the SAMBR effluent in a relatively higher concentration than the other classes (Figure 7.5b), and the majority were dipeptides. The dipeptides are the products of incomplete breakdown of proteins and have potential cell-signalling properties (The Human Metabolome Database).

Sphingolipids detected from the MBR effluent made up 6% among the higher abundant group of compounds. In contrast, 23% of the high abundant compounds in the SAMBR effluent are found to be sphingolipids (including ceramides, ceramide-phosphoethanolamies, and sphinganines). Sphingolipids are a distinctive group of membrane lipids, which are characteristic of certain groups of bacteria, not specifically anaerobes only (Olsen & Jantzen, 2001). Being membrane lipids, they are responsible for cell-signalling, response actions to heat stress, and transport of calcium ions and specific proteins (Huwiler et al., 2000). Since sphingolipids are characteristic of anaerobes, it is therefore abundant in the SAMBR and uncommon in an aerobic MBR.

From the LC-Q-ToF results, the more significant (higher abundance) classes of compounds detected are mainly membrane lipids or cell-signalling compounds. The difference in the compositions in both the effluents highlighted the presence of different dominant microorganism in two distinct systems, aerobic and anaerobic). These chemical composition findings can also act as supporting information for the studies on the microbial ecology in wastewater treatment systems.

7.4 Conclusions

The effluent COD from an industrial WW plant not only consisted of 'end-products' of microbial degradation/cell lysis (SMPs), but also the reaction intermediates, which are often derivatives of the macromolecule making up the presence of the group of higher MW compounds (up to 2000 Da, as detected in this study). The MBR exhibited its capability for degrading or retaining some of these SMPs, while others continued into the downstream processes and most probably continue to degrade and transform (particularly in the disinfection process) down the line until discharge. Comparison of the SAMBR and aerobic MBR effluents treating synthetic and industrial WW respectively showed that there was a small degree of similarity in the SMPs detected by GC-MS. Those detected by the LC-Q-ToF were significantly different most likely due to the difference in the processes i.e. aerobic and anaerobic process, and also the performance of the UASB bioreactor from which the level of cyclooctaatomic sulphur detected by GC-MS suggested the bioreactor to be in a transient state.

This study investigated the performance of a bioreactor through chemical characterisation of the influents and effluents. Although such small molecules are present in concentrations in the ppb level, they should not be neglected because of their effects in the treatment process, such as membrane fouling, and their potential to biotransform into other compounds which might then accumulate in the environment. The shortcoming of this study, however, was the number of samplings from the WWTP. As the influent of the full-scalle WWTP is variable over time, a comparison of SMPs detected in samples collected at different times of the year would make this study more complete and insightful.

Table 7.1 Comparison of (a) number of, and (b) normalized integrated peak area (arbitrary units) of identified SMPs in industrial wastewater

(a)	Alkane	Alkene	Alcohol	Aryl	N	Ester	Acid	Others	Unidentified	Total
UASB inf	22	12	5	44	8	7	5	16	33	152
UASB eff	10	9	7	60	12	12	1	13	75	199
MBR eff	21	8	4	7	17	3	2	3	74	139

(b)	Alkane	Alkene	Alcohol	Aryl	N	Ester	Acid	Others	Unidentified	Total
UASB inf	40	81	22	92	22	11	8.8	51	82	408
UASB eff	12	77	24	1,149	247	57	1.0	1,801	700	4,067
MBR eff	22	67	15	19	97	8.7	1.4	16	346	592

NOTE: Integrate peak areas are relative to the lowest value (Acid, UASB eff); number of compounds and integrated peak area excluded the compounds that were found in the field blank; UASB = up-flow anaerobic sludge blanket; MBR = membrane bioreactor; N = nitrogenous compounds; Others = compounds which were not in the chemical classes mentioned.

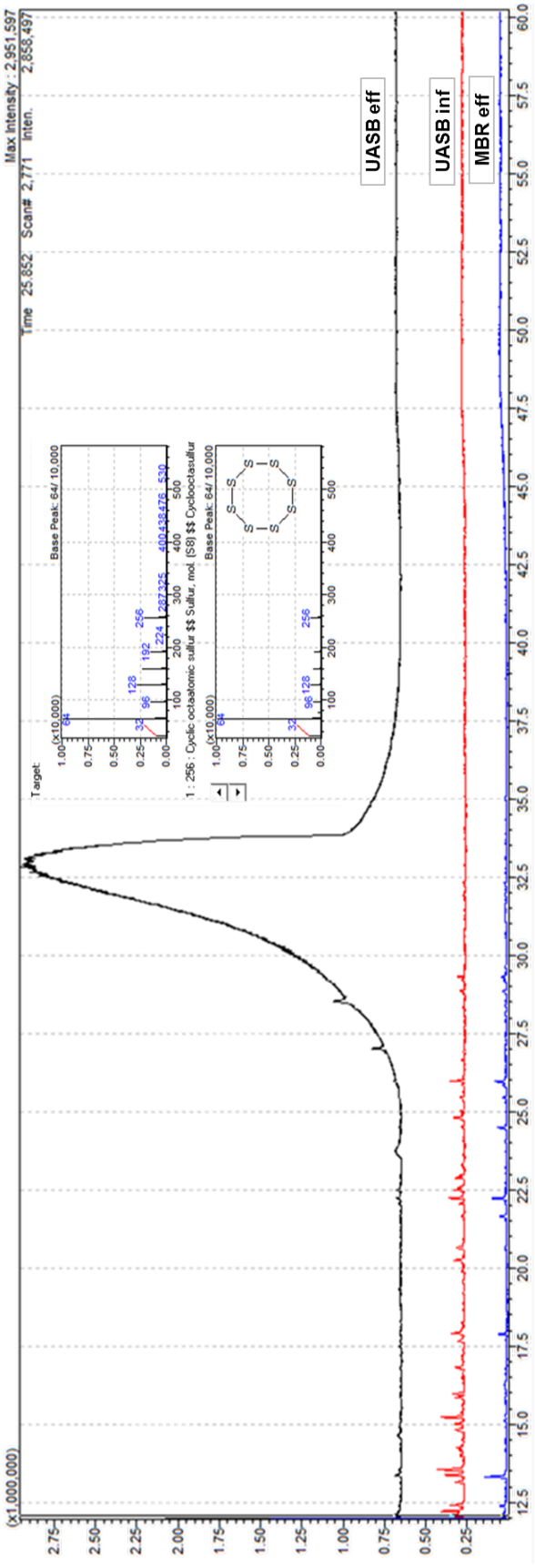
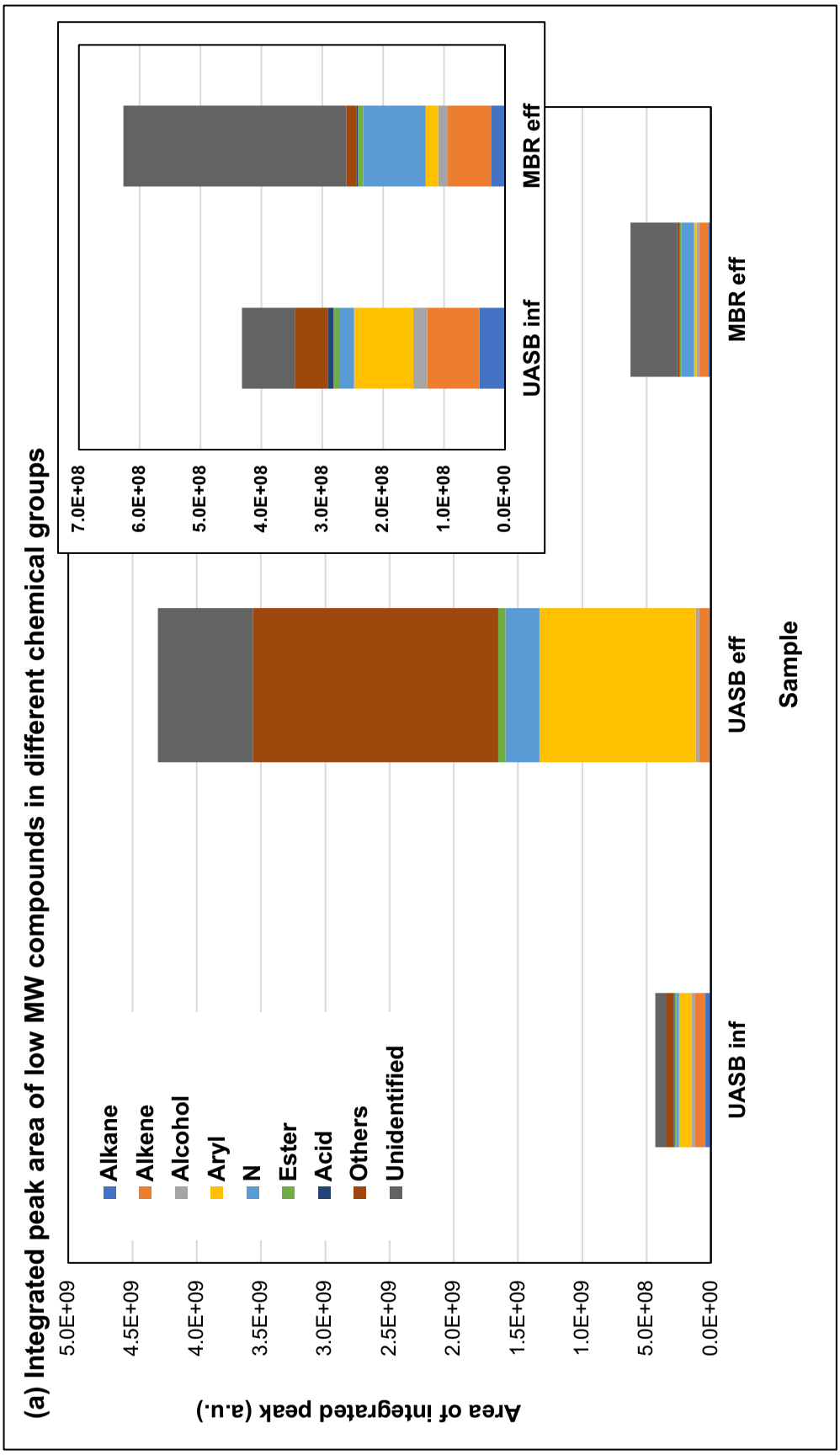
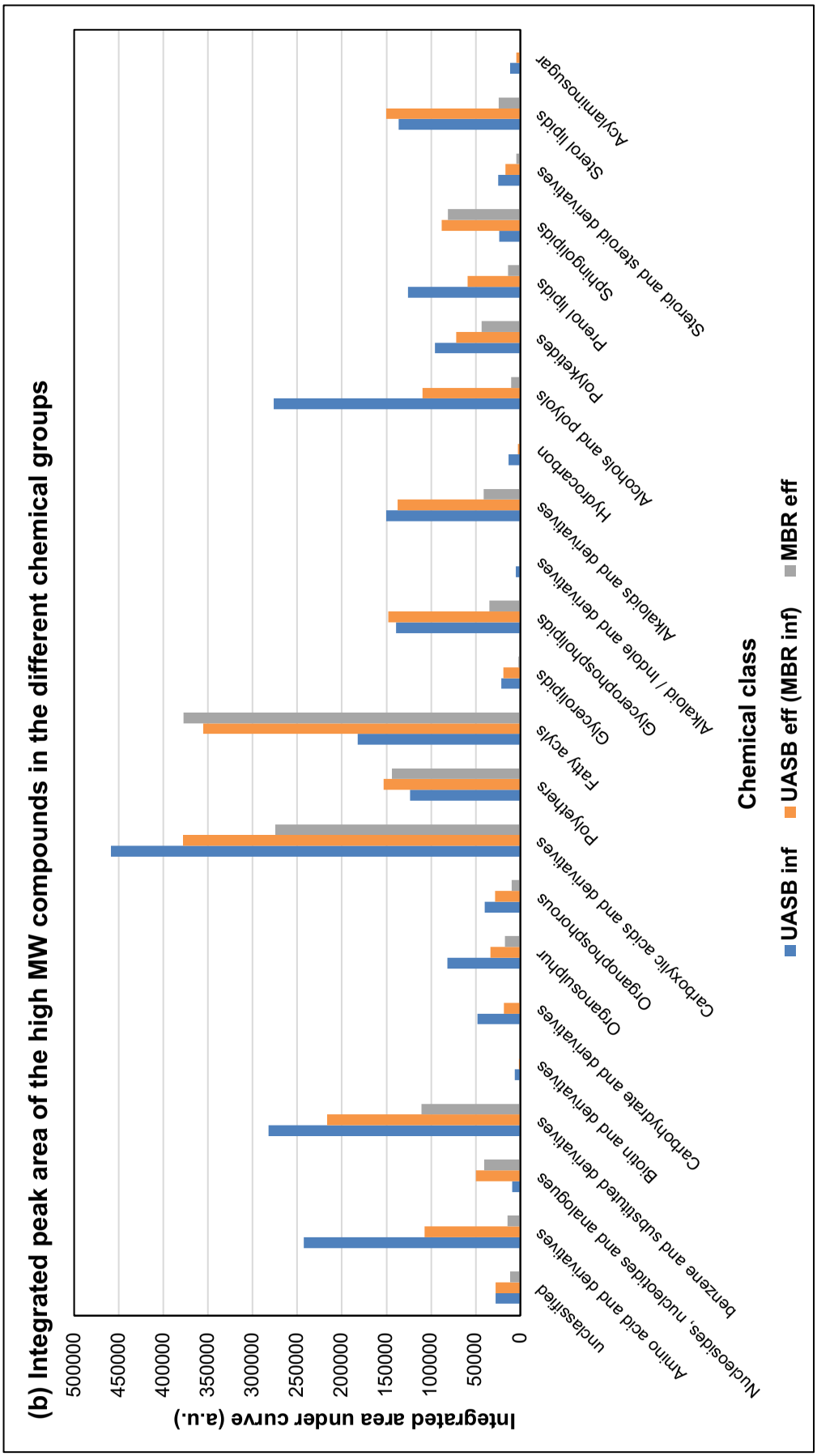


Figure 7.3 GC-MS chromatogram showing S8 having the highest concentration in the UASB effluent (MBR influent)


(a) Integrated peak area of low MW compounds in different chemical groups
Area of integrated peak (a.u.)
5.0E+09
4.5E+09
4.0E+09
3.5E+09
3.0E+09
2.5E+09
2.0E+09
1.5E+09
1.0E+09
5.0E+08
0.0E+00
Alkane
Alkene
Alcohol
Aryl
N
Ester
Acid
Others
Unidentified
UASB inf
UASB eff
MBR eff
Sample
7.0E+08
6.0E+08
5.0E+08
4.0E+08
3.0E+08
2.0E+08
1.0E+08
0.0E+00
UASB inf
MBR eff


(b) Integrated peak area of the high MW compounds in the different chemical groups
Integrated area under curve (a.u.)
0
50000
100000
150000
200000
250000
300000
350000
400000
450000
500000
unclassified
Amino acid and derivatives
Nucleosides, nucleotides and analogues
benzene and substituted derivatives
Carbohydrate and derivatives
Biotin and derivatives
Organosulphur
Organophosphorous
Carboxylic acids and derivatives
Polyethers
Fatty acyls
Glycerolipids
Glycerophospholipids
Alkaloid / Indole and derivatives
Alkaloids and derivatives
Hydrocarbon
Alcohols and polyols
Polyketides
Prenol lipids
Sphingolipids
Steroid and steroid derivatives
Sterol lipids
Acylaminosugar
Chemical class
UASB inf
UASB eff (MBR inf)
MBR eff

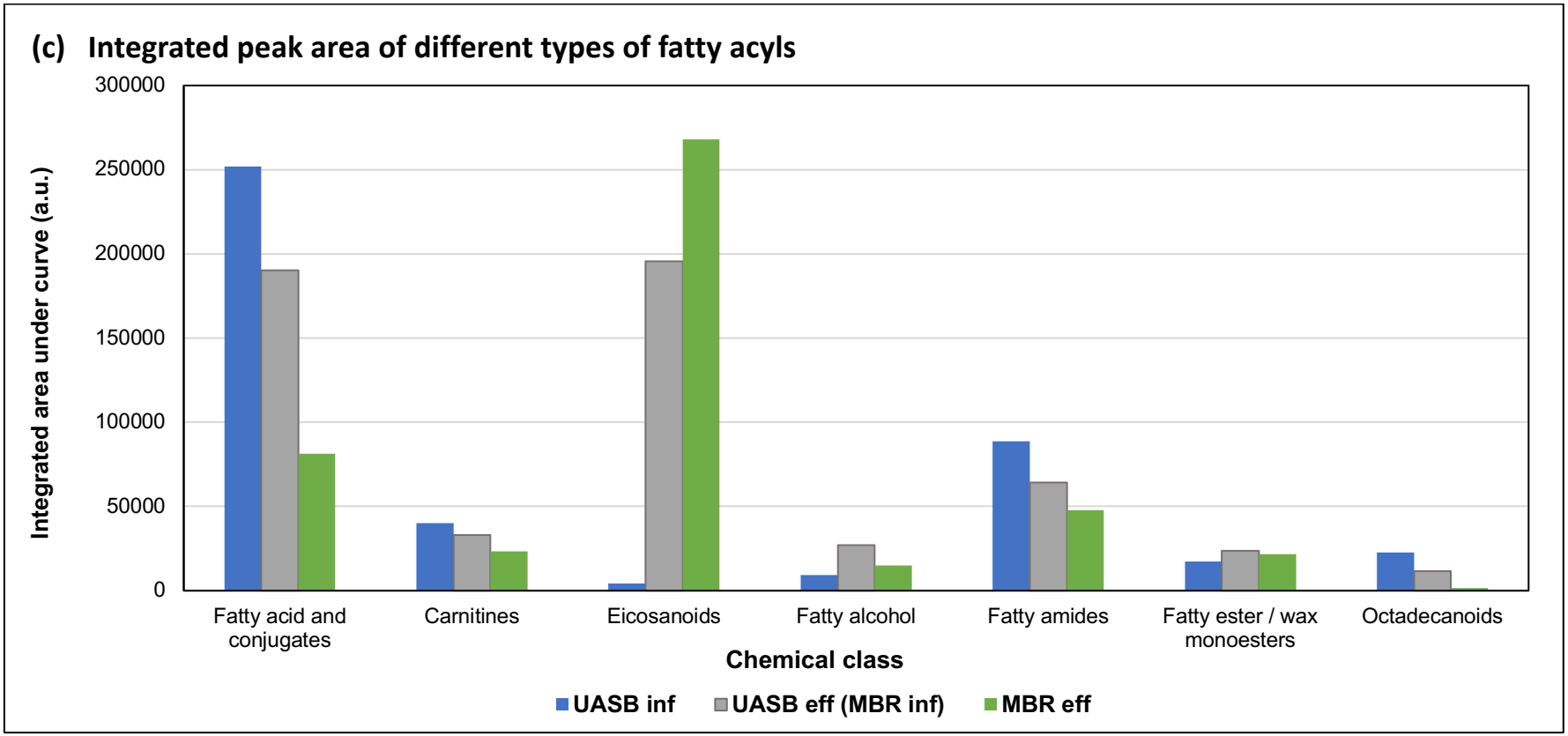


Figure 7.4 (a) Combined plot of integrated peak area of low MW SMPs in UASB influent (inf), UASB effluent (eff) and MBR eff detected using GC-MS. Figure insert is a blown-up plot for SMPs in UASB inf and MBR eff. Area of integrated peak is in arbitrary units (a.u.); (b) Combined plot of integrated peak area of high MW SMPs in UASB influent (inf), UASB effluent (eff) and MBR eff detected using LC-Q-ToF; (c) Extended plot of the different types of fatty acyls.

Table 7.2 Compounds which are common in both SAMBR and aerobic MBR effluents as detected by GC-MS.

RT (min)	Peak Identified	Chemical group
12.19	Decane	Alkane
21.62	3-methyltridecane isomer	Alkane
21.65	unknown (m/z 43 201 83 113 143)	Unknown
22.07	1-Tetradecene	Alkene
22.27	Tetradecane	Alkane
24.38	3,5-Di-tert-butylphenol	Phenol
25.11	4-ethyltetradecane	Alkane
25.76	1-Hexadecene	Alkene
26.04	Hexadecane	Alkane
26.65	Benzophenone	Aryl
28.78	3-methylheptadecane	Alkane
29.06	1-Octadecene	Alkene
29.18	Octadecane	Alkane
30.52	Diisobutyl phthalate	Phthalate ester
31.38	7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione derivative	Others
31.74	Hexadecanoic acid	Acid
32.18	Eicosane	Alkane
34.69	unknown alkane	Alkane
39.48	Di-(6-methylhept-2-yl) phthalate	Phthalate ester
39.60	unknown alkane	Alkane
40.21	unknown (m/z 86 264 58)	Unknown
40.88	2-methylhexacosane	Alkane
39.98	Squalane	Alkane
42.03	cis-11-Eicosenamide	Amide
42.93	2-methyloctacosane	Alkane
44.16	unknown alkane	Alkane
45.90	unknown alkane	Alkane
50.87	unknown	Unknown

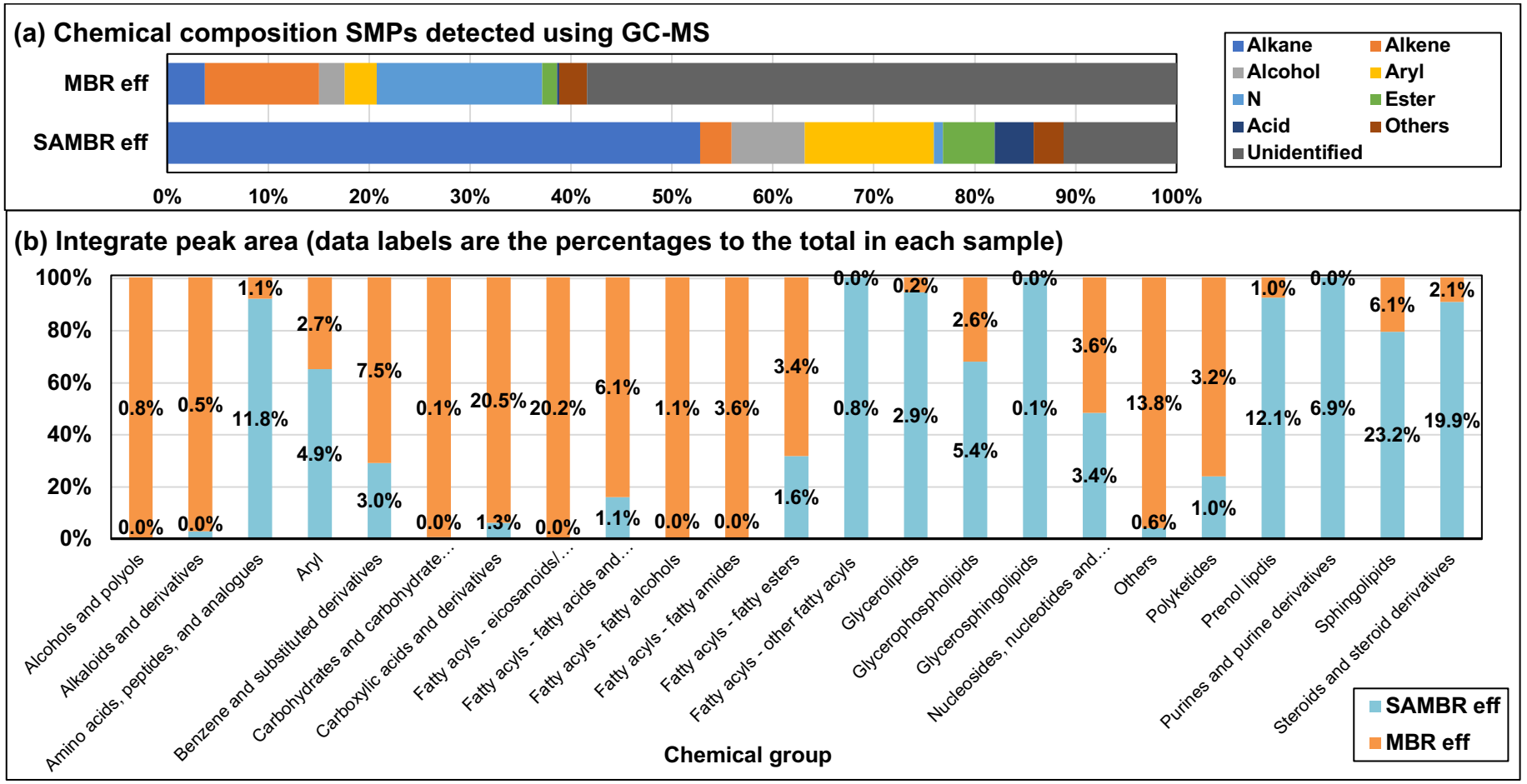


Figure 7.5 Comparison of the chemical compositions of SMPs in the effluents of aerobic MBR and SAMBR detected using (a) GC-MS and (b) LC-Q-ToF.

Chapter 8

Conclusions and Recommendations for future work

8.1 Introduction

The extent to which this work has met the initial objectives outlined in Section 2.5 within the defined scope of work is examined in the first part of this chapter. The important findings and their implications will be discussed. Finally, the research gaps that remain, and the areas which are recommended to be explored further to gain deeper understanding are highlighted in the last section on future work.

8.2 Concluding remarks

The main objectives of this work were:

1. To study the trends in the formation, and biotransformational changes of SMPs during anaerobic wastewater treatment process;
2. To determine the effects of bioreactor feed composition on the production of SMPs, and in turn,
3. To assess the effects of SMPs on membrane fouling, and finally,
4. To analyse the production and changes in SMPs in a full-scale wastewater treatment plant treating industrial wastewater, and compare the SMPs produced in both industrial and synthetic wastewater treatment processes.

Based on experimental results, the following conclusions can be drawn:

8.2.1 Formation and biotransformational changes of SMPs down the length of an anaerobic baffled reactor (ABR)

- From the increasing and decreasing trends of the concentration of SMPs , the low MW compounds tend to accumulate in the last compartment of

the ABR when it is in a transient state (25-30 days after change in feed COD concentration the ABR was operating in a transient state with respect to the COD removal).

- The lowest concentration of SMPs occurred in the 4th compartment of the ABR, where methane gas concentration was also observed to be at its highest. Thus, the increase in SMPs after the 4th compartment suggested a mixture of degraded and biotransformed influent compounds, and new SMPs generated; the decrease in concentration of SMPs to their lowest in the 4th compartment suggested the high activity of methanogens which enhanced the removal of SMPs by a higher rate of conversion of acetate (from acetogenesis) into methane gas.

- For a 24-hour HRT process, concentrations of alkanes and alkenes increased down the ABR as the system approached a pseudo-steady state, implying that they were 'end-products' of organic matter metabolism under such operating conditions. The formation of alkanes has been known to occur via the action of a plant enzyme *Pisum sativum*, suggesting either the presence of the same family of enzymes in the reactor, or that *Pisum sativum* is not just specifically produced by plants. Phthalate esters were classified as recalcitrant in other studies which was using a different bioreactor and/or at different operating conditions such as a shorter HRT, but became undetectable in the last compartment in this experiment – HRT was possibly the reason for incomplete or non-degradation of phthalates, and is likely to be one of the primary causes for other compounds being labelled 'recalcitrant' from other studies. This again showed that process conditions affect the effluent quality to a considerable extent.

- Operation of the ABR involved minimal mechanical cell disruption by stirring – hence the occurrence of lipids and other cell membrane components in the supernatant were likely to be due to cell degradation (lysis) or other cell acitivity; the release of amino acids and their derivatives can also be partly considered as biomass-associated products (BAP). Considering that these are also chemicals released by the

microorganisms to its extracellular environment, this could imply that they are involved in cell-signalling functions which has not been reported in other literature up until now.

- Compounds identified as having the highest integrated peak area in the 4th compartment showed their degradability over 24 hours, however, the highest integrated peak area in the last compartment implied their accumulation and increased chances of entering downstream processes (e.g. chlorination) and undergoing further transformation. Hence further studies are required to find out more about their potential to become disinfection by-products, or recalcitrant compounds.

- Metabolic pathways deduced from the observed appearance and disappearance of compounds in this study were inferred from previous studies of metabolic pathways of similar compounds, and studies of the individual types of compounds will be needed to verify these processes.

8.2.2 Effects of macronutrients on SMP production

- The effects of macronutrients on bioreactor performance have been overlooked as full-scale WWTP often does not receive the same influent type continuously since the influent changes with human activity, and hence the wastewater discharged for treatment. As the influent of industrial WWTP are highly variable, further laboratory studies on varying macronutrients will be helpful in the design of a more dynamic process to handle fluctuating influent types in real situations.

- The change in type of macronutrient – glucose to fructose, and organic nitrogen to inorganic nitrogen did not result in drastic changes to effluent COD and surge in VFAs, but the underlying biochemical processes saw changes, which has been overlooked in most of the previous work.

- Six hours (one HRT cycle) after glucose was replaced by fructose, there was a sudden increase in the total dissolved organic carbon and supernatant COD, but this reversed in the next six hours. The classification of GC-MS analysis results under ‘F only’ and ‘N only’, with

increments from 6 hours to 24 hours after the change in nutrient type showed compounds which were generated by microorganisms in response to this change.

- With a change to fructose, despite it having the same atomic composition ($C_6H_{12}O_6$) as glucose, its ring structure (pentose) disrupted the usual mechanism of metabolic pathways when the reactor had been fed glucose (hexose) since start-up. It is expected that if a system had been continuously fed a certain type of sugar, the switch to other simple sugars will present the same effect as reported here.

- Ammonium chloride (inorganic nitrogen) was added in the same concentration measured by total nitrogen, but it showed signs of inhibition, retarding the glucose metabolism and hence the detection of intermediate aliphatic aldehydes and the 'disappearance' of alkanes over a period of 24 hours. As aliphatic aldehydes are more chemically reactive and are known to be environmental pollutants (Vikrant et al., 2019), it is essential for the development of process control and downstream processes to remove such compounds before effluent discharge.

- Cyclooctaatomic sulphur was detect when the carbon source was initially changed. This indicated the disruption of the stability of the system, although this appeared to be the only major change when switching from a hexose to a pentose sugar. In contrast, the switch from organic to inorganic nitrogen source did not affect the metabolic pathway of the oxidation of sulphides.

- A sudden increase in the concentration of hydroxycinnamic acids was explained by an increase in the production of this metabolic intermediate due to the change in the usual biosynthetic pathway of L-phenylalanine and L-tyrosine. Another possibility was the biotransformation from aryl compounds accumulated during the initial change in carbon source type. Hydroxycinnamic acids and their derivatives have been found to be useful products in the cosmetics industry (Taofiq et al., 2017), and the process

development for the recovery of such chemicals of industrial value could be considered in the future.

- From a PCA statistical plot, LC-Q-ToF analysis results showed significant difference in the analytes detected in the lipid extracts of the two experimental sets. This analysis thus provide more insight to the lipid composition of the higher MW SMPs compared to the conventional spectrometric methods.

- Sphingolipids, glycerophospholipids, purines and their derivatives, and amino acids and their analogues form a majority in the N6 and N24 samples. In particular, the concentration of sphingolipids was exceptionally high when the inorganic nitrogen source was introduced to the SAMBR in place of an organic nitrogen source. This was explained by the breakdown and release of the lipid raft model (cell membrane structure) due to stress induced by the change in feed macronutrient. The ceramides (hydrolysis by-products of sphingomyelin, a type of sphingolipid) which made up 80% of the sphingolipids detected 24 hours after the feed change have a key function of inducing cell death, which in turn might be able to explain the incomplete metabolism of alkanes and the release of aldehydes instead.

8.2.3 Effects of changes in influent macronutrient on membrane fouling and chemical characteristics of the foulant

- Supernatant fractions filtered by membranes larger than 0.45 μm fouled the membrane within 48 hours, even with the gas recycle bubbling kept on. The chemical characterization of these foulants showed that they were mainly comprised of compounds in the MW range of 200 – 799 Da, in addition to the colloids and larger sized particles which may also be present. Steroids and their derivatives were in the MW range of 400 – 699 Da, and fatty acids in the range of 200 – 499 Da made up the majority of the SMPs in the foulant.

- The different fouling patterns of the 0.1 – 0.45 μm and 100 kDa – 0.1 μm fractions was explained by the detection of the octadecanoid, 5,8,12-trihydroxy-9-octadecenoic acid, in these fractions. The same octadecanoid was also found in the foulant with algal growth and apparently did not cause an increase in TMP (fouling). Earlier research had discovered its function as cellular signals to induce a proteinase inhibitor and other microbial products in response to pathogens and cell stresses. Thus, it is possible that protein inhibitor molecules were being generated hence reducing the fouling potential, although this has not been proven anywhere else before.

- The chemical characterization of foulants has not been reported before, and this study provided insight into the biochemical properties of the fouling layer. This information might be able to be utilized by membrane fabricaters to possibly modify membrane surface characteristics, especially the more precise MW distribution of organic matter in the foulants, to better reduce the rate of membrane fouling.

8.2.4 Evaluation of the production of Soluble Microbial Products (SMPs) in full-scale industrial wastewater treatment system

- A comparison of SMPs was made between an industrial WWTP and laboratory scale experiments using synthetic feed. There was only a small degree of similarity between the SMPs in the GC-MS analysis results from the two processes.

- On top of that, LC-Q-ToF analyses were significantly different. From the detection of elevated concentration of cyclooctaatomic sulphur in the UASB effluent (MBR influent) and evidence from previous experiements with the SAMBR operating at low HRT and low pH (extreme conditions), it was likely that the process was not operating at ‘steady-state’ in contrast to the samples from the SAMBR, and this may have explained the difference in the results of SMPs analysis obtained. From this study and slightly earlier studies from our group on the production of SMPs under transient states (Kunacheva et al., 2017b; Kunacheva et al., 2017c), the

analysis of SMPs can be considered as a method of checking the bioreactor performance for metabolic intermediates such as cyclooctaatomic uslphur tend to accumulate when the system is in an unsteady-state.

- This part of the study contributed to the in-depth analysis of the performance of full-scale industrial WW treatment process at the molecular level, an area of research which is lacking as of now.

Anaerobic treatment has proven to offer more attractive and crucial advantages over aerobic processes in terms of lower energy consumption (no need for aeration of the reactor), the biogas generated being contained within the system, and excess waste sludge generated being approximately 90-96% less than aerobic treatment, greatly reducing the need for their treatment and disposal. Most importantly, one of the key goals of wastewater treatment is to achieve sufficiently low effluent COD to meet with the stringent environmental regulations, and to protect the environment from pollution from wastewater discharge. Extensive work has been carried out on improving the performance of anaerobic processes from the technical prespective, while insights into the molecular levels and fundamental cause of the bottleneck issues encountered such as potential disinfection by-product formation and membrane fouling has just started to pick up pace. Analytical methods have been developed, and are still in the process of being fine-tuned to achieve a desirable precision and accuracy of results. This research work has adopted two of the recently developed analytical methods – SPE-LLE-GC-MS and LC-Q-ToF, to look at the production and biotransformation products of SMPs, and their implications in membrane fouling. To avoid identification error (low similarity match to compounds in the libraries and database) when peak abundance is not sufficiently higher than the instrument background signals, only the top 200 analyte peaks with high abundances from LC-Q-ToF were discussed. Hence, there was no direct relationship observed between the total concentration of compounds from the GC-MS and LC-Q-ToF methods for the experiments in this study.

Chapter 4 presented the trends in the formation, disappearance and transformation of the various chemical classes of microbial products which can be detected in anaerobic wastewater treatment processes during transient and at 'steady' states. The detection of SMPs in the first and fourth compartment of the ABR are representative of the acidogenesis and methanogenesis phases respectively, and finally the composition in the last compartment. The findings in Chapters 5 and 6 provided insight into the SMPs produced when macronutrients are being changed, keeping the concentration and all other parameters constant. By switching glucose to fructose, the slight difference in the chemical structure of the two simple sugars disrupted the uptake mechanism of the nutrient, and this was reflected in the production of cyclooctaatomic sulphur (S_8). From past experiences in SMP analysis, the occurrence of S_8 is an indication of incomplete metabolism of sulphur species resulting in the accumulation of elemental sulphur in the system. In the other set of experiments in which the organic nitrogen source was replaced by an inorganic nitrogen source, it resulted in the inhibition of another metabolic pathway, i.e. the retardation of the biosynthesis of alkanes. Since the COD removal was not affected and VFAs were not produced, the effects on alkane biosynthesis were only found after the GC-MS results showed a significant decrease in alkanes and an increase in aldehydes. These observations demonstrated the advantage of SMP analysis in discovering the biochemical changes in the bioreactor in response to changes in operating parameters which the usual monitoring methods such as COD and VFA analysis cannot identify. The analysis of foulants at the molecular level was carried out and reported in Chapter 6. Two sets of supernatants were collected from the experiments performed in the previous chapter, separated into different fractions with membrane filtration using a stirred-cell. The fractions were then introduced to a small set-up similar in configuration to the SAMBR as the influent, to test its membrane fouling properties.

As mentioned by the authors who developed the LC-Q-ToF method (Tipthara et al., 2017) and in the earlier chapters of this thesis, the identification of lipids, or at least the classes of lipids, suggested that naturally produced antifoulants might be present. These compounds are microbial products, but are less studied in wastewater treatment processes, unlike in the research field of marine

microorganisms and their products. The main reason being that the antifouling properties of ship hulls have always been of critical economic importance, and it is necessary for the antifouling coatings to be of low cost and low toxicity to the water bodies, i.e. sea and marine life in general. Identification of low-cost antifouling microbial products with minimum environmental toxicity allow for the development of their extraction methods and incorporation into membrane fabrication or process design to mitigate the membrane fouling problems in wastewater treatment processes.

Despite all the data gathered from the study of SMPs so far, it is still hard to draw lessons from it that can be used to guide practice. Due to the vast and complex microbial communities present in a mixed sludge system, and their everchanging nature in response to their dynamic environment, the formation and biotransformations of SMPs continue to require more study. This will in turn contribute to the development of biological treatment systems, and hence improve effluent quality.

8.3 Recommendations for future work

Based on the findings and issues raised during this study, the following areas for future research are recommended:

- From the chromatograms obtained in this series of experiments, particularly the LLE chromatograms, they tend to show overloading and overlapping signals due to the number of analytes that are present, and the extraction capability of the extraction solvent. Dilution to reduce overloading might sacrifice the identification of analytes which have lower concentrations or signals; extending the temperature ramp in the GC program (the standard procedure to method optimisation) broadened the chromatographic peaks which did not resolve the overlapping peaks well enough for more precise quantification. In view of this, two-dimensional GC-MS (GCxGC-MS) methods can be developed to enhance chromatographic separation. This type of instrument also allows for different modes of analyte separation – using

columns of different stationary phases connected in series by a modulator (to concentrate of eluents from the first column before the separation by the second column). There have been a variety of methods developed for the analysis for river water and sewage water, but these results still show some limitations in identification. The development of chromatographic methods should, therefore, also be combined with the optimisation of extraction methods.

- As per the previous point, the extraction method is equally important for the overall optimisation of chemical characterisation in complex matrices. Other than the combination of SPE and LLE for the extraction of lower MW compounds, initial extraction to separate SMPs broadly into low MW compounds, polysaccharides, lipids, and proteins before chromatography may potentially allow chromatographic separation and mass detection later on to arrive at more precise results. Modification of extraction methods can possibly borrow from the methods used in proteomics and lipidomics; electrophoresis and field-flow fractionation methods which allow for mass and charge separations can also be explored. Current chromatographic columns require samples to be pre-filtered with <0.45 um pore size before analysis which might exclude significant components, especially for the analysis of membrane foulants, and our results from Chapter 6 showed that the fractions greater than 0.45 um, which obviously fouled the membrane fast, contains considerable amounts of analytes as well.
- Isotope-labelled molecules (^{14}C) had been used in the past for determining whether the microbial product belonged to the classes UAP or BAP. Further application by using isotope-labelled macronutrients to study biotransformation pathways will be an interesting area to gain a deeper insight into the metabolic pathways of nutrients.
- More effort should be made to combine microbial ecology with the results from chemical analysis to determine more about the types of microbial products which can be generated at various stages (ABR has shown its applicability in such studies). The development into optimisation to produce certain kinds of useful natural products might be possible in future with the information collected from such cross-disciplinary studies.

- Another branch of studies which could develop from Chapter 6 could be the identification of natural anti-fouling compounds which can be incorporated into membrane surface modifications to mitigate the existing issue of membrane fouling.

Despite the studies carried out to date, there is still much work to be done on SMP characterisation in mixed culture systems where the array of microorganisms within a single system can produce a wide spectrum of SMPs, and SMP biotransformation products due to different process conditions and synergistic effects. As SMPs include a vast range of compounds from biomolecules to low molecular weight hydrocarbons, many of which are still briefly characterised by low accuracy photometric methods, the identification and quantification will take a lot more work combining microbiology, analytical chemistry and engineering conditions in the future.

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Appendix

Table A1 Low MW compounds detected from GC-MS. A1, A4 and A8 refers to the 1st, 4th and 8th compartment of the ABR.

Day 34					
Chemical class	**Suggested compounds**	**RT (min)**	**A1**	**A4**	**A8**
acid	Dodecanoic acid	24.577	6093	0	0
alcohol	2,4,7,9-Tetramethyl-5-decyn-4,7-diol	21.867	23734	0	22518
aldehyde	Pentadecanal isomer	26.613	6047	0	0
alkane	4-ethyl-octane isomer	11.394	273213	246709	0
alkane	3,6-dimethyl-decane	11.455	109432	0	906695
alkane	Decane	11.564	1264497	0	149371
alkane	2,3-dimethyl-undecane	16.269	0	0	0
alkane	3-methyl-undecane	16.393	284517	20616	177195
alkane	Dodecane	17.114	3138306	141166	1798457
alkane	6-methyl-tridecane isomer	20.23	13693	0	9684
alkane	6-methyl-tridecane isomer	20.282	13425	0	11462
alkane	2,6,11-trimethyl-dodecane isomer	20.452	14695	0	0
alkane	2,6,11-trimethyl-dodecane isomer	20.770	7793	0	0
alkane	3,5-Dimethyldodecane isomer	20.826	15655	0	0
alkane	2,6,11-trimethyl-dodecane isomer	20.923	0	0	257124
alkane	3,5-Dimethyldodecane isomer	20.928	205601	56711	0
alkane	3-methylene-tridecane	21.191	0	0	7711
alkane	Tetradecane	21.462	1677087	71330	920294
alkane	Octyl-cyclohexane	22.483	160509	37498	108436
alkane	5-propyl-tridecane isomer	24.079	21610	0	0
alkane	3-methyl-pentadecane	24.726	276304	61887	180759
alkane	Hexadecane	25.208	438034	0	202502
alkane	Decyl-cyclohexane	26.283	12876	0	22592
alkane	alkane	28.096	8532	0	0
alkane	Octadecane	28.542	315139	154259	177619
alkane	Eicosane	31.558	157276	80128	65356
alkane	alkane	33.939	31057	0	14395
alkane	Docosane	34.301	51988	28461	21699
alkane	Tetracosane	37.0	12193	0	0
alkane	Hexacosane	39.139	3071	0	0
alkane	Octacosane	41.286	20655	5208	18114
alkene	7-(Z)-Hexadecene isomer	25.297	0	0	8774
alkene	5-(E)-Tetradecene isomer	21.568	48633	0	28586
alkene	1-Octadecene	28.444	50035	9761	31986
alkene	Cetene	25.084	167296	31567	110186
amine	Methenamine	17.793	0	8014	0
aromatic	Benzophenone	26.032	0	137066	0
sulphur	Cyclic octaatomic sulfur (S8)	32.653	17520	0	0
epoxide	Tetradecyl-Oxirane (m/z 114 57 41 85)	26.607	55023	0	17177
ester	Methyl-pentadecanoate isomer	28.395	27711	0	0
ester	Methyl-pentadecanoate isomer	28.403	0	6566	0
ester	Methyl 12-methyl-tetradecanoate	28.535	36962	0	0
ester	Methyl-pentadecanoate isomer	28.981	64423	0	0
ester	Methyl-cyclopentaneundecanoate	30.513	0	0	13443
ester	cis-10-methyl-Heptadecenoate isomer	31.1	13355	0	0
ester	Methyl 8-(2-hexylcyclopropyl) octanoate isomer	31.808	41037	54066	11313
ester	Methyl-9-(Z)-Octadecenoate isomer	33.124	106367	52228	38516
ester	Methyl-10-Nonadecenoate isomer	34.580	127828	83769	0
ester	Methyl-7-(Z)-Hexadecenoate isomer	30.229	138545	59356	146964
N	Indol-2(3H)-one derivative	23.136	0	0	0
N	N-Butyryl-DL-homoserine lactone (m/z 54 124 151 166 84)	23.837	12910	0	0
N	3-Methyl-1,4-diazabicyclo[4.3.0] nonan-2,5-dione, N-acetyl- isomer (m/z 70 97 125 168)	27.267	13260	0	0
N	3-Methyl-1,4-diazabicyclo[4.3.0] nonan-2,5-dione, N-acetyl- isomer (m/z 70 128 168 44 97 113)	27.554	14397	0	0
N	dl-Alanyl-l-leucine	27.581	22862	0	0
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro- isomer	28.038	319024	0	101326
N	6-Oxabicyclo[3.1.0]hexan-3-one, 2,2,4,4-tetramethyl- isomer (m/z 57 113 156 85 41)	29.102	26050	8792	12585
N	m/z 70 154 1125 13 86 41	29.372	0	0	8936
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(2-methylpropyl)-isomer	29.383	70541	25270	0

N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(2-methylpropyl)- isomer/coleution of cyclic O or cyclic N with aliphatic chain	30.789	107117	25206	8325
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(2-methylpropyl)-isomer	30.879	167581	52061	11200
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(2-methylpropyl)- isomer	30.922	103957	22730	0
N	5,10-Diethoxy-2,3,7,8-tetrahydro-1H, 6H-dipyrrolo[1,2-a:1',2'-d]pyrazine	30.941	0	0	12850
N	Indoles (m/z 117 90 186 42 63)	32.366	23496	0	0
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(phenylmethyl)- (isomer)/Dihydroergotamine	36.357	114342	26198	0
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(phenylmethyl)- isomer	36.731	71708	0	0
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(phenylmethyl)- isomer	37.014	0	11946	0
unknown	Alkane/alcohol	28.104	85358	0	40443
unknown	m/z 73 147 281 327	23.378	8326	0	0
unknown	m/z 54 124 151 166 84	23.542	9090	0	0
unknown	m/z 57 191 206	23.969	11475	0	0
unknown	m/z 57 191 206	24.251	25696	0	0
unknown	m/z 143 221 91 57	27.373	21400	0	0
unknown	m/z 128 113 143 91 57 221	27.509	0	0	13117
unknown	m/z 70 97 125 168 57 85 140	27.664	0	0	12721
unknown	m/z 114	28.196	23933	0	0
unknown	m/z 91 204 170	34.189	160212	0	0
unknown	coelution? m/z 70 86 124 210 41 91	34.408	24777	0	0
unknown	m/z 173 89 117 216 44	34.831	0	0	0
unknown	m/z 91 70 127 208 155 246	35.353	12598	0	0
unknown	m/z 91 113 141 204 169	36.132	11435	0	0
unknown	m/z 91 113 141 204 169	36.439	14881	0	0
unknown	m/z 141 91 169 86 68 260	39.269	10305	0	0
unknown	m/z 68 42 111 152 55 82 137	22.974	15505	0	0
unknown	coelution? m/z 70 74 87 55 43 124 180)	29.952	6304	0	0
unknown	m/z 57 191 206	20.443	0	0	11868
unknown	Z-2-Dodecenol/Dodecanal	21.727	31292	0	0
unknown	m/z 42 68 111 152	22.856	26319	0	0
unknown	Coelution? 10-Methylnonadecane/phthalate	31.154	73411	31379	37099
unknown	Alkane/alcohol	20.872	224964	0	10828
unknown	1-Dodecene/Nonyl-cyclopropane	16.916	283448	9362	169649
unknown	coelution? m/z 70 74 154 87 69 41 55 125	30.515	183788	99945	92404
unknown	Alkane/alcohol	21.311	287392	11772	175066

Day 56

Chemical class	Suggested compounds	RT (min)	A1	A4	A8
acid	Benzeneacetic acid	19.265	36571	0	0
acid	Hydrocinnamic acid	21.139	8505	0	0
alcohol	2-butyl-1-Octanol isomer	21.161	0	0	5367
alcohol	2-butyl-1-Octanol isomer	21.32	0	0	7626
alcohol	7-Tetradecanol	25.923	0	12668	0
alkane	4-ethyl-Octane isomer	12.368	141098	0	324422
alkane	Decane	12.498	105432	0	441741
alkane	Undecane	15.503	44366	69690	44799
alkane	3-methyl-Undecane	17.338	71032	0	163776
alkane	Dodecane	18.052	458008	0	1562095
alkane	2,6,11-trimethyl-Dodecane isomer	21.08	0	0	5067
alkane	2,6,11-trimethyl-Dodecane isomer	21.708	0	0	13318
alkane	3-methyl-Tridecane isomer	21.814	105652	101351	207356
alkane	Tetradecane	22.398	223017	306589	710748
alkane	octyl-cyclohexane	23.431	48873	84400	85096
alkane	5-ethyl-5-propyl-undecane	25.187	0	9799	7921
alkane	3-methyl-pentadecane	25.639	73986	141656	152993
alkane	Hexadecane	26.145	0	48481	29276
alkane	Decyl-cyclohexane	27.233	9231	19194	21750
alkane	3-methyl-Heptadecane	29.043	26142	0	55847
alkane	Octadecane	29.486	52381	156842	127213
alkane	9-methyl-nonadecane isomer	32.113	16084	39863	30634
alkane	Eicosane	32.516	32889	82045	62504
alkane	10-methyl-eicosane isomer	34.905	6786	19869	7133
alkane	Docosane	35.27	13576	27054	22787
alkane	Tetracosane	37.77	0	4659	0
alkane	11-butyl-docosane	38.963	4974	8971	3268
alkane	Hexacosane	40.102	13231	17344	6973
alkane	2-methylhexacosane	41.20	235994	24030	12143
alkane	Octacosane	42.259	26394	66846	14181

alkane	2-methyloctacosane	43.288	0	73183	0
alkane	Triacontane	44.273	0	116435	0
alkene	1-Dodecene	17.861	73786	7320	161571
alkene	1-Tetradecene	22.253	78870	83534	161022
alkene	7-(Z)-Tetradecene isomer	22.511	0	0	20390
alkene	Cetene	26.03	42752	90075	92839
alkene	1-Octadecene	29.396	13943	36755	29967
ester	12-methyl- methyl-tridecanoate	28.304	0	6192	0
ester	Methyl pentadecanoate	29.342	39184	22225	0
ester	Methyl-14-methyl-pentadecanoate	29.928	0	14566	4796
ester	bis(2-methylpropyl) 1,2-Benzenedicarboxyloate isomer	30.74	29179	0	0
ester	Methyl-9-(Z)-hexadecenoate	31.18	106344	70875	55851
ester	Methyl-hexadecenoate	31.464	60313	53539	43714
ester	Butyl 2-methylpropyl-1,2-benzenedicarboxylate	32.16	28985	0	0
ester	Methyl-2-hexyl-cyclopropane-octanoate isomer	32.622	28419	9335	0
ester	Methyl 2-hexyl-cyclopropane-octanoate isomer	32.755	0	0	19039
ester	Methyl 9-(E)-Octadecenoate	34.006	52301	0	0
ester	11-octadecenoate	34.081	65021	40459	48391
N	2-methyl-1H-Indole isomer	22.361	6603	0	0
N	Indole derivative (m/z 117 90 186)	33.382	8662	0	0
N	N-Methyl-1H-benzimidazol-2-amine	25.679	0	5722	0
N	unknown N (m/z 114 85 70)	27.568	7541	0	0
N	N-acetyl-3-Methyl-1,4-diaza-bicyclo [4.3.0] nonan-2,5-dione isomer (m/z 70 125 91 168)	28.283	75728	8506	0
N	N-acetyl-3-Methyl-1,4-diaza-bicyclo [4.3.0] nonan-2,5-dione isomer (m/z 70 125 91 168)	28.682	57105	6356	0
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-isomer (m/z 83 111 154 70 98 126)	28.977	0	18656	13011
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro- isomer (m/z 83 111 154 70 98)	29	0	70799	0
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-isomer (m/z 83 111 154 70 98 126)	29.094	971148	0	0
N	N-glycyl-DL-Threonine isomer (m/z 114)	29.213	14523	0	0
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(2-methylpropyl)-isomer (m/z 70 154 125)	30.028	18611	4769	0
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(2-methylpropyl)-isomer (m/z 70 154 125)	30.410	52436	13508	5278
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(2-methylpropyl)-isomer (m/z 70 154 125)	31.515	9270	0	0
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(2-methylpropyl)-isomer (m/z 70 154 125)	31.766	41276	5812	0
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(2-methylpropyl)- (RI 1699 m/z70 154 125)	31.885	7664	12201	4798
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(2-methylpropyl)-isomer (m/z 70 154 125)	31.904	53932	0	0
N	5,10-Diethoxy-2,3,7,8-tetrahydro-1H,6H-dipyrrolo[1,2-a:1',2'-d]pyrazine (m/z 70 154 96)	31.998	72241	15840	0
N	2,5-Piperazinedione, 3,6-bis(2-methylpropyl)- isomer (RI 1636 m/z 170 86 140)	35.108	47869	0	0
N	2,5-Piperazinedione, 3-(phenylmethyl)- isomer (m/z 91 204)	35.264	35808	0	0
N	unknown N (m/z 70 86 124 210)	35.434	72993	0	0
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(phenylmethyl)- isomer (m/z 125 70 153 91 244)	37.442	25121	5097	0
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(phenylmethyl)- isomer (m/z 125 70 153 91 244)	37.989	18186	0	0
Aromatic	p-Cresol isomer	14.953	524231	210199	182363
unknown	m/z 85 57 128 100	25.465	17301	0	0
unknown	m/z 118 147 92 77	25.69	21194	0	0
unknown	alkane/alcohol	26.238	0	11734	0
unknown	alkane/alcohol	29.036	0	23641	0
unknown	m/z 70 86 124 210	34.775	16254	0	0
unknown	m/z 70 86 124 210	35.417	0	6125	0
unknown	m/z 141 91 169 260	40.297	6903	0	0

Day 96

Chemical class	Suggested compounds	RT (min)	A1	A4	A8
alcohol	2-Hexyl-1-octanol isomer	25.341	6954	0	15487
alkane	Decane	12.31	0	519580	1187884
alkane	Undecane	15.297	29091	42595	36984
alkane	unknown alkane	16.474	0	0	4040
alkane	3-methyl-undecane (RI 1150)	17.130	50145	85259	185965
alkane	Dodecane	17.856	121234	584727	1948701
alkane	Tridecane	20.137	0	0	18780
alkane	2,6,11-trimethyl-dodecane isomer	20.892	4392	3349	20093
alkane	6-methyl-tridecane	20.975	0	0	17815

alkane	5-methyl-tridecane (RI 1349)	21.263	3904	0	0
alkane	2,6,10-trimethyl-dodecane isomer	21.506	6555	3869	29131
alkane	3,5-Dimethyldodecane isomer	21.614	111762	101512	259216
alkane	Tetradecane	22.206	269955	188292	876141
alkane	Octyl-cyclohexane (RI 1476)	23.226	41880	32909	91686
alkane	7-Methyl pentadecane isomer	24.986	5082	2760	16790
alkane	3-Methyl pentadecane isomer	25.435	91026	72566	167361
alkane	Hexadecane	25.952	0	0	50099
alkane	2-cyclohexyl-decane (RI 1611)	27.025	12662	0	17884
alkane	3-Methyl-heptadecane (RI 1746)	28.834	0	0	21688
alkane	Octadecane	29.288	52368	20454	143448
alkane	10-Methylnonadecane isomer	31.881	28381	11013	29720
alkane	Eicosane	32.303	28868	25872	76317
alkane	Eicosane, 2-methyl- isomer	34.684	0	0	14639
alkane	Docosane	35.052	10835	8527	19360
alkane	Hexacosane	39.899	0	4225	0
alkene	1-Dodecene	17.652	48120	88075	189283
alkene	3-methylene-tridecane	21.928	6927	4088	22061
alkene	1-Tetradecene	22.055	135630	90920	195153
alkene	5-(E)-Tetradecene isomer	22.306	9522	14823	31942
alkene	4-(Z)-Tetradecene isomer	22.444	3045	0	0
alkene	Unknown alkene (m/z 70 55)	25.724	3270	0	151356
alkene	Cetene	25.830	53151	36473.52	129387
alkene	7-(Z)-Hexadecene	26.037	0	0	11561
Aromatic	Phenol	12.013	407615	0	0
Aromatic	p-Cresol isomer	14.78	4593518	0	0
Aromatic	2,3-Dimethylphenyl isocyanate isomer	24.133	76279	4511	0
Aromatic	2,6-Dimethylphenyl isocyanate isomer	25.336	10239	0	0
ester	Methyl 2-Butenoate isomer	19.386	0	0	6293
ester	2,2,4-Trimethyl-1,3-pentanediol diisobutyrate isomer	26.04	0	4118	6169
ester	Methyl tetradecanoate isomer	28.108	15944	0	0
ester	Methyl pentadecanoate isomer	29.132	18512	19898	18430
ester	Methyl 12-methyl-tetra decanoate isomer	29.142	0	0	18430
ester	Methyl 12-methyl-tetra decanoate isomer	29.286	0	3174	0
ester	Methyl pentadecanoate isomer	29.718	28049	0	0
ester	Methyl 9-(Z)-hexadecenoate isomer	30.969	265833	61595	50636
ester	Methyl cyclopentane-undecanoate isomer	31.246	0	0	15530
ester	Methyl hexadecanate isomer	31.254	145519	49172	54698
ester	Methyl 9-(Z)-Octadecenoate isomer	32.405	9998	6953	0
ester	Methyl 9-(Z)-Octadecenoate isomer	32.553	0	0	3469
ester	Methyl 6-(Z)-Octadecenoate isomer	33.786	12259	3885	0
ester	Methyl 11-Octadecenoate isomer	33.861	32568	52553	247304
ester	Methyl stearate (RI 2077)	34.118	0	0	8809
ester	Methyl 10-Nonadecenoate isomer	35.318	6598	0	40791
ester	Methyl 9-(Z)-Octadecenoate isomer	35.324	0	12301	0
N	2-Pyrrolidinone derivative (m/z 85 41)	14.497	12099	0	0
N	2-Piperidinone derivative (m/z 99 70 42)	17.455	363863	0	0
N	Oxazolidin-2-one, N-[(E)-butenoyl]- (m/z 69)	20.873	0	0	13388
N	4-methyl-1H-Benzotriazole (m/z 104 133 78 51)	23.796	34944	9714	0
N	5-methyl-1H-Benzotriazole (m/z 104 133 78 51)	23.881	308049	0	0
N	N (m/z 70 44 97 125 168)	28.057	46970	22357	0
N	3-Methyl-1,4-diazabicyclo [4.3.0]nonan-2,5-dione, N-acetyl- isomer (m/z 70 91 125 168)	28.443	14738	17003	0
N	N (m/z 70 97 125 168)	28.463	17139	0	0
N	Pyrrolo[1,2-a]pyrazine-1,4-dione,hexahydro- isomer (m/z 83 111 154 70 98)	28.776	58437	164003	39574
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro- isomer (m/z 83 111 154)	28.818	156465	0	0
N	Glycyl-D-threonine derivative (m/z 114 57 85)	28.974	10170	0	0
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(2-methylpropyl)- isomer (m/z 70 154 125)	30.181	76330	37097	5186
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(2-methylpropyl)- isomer (m/z 70 154 125)	31.531	83207	21316	0
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(2-methylpropyl)- isomer (m/z 70 154 125)	31.678	150062	56791	9625
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(2-methylpropyl)- isomer (m/z 70 154 125)	31.761	85509	39052	6028
N	2,5-Piperazinedione, 3-(phenyl methyl)- isomer (m/z 91 204)	34.995	14343	0	0
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(2-methyl propyl)- isomer (m/z 70 154 139)	35.849	7092	0	0
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(2-methylpropyl)- isomer (m/z 70 154 139)	36.035	7426	0	0
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(phenylmethyl)- isomer	37.193	42987	16342	0

N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(phenylmethyl)- isomer(m/z 125 70 153 91 244)	37.738	17524	3605	0
N	Indole derivative (m/z 117 90)	20.171	212941	0	0
N	3-methyl-1H-Indole derivative	22.144	118098	0	0
N	2,3-dihydro-1H-Indole-1-carboxalde-hyde derivative (m/z 118 147 92 77)	25.523	119026	0	0
Other	Hexyl octyl ether (RI 1489)	25.098	2988	0	0
Other	Octane, 1,1'-oxybis- (RI 1688)	26.042	0	0	11978
Other	Pentadecanal (RI 1701)	27.343	12659	0	0
Other	2(1H)-Quinolinone isomer (m/z 117 145 90)	27.79	25253	0	0
Other	aldehyde	29.621	0	0	4424
unknown	unknown	20.968	5000	4296	5416
unknown	alkene/alcohol	21.129	5556	4404	25627
unknown	alkene/alcohol	21.455	3892	0	0
unknown	alkene/alcohol	21.465	0	0	2466
unknown	unknown (alkane?)	22.521	2923	0	0
unknown	unknown (alkane?)	24.672	3324	0	5932
unknown	unknown (alkane?)	24.718	4118	0	12764
unknown	unknown (m/z 120 135 92 163)	24.817	16075	0	16304
unknown	coelution (m/z 57 71 85 43 147)	25.45	23879	0	0
unknown	coelution (m/z 55 69 83 97 120 135)	25.82	16854	0	0
unknown	m/z 55 41 83 67 101 111 129)/ m/z 41 57 114)	28.929	12231	0	0
unknown	coelution? (m/z 70 154 199 128 171 115 214)	29.781	46848	7583	0
unknown	m/z 89 75	35.349	2632	0	0

Day 120

Chemical class	Suggested compounds	RT (min)	A1	A4	A8
acid	2-methyl-pentanoic acid	10.982	0	39254	0
acid	Octanoic acid	17.293	0	0	7597
acid	Benzeneacetic acid (RI 1249)	19.093	0	0	55417
acid	Nonanoic acid	19.471	0	0	6238
acid	Hydrocinnamic acid (RI 1349)	20.966	0	0	23350
alcohol	1-Heptanol, 2-propyl- (RI 1194)	16.576	4926	0	0
alkane	Octane, 4-ethyl- (RI 951)	12.113	397746	207889	0
alkane	Decane	12.265	235224	273181	25287
alkane	Undecane (RI 1115)	15.234	34843	63679	19931
alkane	2,5,6-trimethyl-decane isomer	15.276	0	0	35372
alkane	unknown alkane	16.978	0	7223	0
alkane	2,3,7-trimethyl-decane isomer	16.985	0	6049	0
alkane	3-methyl-undecane isomer	17.103	105199	0	4877
alkane	3-methyl-undecane isomer	17.125	0	120074	0
alkane	Dodecane	17.840	1542573	1222978	104134
alkane	1-Ethyl-2-(4-methylpentyl) cyclopentane (m/z 83 55 70 112)	18.805	2317	0	0
alkane	Tridecane	20.127	21245	0	0
alkane	3,5-Dimethyldodecane isomer	20.957	11059	11605	0
alkane	alkane	21.118	9210	13152	0
alkane	alkane (m/z 43 85 57 69 101)	21.247	0	5778	0
alkane	2,6,11-trimethyl-dodecane isomer	21.496	5117	11965	0
alkane	Tetradecane (RI 1413)	22.192	640553	689786	158333
alkane	Octyl-cyclohexane (RI 1476)	23.209	43847	56527	23864
alkane	alkane (m/z 57 71 43 85 99)	24.71	2317	0	0
alkane	3-methyl-pentadecane isomer	24.811	2858	0	0
alkane	unknown alkane	24.984	4141	2398	0
alkane	3-methyl-pentadecane isomer	25.424	83582	101825	41436
alkane	Hexadecane (RI 1612)	25.936	201698	5968	130720
alkane	Decyl-cyclohexane (RI 1675)	27.007	4152	4861	0
alkane	3-methyl-heptadecane	28.820	21242	27091	20178
alkane	Octadecane	29.269	91770	115720	78988
alkane	10-Methylnonadecane isomer	31.881	13632	18442	14237
alkane	Eicosane	32.286	31687	49688	26829
alkane	5-Ethyl-5-methylnonadecane isomer	34.669	2806	4756	2791
alkane	Docosane	35.03	8675	15257	8688
alkane	Hexacosane	39.873	1526	0	0
alkane	2-methylhexacosane (RI 2641)	40.968	2357	0	0
alkane	Octacosane	42.022	2650	1761	0
alkane	2-methyloctacosane	43.041	2860	0	0
alkane	Triacontane	44.027	1865	0	0
alkene	alkene	11.806	0	33407	0
alkene	1-Dodecene	17.642	21421	125814	4145
alkene	3-(E)-Dodecene	17.971	3552	8599	0
alkene	unknown alkene	21.437	0	2338	0
alkene	1-Tridecene	21.44	8239	3801	0
alkene	3-methylene-tridecane	21.915	6643	8143	0

alkene	1-Tetradecene (RI 1403)	22.041	137215	123816	18438
alkene	7-Tetradecene (RI 1421)	22.302	25227	20146	0
alkene	7-(E)-Tetradecene isomer	22.515	2186	0	0
alkene	Cetene (RI 1602)	25.812	54743	63045	24207
alkene	1-Octadecene	29.171	16075	19312	12709
aromatic	Phenol, 2-methyl- isomer	11.135	0	45668	0
aromatic	Phenol, 3-methyl- isomer	14.703	9114	0	57434
aromatic	p-Cresol isomer	14.718	0	22866	0
aromatic	p-Cresol isomer	14.815	396817	9540234	798522
aromatic	p-Cresol isomer	15.338	50944	0	0
aromatic	2,6-Dimethylphenyl isocyanate isomer	24.101	0	0	13229
aromatic	2,6-Dimethylphenyl isocyanate isomer	25.508	0	0	62697
ester	2,2,4-Trimethyl-1,3-pentanediol diisobutyrate (m/z 71 43 97)	26.035	12387	0	0
ester	Methyl pentadecanoate	29.129	0	21031	0
ester	Methyl pentadecanoate isomer (m/z 253)	29.166	9237	0	0
ester	Methyl pentadecanoate isomer	29.709	13365	18763	0
ester	Methyl-9-(Z)-hexadecenoate isomer	30.975	47290	377801	0
ester	Methyl hexadecanoate isomer	31.243	34150	38636	7968
ester	Methyl-9-(Z)-octadecenoate isomer	32.394	20354	25834	0
ester	Methyl cis-10-heptadecenoate isomer	32.534	8007	6282	0
ester	unknown methyl ester	32.701	6781	8126	0
ester	Methyl 9-(E)-octadecenoate isomer	33.392	0	9626	0
ester	Methyl 9,12-(E,E) octadeca-dienoate isomer	33.702	0	0	29070
ester	Methyl 9,12-(E,E) octadeca-dienoate isomer	33.715	0	0	7004
ester	Methyl 9-(E)-octadecenoate isomer	33.769	0	0	9973
ester	Methyl 11-(E)-octadecenoate isomer	33.851	52171	0	0
ketone	3-Methyl-2-cyclohexen-1-one isomer	14.055	0	27369	0
ketone	3-Methyl-2-cyclohexen-1-one isomer	14.086	0	9835	0
N	Pyrrole, 1-methyl-3-(1,1-dimethyl ethyl)- (m/z 122 137 79 94 107)	11.03	0	26563	0
N	2,2,6,6-tetra methyl-4-Piperidinone isomer (m/z 83 140 42 58 98)	15.796	7587	0	0
N	THP/thiophene (m/z 85 56)	25.22	0	0	3386
N	(2-Benzimidazolyl)-methyl amine (m/z 118 147 92 77)	25.519	31416	0	0
N	3-Methyl-1,4-diazabicyclo [4.3.0] nonan-2,5-dione, N-acetyl- isomer	28.091	81384	48986	60233
N	3-Methyl-1,4-diazabicyclo [4.3.0] nonan-2,5-dione, N-acetyl- isomer	28.486	25145	28716	48695
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro- isomer	28.806	0	99962	0
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro- isomer	28.879	241249	0	600601
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro- isomer	28.971	473689	241985	0
N	unknown N (m/z 114 85 57)	29.037	15984	6573	7915
N	unknown N (m/z 114 74 57 87)	29.141	41043	0	0
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hex ahydro-3-(2-methylpropyl)- isomer	29.812	65120	29368	17205
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hex ahydro-3-(2-methylpropyl)- isomer	29.861	0	0	2795
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hex ahydro-3-(2-methylpropyl)- isomer	30.197	0	58273	55156
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hex ahydro-3-(2-methylpropyl)- isomer (m/z 70 154 125)	30.208	8946	0	0
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hex ahydro-3-(2-methylpropyl)- isomer (m/z 70 154 125)	30.279	93043	0	0
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hex ahydro-3-(2-methylpropyl)- isomer	31.321	32026	0	5444
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hex ahydro-3-(2-methylpropyl)- isomer	31.449	17988	0	0
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hex ahydro-3-(2-methylpropyl)- isomer	31.520	6658	52770.21	18136
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hex ahydro-3-(2-methylpropyl)- isomer	31.615	154210	0	0
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hex ahydro-3-(2-methylpropyl)- isomer	31.682	4335	67145	36156
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hex ahydro-3-(2-methylpropyl)- isomer	31.743	0	48058	30932
N	5,10-Diethoxy-2,3,7,8-tetrahydro-1H, 6H-dipyrrolo [1,2-a:1',2'-d]pyrazine isomer	31.764	12927	0	0
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hex ahydro-3-(2-methylpropyl)- isomer	31.79	290508	0	0
N	2,5-Piperazinedione,3-methyl-6-(phen ylmethyl)-isomer (m/z 91 99 127 218)	34.212	0	0	2916
N	2,5-Piperazinedione,3-methyl-6-(phen ylmethyl)-isomer (m/z 91 127 99 218)	34.706	27394	0	0
N	2,5-Piperazinedione, 3,6-bis(2-meth ylpropyl)- isomer (m/z 86 170 135)	34.905	6671	29675	0
N	2,5-Piperazinedione, 3-(phenyl methyl)- isomer	34.976	0	0	47534
N	2,5-Piperazinedione, 3-benzyl-6-isopropyl- isomer (RI 1976 m/z 91 127 155 170 246)	35.77	5413	0	0

N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hex ahydro-3-(2-methylpropyl)- isomer	35.895	42430	18273	0
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hex ahydro-3-(2-methylpropyl)- isomer	36.09	37926	17063	0
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(phenylmethyl)- isomer	37.19	0	37521	34951
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(phenylmethyl)- isomer	37.249	116996	0	0
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(phenylmethyl)- isomer	37.75	76094	25879	20939
N	Indole derivative (m/z 117 90)	20.187	33112	0	0
N	1H-Indole, 3-methyl- derivative (m/z 30 77 103)	22.146	0	0	3411
N	2H-Indol-2-one, 1,3-dihydro- isomer	23.815	14185	7345	17918
N	1H-Indole-1-carboxaldehyde, 2,3-dihydro- isomer (m/z 118 147 77)	25.484	0	24619	0
N	Indole derivative (m/z 117 90 186)	33.185	19765	11320	7235
N	DL-Norleucine (m/z 86 69)	19.051	8541	0	0
N	D-Proline (m/z 70 86)	19.161	35195	0	0
N	dl-Alanyl-l-leucine isomer(m/z128 113 44 99 151)	28.411	32234	0	0
others	Decamethylcyclopentasiloxane isomer	16.719	0	13236	0
others	Dodecamethylcyclopentasiloxane isomer	20.65	0	3792	0
others	Pentacyclo[9.5.1.1(3,9).1(5,15).1(7,13)]octasiloxane, octa methyl- isomer (m/z 521 253)	24.659	34590	0	0
others	Pentacyclo[9.5.1.1(3,9).1(5,15).1(7,13)]octasiloxane, octa methyl- isomer (m/z 521 253)	25.041	1700	0	0
unknown	m/z 55 69 93 140	11.93	0	11704	0
unknown	m/z 41 68 112 95	16.306	11157	0	0
unknown	m/z 43 71 85 99 140	16.445	4740	4263	0
unknown	m/z 43 57 71 85 140	16.564	0	4217	0
unknown	m/z 72 55	16.715	0	0	0
unknown	m/z 72 99 55	16.96	29529	0	0
unknown	m/z 99 42 55 70	17.23	33173	0	0
unknown	m/z 99 42 55 70	17.77	774954	0	0
unknown	m/z 99 42 55 70	17.905	179095	0	0
unknown	m/z 54 82 133 109 126 148	19.438	23712	0	0
unknown	m/z 98 42 133	19.897	5056	0	0
unknown	m/z 98 42 82	19.923	13545	0	0
unknown	m/z 58 43 71 98	20.045	5862	0	0
unknown	m/z 69 56 110 94	20.341	15155	0	0
unknown	m/z 56 69 110 94	20.459	6612	0	0
unknown	m/z 387 97 69 186	20.717	2562	0	0
unknown	m/z 69 41 103	20.851	14007	0	0
unknown	unknown	20.88	7022	8585	0
unknown	m/z 41 60 73 84 137 124 152	21.503	0	0	3653
unknown	m/z 71 57 43 85 99 113 124	21.504	3933	0	0
unknown	unknown	21.600	121409	61184	8787
unknown	m/z 42 98 111 69 138 125 83	22.135	7929	0	0
unknown	m/z 91 55 65 135 152	22.282	0	0	3433
unknown	m/z 55 41 111 69 82 91 138 167	22.433	4976	0	2351
unknown	m/z 42 68 111 152	22.905	6073	0	0
unknown	m/z 18 147 69	23.495	0	0	2219
unknown	m/z 42 68 111 152	23.579	6303	0	8511
unknown	m/z 68 111 42 152	23.643	46234	13935	0
unknown	m/z 42 68 152 137	23.768	9404	0	0
unknown	m/z 57 463 84 166 224 281	24.035	4664	0	0
unknown	m/z 118 147 57 91	24.14	7410	5393	0
unknown	m/z 54 124 151 166	24.223	0	3504	5812
unknown	m/z 165 151 55 68 123 109 84	24.293	18563	0	0
unknown	m/z 165 68 122	24.38	6253	0	0
unknown	m/z 125 166 151 56 68 82	24.804	2762	0	3106
unknown	m/z 125 68 56 166	24.831	21784	0	0
unknown	m/z 57 71 43 85 99 166 151 125	24.996	8731	0	0
unknown	m/z 85 57 43 71 128	25.339	15124	0	7952
unknown	m/z 138 123 165 68	25.6	17267	0	0
unknown	m/z 70 55 41 83 97 111 165	25.721	3908	4043	0
unknown	m/z 165 68 179 41	25.885	0	243219	0
unknown	m/z 71 151 43	26.022	0	6238	2810
unknown	m/z 151 68 137 179	26.08	5954	0	0
unknown	m/z 151 68 82 194 110 137	26.652	4864	0	0
unknown	m/z 120 124 73 91	26.826	54679	0	0
unknown	m/z 84 179 41	27.288	4479	0	0
unknown	m/z 179 68 43 96	27.364	12199	0	0
unknown	m/z 283 114 246	27.386	18206	0	0
unknown	m/z 114 165 85 68	27.53	10062	0	0
unknown	m/z 145 117 90	27.767	0	0	10191
unknown	m/z 138 123 41 84 151 179	27.774	14709	0	0

unknown	m/z 128 113 44 70	28.29	14117	5295	0
unknown	m/z 70 128 97 168	28.52	40230	0	0
unknown	m/z 114	29.208	0	2482	0
unknown	m/z70 56 180	29.215	0	0	15896
unknown	m/z 156 113 72 85	29.993	15689	0	0
unknown	(m/z 70 180 124 110	30.74	0	0	5775
unknown	m/z 130 55 43 121 71 91 99 147	31.105	3455	0	0
unknown	m/z 117 200 90 56	34.081	5958	0	0
unknown	m/z 91 113 99 127 156 218	34.292	21384	0	0
unknown	m/z 113 156 169	34.492	4505	0	0
unknown	m/z 70 86 124 210	34.635	0	0	3101
unknown	m/z 1 99 127 218	34.64	0	0	3934
unknown	m/z 91 204 170	35.154	107376	0	0
unknown	m/z 70 86 124 210	35.257	0	0	6205
unknown	m/z 70 86 170 124	35.315	27050	0	0
unknown	unknown silane (m/z 75)	35.335	0	0	3199
unknown	m/z 186 117 86 170 213 228	35.444	14050	0	0
unknown	m/z 86 170 70 114	35.676	15896	0	0
unknown	m/z 91 113 141 204	36.999	5230	0	0
unknown	m/z 186 117 90	37.115	1919	0	0
unknown	m/z 41 91 169 86 68	40.079	0	0	4749
unknown	m/z 154 107 70	41.357	0	0	4630
unknown	m/z 154 107 70	41.843	0	0	3311

Day 158					
Chemical class	**Suggested compounds**	**RT (min)**	**A1**	**A4**	**A8**
alcohol	2-Hexyl-1-octanol	25.338	0	0	1810
alcohol	1-Decanol, 2-hexyl- isomer	28.742	2035	13884	0
alcohol	n-Heptadecanol-1	32.198	0	2199	0
alcohol	unknown alcohol	33.526	0	4927	0
alkane	Decane	12.282	111544	232352	30650
alkane	Undecane	15.26	12581	28405	15858
alkane	2,6,7-trimethyl-decane isomer	15.285	14867	0	0
alkane	2,3,5-trimethyl-decane isomer	15.872	0	0	11142
alkane	4-ethyl-decane isomer	16.585	0	0	4647
alkane	2,6-Dimethyldecane isomer	16.744	0	9388	0
alkane	3-methyl-undecane isomer	16.938	13960	0	0
alkane	3-methyl-undecane isomer	17.121	0	18127	70080
alkane	Dodecane	17.849	201287	232478	752410
alkane	2,6,11-trimethyl-dodecane isomer	20.881	0	0	4567
alkane	3,5-Dimethyldodecane	20.965	0	0	8650
alkane	alkane	21.132	0	0	2427
alkane	2,4-Dimethyldodecane	21.248	0	4395	0
alkane	2,6,11-trimethyl-dodecane isomer	21.501	0	0	8263
alkane	2,6,10-trimethyl-dodecane isomer	21.597	14350	19842	41100
alkane	Tetradecane	22.195	161121	139115	397558
alkane	Octyl-cyclohexane (RI 1476)	23.203	15886	14014	26359
alkane	unknown alkane	24.717	0	0	1743
alkane	unknown alkane	24.921	0	0	2861
alkane	7-propyl-tridecane isomer	25.088	3690	1576	2772
alkane	3-methyl-pentadecane	25.417	28688	23731	47260
alkane	Hexadecane	25.937	100828	82086	141233
alkane	Decyl-cyclohexane (RI 1675)	27.013	4435	2036	2668
alkane	unknown alkane	28.494	2416	0	0
alkane	3-methyl-heptadecane isomer	28.815	18005	17841	18902
alkane	Octadecane	29.272	56640	45237	60751
alkane	Nonadecane	30.814	0	0	4728
alkane	9-methyl-nonadecane isomer	31.887	7751	4473	10720
alkane	Eicosane	32.279	21295	16196	26215
alkane	unknown alkane	32.515	0	0	3057
alkane	Heneicosane	33.69	0	0	5282
alkane	5-Ethyl-5-methylnonadecane isomer	34.673	4210	2113	4414
alkane	Docosane	35.023	5978	3286	12507
alkane	Tetracosane	36.533	6803	1746	0
alkane	Hexacosane	39.87	4365	3320	3279
alkane	2-methylhexacosane	40.965	3078	4900	3075
alkane	Octacosane	42.023	6807	6543	7204
alkane	2-methyloctacosane	43.042	8086	7082	5253
alkane	Triacontane	44.026	3592	4640	4009
alkane	unknown alkane	44.979	1732	2142	2131
alkene	3-methyl-5-(E)-undecene	17.493	0	0	5351
alkene	1-Dodecene	17.655	10432	20771	79091
alkene	3-(E)-dodecene isomer	17.96	0	0	4613

alkene	3-methylene-tridecane (m/z 70 55)	21.91	0	0	13440
alkene	1-Tetradecene	22.037	65297	19895	84814
alkene	7-(E)-Tetradecene isomer	22.304	0	2867	15642
alkene	2-methyl-1-pentadecene (m/z 70 55 41 83 111 145 172)	25.718	3663	0	1964
alkene	1-Hexadecene	25.813	23536	19011	39768
alkene	Hexadecene isomer	26.033	3949	0	0
alkene	1-Octadecene	29.175	11104	4913	8382
alkene	1- Eicosene	32.209	3801	0	2553
alkene	3-(E)-Eicosene isomer	33.508	0	0	3616
aromatic	3,5-bis(1,1-dimethyl ethyl)-Phenol isomer,	24.434	0	0	2984
aromatic	Benzophenone derivative (m/z 105 77 182 51)	26.764	4485	6457	2927
ester	2,2,4-Trimethyl-1,3-pentane diol diisobutyrate isomer (m/z 7 43)	26.014	17182	7817	9179
ester	Methyl 12-methyl-tetradecanoate isomer	27.475	0	2581	0
ester	Methyl tetradecanoate isomer	28.074	3507	4452	0
ester	Methyl 6-ethyloct-3-yl propyl oxalate isomer	28.499	0	0	1619
ester	Methyl Pentadecanoate isomer	29.113	7323	19950	13986
ester	5,9,13-trimethyl-tetradecanoate isomer	29.262	7385	0	0
ester	Methyl 14-methyl-pentadecanoate isomer	29.694	9805	5563	2878
ester	Methyl bis(2-methylpropyl)-1,2-Benzenedicarboxyloate	30.49	0	3949	2975
ester	Methyl 9-(Z)-hexadecenoate isomer	30.943	41707	27645	32796
ester	Methyl hexadecanoate isomer	31.234	69714	36057	33150
ester	Methyl butyl 2-methylpropyl 1,2-benzenedicarboxyloate isomer	31.919	6106	4547	3142
ester	Methyl cis-10-heptadecenoate isomer	32.382	17284	3780	0
ester	Methyl cis-10-heptadecenoate isomer	32.485	43414	0	0
ester	Methyl 9-(Z)-octadecenoate isomer	32.527	0	12845	6766
ester	Methyl stearate isomer	32.689	8550	0	0
ester	Methyl 6-octadecenoate isomer	33.772	15115	0	0
ester	Methyl 11-(E)-octadecenoate isomer	33.837	129959	24433	28531
ester	unknown methyl ester	35.294	0	0	4513
ester	Methyl 9-(Z)-octadecenoate isomer	35.302	41678	10811	6519
ester	Methyl cis-10-heptadecenoate isomer	35.311	3365	0	0
ester	di(6-methylhept-2-yl) Phthalate	39.455	0	0	3059
N	5-methyl-1H-Benzotriazole	23.804	46583	0	0
N	2,6-Dimethylphenyl isocyanate	24.11	8418	0	0
N	2,3-dihydro-1H-Indole-1-carboxalde hyde derivative (m/z 118 147 91 77 59)	25.45	0	5553	0
N	2,6-Dimethylphenyl isocyanate	25.526	136524	0	0
N	(2-acetylphenyl)-formamide, (RI 1529 m/z 120 135 92 163)	25.742	15423	0	0
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hex ahydro- isomer (m/z 83 111 70 41 114 154 55)	28.759	21006	3127	0
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hex ahydro-3-(2-methylpropyl)- isomer (m/z 70 154 125)	30.148	0	7452	0
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hex ahydro-3-(2-methylpropyl)- (m/z 70 154 125)	30.185	11124	0	0
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hex ahydro-3-(2-methylpropyl)- isomer	31.504	0	8279	0
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexa hydro-3-(2-methylpropyl)- isomer	31.631	0	15372	0
N	Pyrrolo[1,2-a]pyrazine-1,4-dione, hex ahydro-3-(2-methylpropyl)- isomer	31.716	0	8153	3827
N	5,10-Diethoxy-2,3,7,8-tetrahydro-1H, 6H-dipyrrolo[1,2-a:1',2'-d]pyrazine isomer (m/z 70 154 194)	31.742	5794	0	0
other	Lenthionine isomer(m/z 78 45 142 188)	26.95	0	2439	0
other	8-Hydroxyquinoline isomer	27.831	40108	0	0
other	1-Cyclohexene-1-carboxylic acid, 4-(1,5-dimethyl-3-oxohexyl)-, methyl methyl ester, [S-(R*,R*)]- isomer	32.764	10108	0	2635
other	Cyclic octaatomic sulfur (S_8)	33.605	13510	13025	120082
other	2-Dodecen-1-yl(-)succinic anhydride (RI 2159 m/z 69 55 91 41 125 139)	34.199	7248	0	0
other	17.alfa.,21.beta.-28,30-Bisnor hopane isomer	46.139	0	0	2938
unknown	m/z 57 43 71 85 113)	16.737	0	0	7319
unknown	m/z 71 43 57 85 99 140	16.996	0	0	6837
unknown	m/z 57 85 43 71 99 113	21.124	0	0	9636
unknown	m/z 85 43 57 71 99 140)	21.257	7700	0	12438
unknown	unknown	21.592	0	0	42866
unknown	m/z 130 77 103	22.105	0	0	8789
unknown	m/z 98 125 42 69 138 56 83 151	22.117	36455	0	0
unknown	m/z 521 253	24.65	13560	0	0
unknown	m/z 120 92 135 57 65 43 166	24.809	3005	0	0
unknown	m/z 57 71 85 43 99 113 141 169	33.879	0	3791	0
unknown	unknown alkane	35.51	0	2671	14457

Table A2 LC-Q-ToF analysis from ABR samples collected on Day 34, 56, 96, 120 and 158 (Chapter 4). A1, A4 and A8 refers to the 1st, 4th and 8th compartment of the ABR.

Day 34

RT (min)	Chemical class	Suggested compound	A1	A4	A8	Score	Mass Error (ppm)	Isotope Similarity
1.275	Prenol lipids	Vomitoxin	1092149	976559	795776	38.6	2.86	96.24
1.473	Prenol lipids	Vomitoxin	525433	500057	299961	38.6	2.49	96.05
3.235	(unclassified)	Distichonic acid A	312314	107003	16670	36.3	0.26	81.93
1.637	(unclassified)	5'-(dimethylsulfonio)-5'-deoxyadenosine	64175	104547	73278	38.8	1.68	96.19
6.609	Glycerophospholipid	PI(O-16:0/20:5(5Z,8Z,11Z,14Z,17Z))	210735	210000	211669	38.1	2.30	93.19
6.552	Benzene and substituted derivatives	8-anilino-1-naphthalenesulfonate	27634	29383	42896	37.1	2.93	89.07
12.00	Polyketides/phenylpropanoids	2'-Hydroxy-4',6'-dimethoxy-3'-methyldihydrochalcone	8077451	8997813	9219266	38.8	-3.58	98.26
3.214	Glycerolipids	MG(0:0/22:2(13Z,16Z)/0:0)	48918	47732	54511	39.2	0.93	97.19
2.043	Polyketides/flavonoids	(S)-(E)-2'-(3,6-Dimethyl-2-heptenyl)-3',4',7-trihydroxyflavanone	241042	268398	688634	38.6	0.86	94.18
9.251	Indoles and derivatives	Alkaloid AQC2	229699	152063	123771	37.5	2.93	90.76
0.710	Indoles and derivatives	Indole-3-carbinol	120063	81470	68289	38.3	3.11	95.19
2.873	Polyketides/ flavonoids	7-Chloro-3,4',5,6,8-pentamethoxyflavone	308670	206779	70417	37.9	1.41	91.01
0.798	Benzene and substituted derivatives	N-Acetylprocainamide	357406	349777	142105	38.5	2.32	95.28
0.799	Amino acid and derivatives	(S)-N-(4,5-Dihydro-1-methyl-4-oxo-1H-imidazol-2-yl)alanine	1426284	805739	366430	38.1	1.41	92.30
2.290	Alcohols and polyols	Pantothenic acid	192094	115012	46034	35.9	0.93	80.45
0.647	Alcohols and polyols	D-4-O-Methyl-myo-inositol	799963	168663	23919	37.5	-0.87	88.32
3.495	Alkaloids and derivatives	SN-38	327525	217163	167704	36.3	0.93	82.56
7.662	Diacylglycerol/diglyceride	DG(P-14:0/18:1(9Z))	132712	148938	90196	37.4	1.51	88.58
1.330	alkyl phenylketones	Hydroxykynurenine	1396760	502341	133644	38.5	0.43	93.13
1.386	alkyl phenylketones	N'-Formylkynurenine	628240	419716	65092	36.6	-2.97	86.30
1.806	Purines and purine derivatives	1-ethyladenine	641147	581101	104560	38.9	1.70	96.38
1.505	alkyl-phenylketones	N'-Formylkynurenine	1078886	426493	116004	38.3	2.90	94.84
1.607	alkyl-phenylketones	fluorobenzoylpropionic acid	83681	47300	28264	38.8	1.13	95.22
3.605	Amino acid and derivatives	L-cis-Cyclo(aspartylphenylalanyl)	192257	101784	23405	38.5	0.07	92.59
3.193	Amino acid and derivatives	L-cis-Cyclo(aspartylphenylalanyl)	115609	102437	20996	35.6	-3.32	81.70
3.025	Amino acid and derivatives	L-cis-Cyclo(aspartylphenylalanyl)	88592	99135	5331	36.7	-0.67	84.41
3.084	Amino acid and derivatives	Levetiracetam	1156155	152933	12472	39.5	1.74	99.39
0.952	Aldehyde	1-(3-Aminopropyl)-4-aminobutanal	753506	144383	1114	39.2	2.83	99.14
1.448	Amino acid and derivatives	Descarbonyl-lacosamide	2283450	511192	136460	38.7	1.31	94.95
2.259	Amines (alkyldiarylamines)	Isothipendyl	361203	162290	47809	38.1	0.89	91.62
4.661	Amino acid and derivatives	L,L-Cyclo(leucylprolyl)	845461	423167	34384	39.6	1.34	99.83
3.403	Amino acid and derivatives	L-alpha-Amino-1H-pyrrole-1-hexanoic acid	1606414	931656	119948	39.3	1.76	98.62
2.031	Amino acid and derivatives	L-Phenylalanine	217623	146926	56817	37.2	3.25	90.04

3.339	Amino acid and derivatives	L-Tryptophan	1889535	143482	18076	39	1.95	97.19
2.500	Amino acid and derivatives	N-Acetylglutamine	518881	333179	69599	38.7	1.86	95.72
0.666	Amino acid and derivatives	N-Acetylhistidine	525335	248195	55543	39.4	0.81	98.06
0.856	Amino acid and derivatives	N-(1-Deoxy-1-fructosyl)valine	296898	175217	65366	38.5	0.83	93.39
0.834	Amino acid and derivatives	N-Carbamoyl-2-amino-2-(4-hydroxyphenyl)acetic acid	385272	160794	50434	39.6	0.27	98.28
1.003	Amino acid and derivatives	Coutaric acid	383895	324798	129334	37.8	1.28	90.38
0.811	Amino acid and derivatives	N-a-Acetyl-L-arginine	854039	800055	89263	38.7	0.33	93.87
1.238	Fatty acyl / amino fatty acid	11-amino-undecanoic acid	3905683	3500990	3048616	39	2.49	98.14
3.254	Alcohol and polyol	Paromomycin	191797	148714	173264	35.5	2.31	80.15
1.001	Alcohol and polyol	Voglibose	277264	181637	79754	38.2	-3.78	95.32
1.037	Purines and derivatives	N1-methyladenine	549890	478689	148502	38.2	2.55	94.16
12.00	Benzene and substituted derivatives	Methamphetamine	98148	110321	107210	36.4	0.33	82.27
6.005	Fatty acyl	Cohibin A	10759005	5939352	909300	38.9	2.15	97.05
4.827	Fatty acyl	Cohibin A	2828888	2436138	129180	38.6	1.72	95.26
7.132	Fatty acyl	Cohibin A	2098596	1250756	163479	38.5	1.86	94.73
1.729	Benzene and substituted derivatives	Sennidin C	73828	75343	17984	36.6	2.25	85.74
2.222	Aralkylamines / amines	Porphobilinogen	199959	152897	50856	38.1	2.91	93.72
2.031	Aralkylamines / amines	Porphobilinogen	161998	78349	29123	38.6	2.44	95.86
0.689	Organosulfur	S-2,5-Dimethyl-3-furanyl 3-methylbutanethioate	122668	166074	104252	38.3	-0.13	91.62
1.863	Pyrimidines and derivatives	Aprobarbital	294047	212157	105882	38.3	2.36	94.18
1.985	Pyrimidines and derivatives	Metharbital	288067	148064	65059	37.1	2.50	88.44
9.396	Benzene and substituted derivatives	Procarbazine	998317	2129092	912587	38.7	0.86	94.57
0.710	Benzene and substituted derivatives	Acidissiminol epoxide	105864	106977	78719	35.9	-1.00	80.78
1.196	Benzene and substituted derivatives	N-Acetylarylamine	188790	89736	33071	38.1	3.33	94.23
3.006	Benzene and substituted derivatives	5-Phenyl-1,3-oxazinane-2,4-dione	243162	170028	286684	39.1	1.73	97.63
10.01	Benzene and substituted derivatives	1,3,5-Triphenylcyclohexane	75446	133359	230412	37.3	-2.33	89.17
2.937	Benzene and substituted derivatives	Udenafil	4957466	1022270	94424	36.9	1.14	85.92
1.740	Benzene and substituted derivatives	N-Undecylbenzenesulfonic acid	713044	625114	619321	38.8	-1.80	96.18
0.677	Benzene and substituted derivatives	Tiapride	174890	75058	17812	38.1	-0.25	90.76
0.737	Benzene and substituted derivatives	Dimethylbenzimidazole	341353	78678	10881	39	2.73	98.03
2.758	Benzene and substituted derivatives	Desloratadine	872585	891433	383999	36.1	3.73	85.07
2.801	beta hydroxy acids and derivatives	2-Hexenoylcarnitine	402723	103689	49850	36.7	0.00	83.45
1.535	beta hydroxy acids and derivatives	Glutarylcarnitine	303675	232645	71122	38.1	1.97	93.08
2.732	beta hydroxy acids and derivatives	Pimelylcarnitine	369783	148525	31932	38.1	3.16	94.31
2.591	Biotin and derivatives	Biotin	33716	28374	17290	36.7	1.56	85.32
4.055	Biotin and derivatives	Biotin	60887	99684	49949	38.6	1.05	94.33
2.976	Benzene and substituted derivatives	Telmisartan	538956	302663	51382	38.4	0.87	92.90
2.709	Benzene and substituted derivatives	Diflunisal	29401	27704	6944	38.1	2.84	93.70
1.523	Benzene and substituted derivatives	Olmesartan	82292	77078	22794	36.9	-2.61	87.71
1.961	Benzene and substituted derivatives	Telmisartan	764122	672302	76714	36.3	-2.06	84.00
2.987	Benzene and substituted derivatives	Telmisartan	468436	352775	25733	38.4	0.84	93.11

3.517	Benzene and substituted derivatives	Biphenyl	79431	87407	72194	38	-2.51	92.88
1.333	Benzene and substituted derivatives	Telmisartan	72386	89237	19050	35.8	-1.43	80.93
3.256	Fatty acyl / fatty acid	13:0(12Me,12Me)	99105	47857	26173	38.7	-1.90	95.74
3.335	Fatty acyl / fatty acid	13:0(12Me,12Me)	76720	46738	14474	38.6	-1.99	95.42
5.152	Fatty acyl / fatty acid	19:0(11Me)	188760	109860	54447	38.7	-1.52	95.56
1.878	Furanones	Ascorbic acid	26834	45341	29742	39.3	0.31	96.71
1.326	Prenol lipids	Lamioside	1263103	336037	61507	36.5	-0.24	82.83
1.348	Prenol lipids	Flakinin A	262159	273140	153396	38.9	0.71	95.45
1.759	Prenol lipids	Flakinin A	103987	111097	90075	38.2	3.19	94.62
1.355	Prenol lipids	Parthenin	245562	255763	75446	35.9	3.55	83.46
3.412	Steroids and derivatives	Estradiol dipropionate	170624	167450	196467	37.7	3.68	92.63
4.909	Prenol lipids	(-)-Jolkinol A	197341	118445	55640	35.7	1.57	80.34
5.032	Prenol lipids	Helvolic acid	91093	92973	98068	38.1	0.86	91.77
5.434	Prenol lipids	2,2'-Diketospirilloxanthin	37392	37098	38313	35.8	-2.03	81.49
3.267	Prenol lipids	7,8,7',8'-Tetradehydroastaxanthin	110306	127546	76509	37.4	-2.53	89.92
1.036	Carboxylic acid esters	Ethyl 2-(methyldithio)propionate	2560067	488420	62130	37.1	-3.82	90.07
6.735	Carotenoid	Ketospirilloxanthin	374786	252702	331592	38.9	3.41	98.72
4.676	Benzene and substituted derivatives	3,4-Dihydroxyphenylvaleric acid	121212	172089	50306	38.7	-3.59	97.51
5.940	Sphingolipid	Cer(t18:0/16:0)	158870	110695	31279	38.7	1.91	95.78
5.937	Sphingolipid	Cer(d14:1/20:0)	225857	71154	8758	37.1	-3.80	89.76
6.575	Sphingolipid	Cer(d18:0/18:0(2OH))	152329	63732	11212	39	1.74	97.27
6.365	Sphingolipid	Cer(d18:1/17:0)	95504	74705	29081	37.2	-0.81	86.75
6.853	Sphingolipid	N-Stearoylsphingosine	32032	213978	260410	38.4	2.03	94.39
1.557	Polyketides / flavonoids	Antiarone J	99342	99545	47082	37.8	2.18	91.66
2.347	Steroid and derivatives	(25S)-5alpha-cholestan-3beta,6alpha,-7beta,8beta,15alpha,16beta,26-heptol	31627	36396	188873	36	0.97	81.41
1.473	Polyketide	(Z)-3-Phenyl-2-propenal	279991	282109	123969	38.9	3.95	98.98
1.406	Sugar and derivatives	D-arabinonate	161650	47811	55476	37.8	1.33	90.55
2.412	Coumaric acid and derivatives	Caffeoylmalic acid	121702	100635	27265	36.4	-0.65	82.99
0.919	Amino acids and derivatives	Coutaric acid	476828	391056	121566	37.6	1.90	90.39
7.658	Glycerolipid	DG(16:0/18:3(9Z,12Z,15Z)/0:0)[iso2]	109762	98343	77806	36.2	-1.42	82.89
7.224	Glycerolipid	DG(18:4(6Z,9Z,12Z,15Z)/18:1(9Z)/0:0)[iso2]	166061	50523	74478	36.4	-3.15	85.92
8.189	Glycerolipid	DG(14:1(9Z)/22:2(13Z,16Z)/0:0)[iso2]	102297	103451	44550	36.2	-2.63	83.93
0.539	Glycerophospholipids	PA(22:6(4Z,7Z,10Z,13Z,16Z,19Z)/20:5(5Z,8Z,11Z,14Z,17Z))	96765	40602	18342	36.4	-3.01	85.37
4.826	Glycerophospholipids	PG(14:0/18:1(9Z))	4510809	1820234	147224	39.3	-0.81	97.59
4.617	Glycerophospholipids	PG(15:0/18:2(9Z,12Z))	2400017	498061	6738	39.2	-0.80	96.89
4.903	Glycerophospholipids	PG(12:0/19:0)	95051	8490	0	35.4	3.63	81.43
5.442	Glycerophospholipids	PG(20:5(5Z,8Z,11Z,14Z,17Z)/18:0)	83682	25497	2381	38.7	-2.72	96.56
0.919	Glycerophospholipids	PI(12:0/12:0)	299049	262112	58284	38.6	-2.88	96.60
1.003	Glycerophospholipids	PI(12:0/12:0)	350190	304941	71845	38.7	-2.84	96.62
5.538	Glycerophospholipids	PI(17:2(9Z,12Z)/0:0)	341664	187387	50513	36.8	0.93	85.29
3.057	Dialkyldisulphides	1-(1-Propenylthio)propyl propyl disulfide	76166	50354	52620	36.6	1.32	84.48

7.028	Dialkyldisulphides	1-(1-Propenylthio)propyl propyl disulfide	85404	92624	110615	36.6	3.20	86.94
3.553	Dialkyldisulphides	1-(1-Propenylthio)propyl propyl disulfide	68440	76100	83951	36.6	1.46	84.55
5.995	Dicarboxylic acid and derivatives	Genipinic acid	3012422	2203464	149162	39.3	0.62	97.40
3.659	Dicarboxylic acid and derivatives	Tricosanedioic acid	238434	250012	112065	39.2	2.17	98.70
7.708	Glycerolipid	DG(18:4(6Z,9Z,12Z,15Z)/18:0/0:0)[iso2]	32134	21906	24148	37.5	-2.00	89.70
0.757	Purines and derivatives	Adenosine monophosphate	37575	34096	14268	37.8	0.60	89.72
1.326	Amino acids and derivatives	Alanyl-Glutamine	1197281	876555	510064	37.1	1.75	87.60
0.860	Amino acids and derivatives	Arginyl-Valine	175557	95480	26640	36.2	-0.31	81.60
1.216	Amino acids and derivatives	Asparaginyl-Proline	2360276	315125	123672	37.8	2.96	92.39
1.497	Amino acids and derivatives	Asparaginyl-Proline	963779	340941	177107	38.5	3.58	96.76
1.547	Amino acids and derivatives	Asparaginyl-Proline	906264	257662	138044	38.1	3.32	94.53
2.923	Amino acids and derivatives	Glutaminyl-Glutamate	653367	336609	116265	35.4	-2.94	80.37
1.414	Amino acids and derivatives	Glutaminyl-Isoleucine	62271	45717	2300	37.8	0.92	89.89
1.341	Amino acids and derivatives	Glutaminyl-Isoleucine	56661	25307	4592	38.7	1.46	95.36
1.086	Amino acids and derivatives	Glutaminyl-Proline	840613	305382	144556	37	0.11	84.99
0.761	Amino acids and derivatives	Glycyl-L-leucine	2994170	954157	48946	39.1	1.98	98.08
2.424	Amino acids and derivatives	Glycyl-L-leucine	121154	66391	16177	39.4	1.99	99.52
3.491	Amino acids and derivatives	Glycyl-Methionine	1236671	1132762	908689	38.4	-1.23	93.33
1.444	Amino acids and derivatives	Glycyl-Methionine	37896	24244	6973	38	1.98	92.54
2.812	Amino acids and derivatives	Glycyl-Phenylalanine	322901	152474	49635	36.6	2.18	85.41
0.849	Amino acids and derivatives	Glycylproline	1043600	909619	262113	38.2	1.42	92.89
1.615	Amino acids and derivatives	Glycyl-Tyrosine	68239	27368	8356	38.3	-3.62	95.83
0.956	Amino acids and derivatives	Hydroxyprolyl-Glutamine	1851804	1709226	362380	37.3	2.21	88.93
1.947	Amino acids and derivatives	Hydroxyprolyl-Isoleucine	1583434	329232	86230	38.8	2.75	97.16
1.459	Amino acids and derivatives	Isoleucyl-Lysine	284674	117635	13013	39.4	1.01	98.23
0.830	Amino acids and derivatives	Isoleucyl-Lysine	60882	35476	2281	39.3	1.30	98.15
2.435	Amino acids and derivatives	Isoleucyl-Threonine	167396	136511	7273	39.4	0.77	98.14
2.633	Amino acids and derivatives	Isoleucyl-Valine	55316	31665	9312	39.5	1.16	98.66
4.810	Amino acids and derivatives	L,L-Cyclo(leucylprolyl)	397876	85771	7999	39.5	1.25	98.87
4.942	Amino acids and derivatives	Leucyl-phenylalanine	130174	60963	2407	37.8	-2.97	92.46
4.649	Amino acids and derivatives	Leucyl-phenylalanine	31277	18124	1291	37.9	-4.00	94.11
2.827	Amino acids and derivatives	L-gamma-glutamyl-L-valine	757801	613541	183457	35.3	-3.02	80.30
3.715	Amino acids and derivatives	L-phenylalanyl-L-proline	44138	34818	923	36.6	2.33	85.58
1.326	Amino acids and derivatives	Prolyl-Alanine	263278	208032	54032	38.6	0.17	93.25
2.591	Amino acids and derivatives	Prolyl-Tyrosine	2138010	1205168	388552	36.1	2.67	83.66
2.321	Amino acids and derivatives	Trandolaprilat	64056	56014	61941	39	-0.22	95.04
2.420	Amino acids and derivatives	Alanyl-Isoleucine	67588	94158	1937	39.1	1.16	97.06
0.677	Amino acids and derivatives	Asparaginyl-Hydroxyproline	171784	233229	171480	38.9	0.38	94.73
2.070	Amino acids and derivatives	Asparaginyl-Isoleucine	425711	1199621	418506	38.7	1.89	95.94
0.651	Amino acids and derivatives	Glycyl-L-leucine	223409	270550	29987	38.5	2.62	95.65
2.976	Amino acids and derivatives	N5-Acetyl-N2-gamma-L-glutamyl-L-ornithine	659405	542860	49291	36.6	0.03	83.24

2.766	Amino acids and derivatives	N5-Acetyl-N2-gamma-L-glutamyl-L-ornithine	643763	331545	45198	36.1	1.71	82.69
3.224	Amino acids and derivatives	Isoleucyl-Valine	159070	107360	10604	39.4	1.53	98.88
2.207	Amino acids and derivatives	N5-Acetyl-N2-gamma-L-glutamyl-L-ornithine	559144	106813	29874	37.5	-2.09	89.75
5.438	Glycerolipid	1-(14-methyl-pentadecanoyl)-2-(8-[3]-ladderane-octanyl)-sn-glycerol	210069	84974	9205	39.1	1.72	97.45
1.707	Prenol lipid	16,17-Dihydro-16a,17-dihydroxygibberellin A4 17-glucoside	2340211	1268819	198084	35.7	-3.35	82.55
4.823	Prenol lipid	Narasin	67210	62231	1693	37.3	-3.97	91.27
0.767	Prenol lipid	Persicachrome	372997	380906	151929	35.8	2.59	82.07
4.356	Fatty acyl	LTE4	252101	45925	70178	37.1	3.95	90.05
5.948	Fatty acyl	Dichotellate A	47216	53153	76800	36.5	-0.97	83.88
3.404	Steroid and derivatives	Norselic acid C	73832	66143	70235	38.9	1.14	95.68
2.496	Benzene and substituted derivatives	Phenethyl 6-galloylglucoside	172804	98895	128043	37.2	-3.70	90.21
5.144	Fatty acyl / fatty acid	4Z,7Z,10Z,13Z,16Z,19Z,22Z,25Z-octacosaoctaenoic acid	2882237	1946100	2503789	39.5	-0.71	98.38
3.160	Fatty acyl / fatty acid	cis-9-palmitoleic acid	223821	105215	25589	39.2	-1.67	98.08
3.667	Fatty acyl / fatty acid	Palmitic acid	11330614	6989258	3279703	39.8	-0.36	99.48
3.037	Fatty acyl / fatty acid	3R,5S-Dimethyldodecanoic acid	414188	250344	138980	38.9	-2.10	97.00
4.017	Fatty acyl / fatty acid	Heptadecanoic acid	1335062	1066260	978322	39.8	-0.55	99.48
1.839	Fatty acyl / fatty acid	2-Methylacetophenone	136585	109031	101009	36.5	-2.40	85.33
5.666	Fatty acyl / fatty acid	Polyoxyethylene dioleate	37211	14442	2915	38.6	0.14	93.00
2.420	fatty acyl carnitines	(7Z,10Z,13Z,16Z)-docosatetraenoylcarnitine	284704	262420	127860	37.6	1.61	90.11
2.648	Fatty acyl carnitines	3-hydroxy-cis-5-octenoylcarnitine	5662671	2398921	1117416	39.4	0.41	97.53
0.554	fatty acyl carnitines	3-hydroxy-cis-5-octenoylcarnitine	818131	774952	404009	37.8	3.76	93.61
4.518	fatty acyl carnitines	Arachidyl carnitine	145391	150498	220349	39.4	1.54	98.71
5.255	fatty acyl carnitines	O-behenoylcarnitine	79369	83233	112141	38.9	1.53	96.51
0.855	fatty acyl carnitines	(9Z)-3-hydroxydodecenoylcarnitine	237873	239100	79370	38.9	0.80	95.70
4.244	fatty acyl carnitines	Palmitoylcarnitine	1585599	1741861	1711250	38.7	2.01	96.07
1.184	fatty acyl carnitines	(9Z,12Z,15Z)-3-hydroxyoctadecatrienoylcarnitine	136023	131639	143831	39.5	0.73	98.36
2.378	fatty acyl carnitines	O-(17-carboxyheptadecanoyl)carnitine	21723	16569	123565	39.2	0.67	96.83
1.954	fatty acyl glycosides	Prenyl apiosyl-(1->6)-glucoside	489345	450993	50792	38.3	0.10	91.80
1.303	fatty acyl glycosides	1-(3-Methyl-2-butenoyl)-6-apiosylglucose	279440	225872	60393	37.9	-1.85	91.49
2.923	fatty acyl glycosides	3-Methyl-3-butenyl apiosyl-(1->6)-glucoside	340315	199034	49242	37.9	2.98	93.17
2.945	fatty acyl glycosides	3-Methyl-3-butenyl apiosyl-(1->6)-glucoside	194076	144949	29406	38.3	-0.18	91.75
2.846	fatty acyl glycosides	3-Methyl-3-butenyl apiosyl-(1->6)-glucoside	778663	787571	406318	37.5	-0.31	87.65
0.824	fatty acyl / fatty amides	N-(3-oxododecanoyl) homoserine lactone	104404	92867	91571	36.5	0.31	82.86
1.599	fatty acyl / fatty amides	N-(3-oxododecanoyl) homoserine lactone	50729	75685	40068	38	1.05	91.04
6.605	fatty acyl/fatty alcohol	phenolic phthiocerol	1302400	743586	112241	38.1	1.76	92.70
2.469	Fatty acyls	2R-hydroxy-oleic acid	19793	13346	15800	36.9	-2.65	87.45
5.373	fatty alcohol	phenolic phthiocerol	388005	233455	10965	39.3	2.26	99.08
7.708	fatty alcohol	phenolic phthiocerol	101728	49375	28229	38.2	1.40	92.72
2.412	Fatty aldehyde	9Z,11E,13-Tetradecatrienal	388814	319485	369746	39.1	-2.92	98.88
5.156	fatty amides	Docosanamide	181106	170830	85458	38.9	2.02	97.04
4.343	fatty ester	Mayolene-17	1514545	471765	24148	39.1	1.56	97.37

6.076	Fatty ester	Mayolene-19	3214155	1250635	287767	39.3	1.99	98.96
4.891	fatty ester	Mayolene-19	1576477	721765	48973	39.2	1.97	98.54
7.213	fatty ester	Mayolene-19	855989	332853	85789	37.9	1.44	91.15
6.365	fatty ester	Mayolene-19	273865	211394	79440	35.2	1.88	78.31
6.377	fatty ester	Mayolene-20	638287	301516	43200	38.5	-0.46	93.29
5.167	fatty ester	Mayolene-20	323075	144336	3261	38.4	1.33	93.70
6.651	fatty ester	Mayolene-20	38195	38031	27566	37.1	1.43	87.30
1.432	fatty ester / fatty acyl carnitines	3-hydroxy-cis-5-octenoylcarnitine	1117914	640533	307395	35.6	3.20	81.93
4.731	Polyketides / flavonoids	Laxiflorin	216295	267252	129829	39.5	0.81	98.69
6.609	Polyketides / flavonoids	Laxiflorin	168760	177058	201937	38.9	0.85	95.49
0.936	Polyketides / flavonoids	2',4',5,7-Tetramethoxy-8-methylflavanone	268818	543026	232298	38.4	3.68	96.32
0.504	Polyketides / flavonoids	5,7-Dihydroxyflavone 7-benzoate	154011	39071	29246	38.2	2.79	94.12
8.979	Polyketides / flavonoids	Demethyltorosaflavone C	133773	110725	75111	38.1	-2.90	93.81
5.816	Polyketides / flavonoids	Demethyltorosaflavone D	1344673	47273	10994	38.7	0.72	94.41
2.030	Polyketides / flavonoids	Epilumaflavanone B	271657	250864	41584	39	1.66	97.04
1.958	Polyketides / flavonoids	Euchrenone a14	217972	117591	19932	36	-2.16	82.71
1.226	Polyketides / flavonoids	Prebarbigerone	208028	183958	45765	38.7	0.70	94.52
0.635	Polyketides / flavonoids	Galangin 5,7-dimethyl ether	77278	93207	38586	36.4	-1.00	83.29
3.780	Polyketides / flavonoids	Lonchocarpenin	309775	129088	19429	38.4	1.32	93.71
1.215	Polyketides / flavonoids	Heteroflavanone B	678418	577451	234467	39	0.30	95.61
3.517	Polyketides / flavonoids	Artocommunol CA	366480	302559	117853	36.4	-0.63	82.89
1.470	Polyketides / flavonoids	Heteroflavanone B	172569	138162	36547	38.8	1.14	95.18
4.425	Polyketides / flavonoids	Isochamanetin	157963	130041	26890	36.6	-2.26	85.87
2.050	Polyketides / flavonoids	Quercetol B	63446	58846	44409	38.2	3.04	94.46
2.416	Benzene and substituted derivatives	Fluconazole	1272571	1364248	859086	38.9	-2.86	97.92
1.355	furopyrans	Cyclocalopin F	408538	442341	192596	38.5	2.53	95.62
8.979	amino acid and derivatives	Avenic acid A	1355595	1163306	816233	39.2	0.91	97.35
0.647	amino acid and derivatives	4-Guanidinobutanoic acid	649677	542629	824649	38.3	3.17	95.44
0.670	amino acid and derivatives	(S)-4-Amino-5-oxopentanoate	169477	129189	45822	36	3.45	83.82
4.404	sugar acids and derivatives	Alginic acid	27385	25129	21290	36.9	-0.77	85.24
1.269	amino acid and derivatives	gamma-Glutamyl-beta-aminopropiononitrile	1597406	655140	214678	37.4	1.66	88.86
0.670	amino acid and derivatives	gamma-glutamyl-ethylamide	82934	104300	29296	37.8	-1.42	90.76
2.564	Fatty acids	(2S,4S)-Pinnatanine	89943	59398	18889	36.7	1.95	85.67
4.560	Glycerolipids	SQDG(16:0/16:1(9Z))	3664	1	55	38.6	-1.09	94.25
6.609	Glycerophospholipids	PI(O-20:0/20:5(5Z,8Z,11Z,14Z,17Z))	180063	180297	189277	36.9	2.40	87.51
1.599	Glycerophospholipids	PI(13:0/12:0)	1826127	1543222	1343956	38.8	-1.91	96.49
4.537	Glycerophospholipids	PS(O-16:0/14:1(9Z))	307582	63698	461	36.7	0.09	83.56
4.826	Glycerophospholipids	PS(P-16:0/16:1(9Z))	966759	1071759	35177	39.2	0.31	96.61
4.268	Amino acid and derivatives	N-[(3a,5b,7b)-7-hydroxy-24-oxo-3-(sulfoxy)cholan-24-yl]-Glycine	195668	73279	13932	36.3	1.64	83.41
6.365	Glycerolipids	MGDG(18:2(9Z,12Z)/18:3(9Z,12Z,15Z))	59729	146672	26735	39.3	-2.46	99.27
0.538	Sphingolipids	Glucosylceramide (d18:1/25:0)	35004	32454	20475	35.5	3.19	81.41

0.623	Alkaloids and derivatives	Flazine methyl ether	128641	207312	51383	36.2	-1.77	83.02
0.651	Benzene and substituted derivatives	4-Aminohippuric acid	476803	412853	111989	38.1	-3.68	94.93
1.638	Benzene and substituted derivatives	4-Aminohippuric acid	316711	159407	43444	39.1	0.11	95.77
1.033	Amino acid and derivatives	N-Ribosylhistidine	1211315	1889083	540966	37.2	2.17	88.64
5.769	Prenol lipids	2-methylbacteriohopane-32,33,34,35-tetrol	1822146	771985	79323	38.9	2.20	97.29
5.369	Prenol lipids	bacteriohopane-,32,33,34-triol-35-cyclitol	712060	633117	133820	39.2	1.88	98.29
4.366	Prenol lipids	adenosylhopane	138390	307539	28819	37.1	2.21	88.35
5.228	Fatty acyl	5-Oxo-ETE-d7	49103	22283	10897	39.3	-0.41	96.86
0.862	Hydroxycoumarin	Mammea E/BB	1101893	438192	523512	35.9	2.24	81.93
1.001	Purine and derivatives	7-Methylguanine	2087056	1213342	71730	39	2.21	97.73
1.452	Purine and derivatives	Hypoxanthine	36400	53693	10549	38.7	3.83	97.83
3.095	Benzene and substituted derivatives	Sulindac sulfide	212893	229722	27672	37.5	-0.45	88.15
6.887	Indole	Cyclobrassinone	113071	94253	109139	37.6	-2.72	91.32
5.995	Indole	Indoleacetic acid	1921557	1286441	32991	39.1	2.40	98.16
1.950	Amino acids and derivatives	5-Hydroxy-L-tryptophan	265032	47822	18733	38.8	-3.32	97.93
4.932	Indole	2-Indolecarboxylic acid	847852	571049	120932	39	2.27	97.88
3.065	Indole	2-Indolecarboxylic acid	493532	356580	10068	38.6	2.35	95.96
3.609	Indole	1H-Indole-3-carboxaldehyde	715616	323499	34190	36.6	3.52	86.90
2.766	Indole	Indoleacrylic acid	124399	74182	26394	38.4	2.84	95.54
3.323	Amino acids and derivatives	5-Methoxytryptophan	643443	180845	30267	37.5	2.00	90.04
9.533	Prenol lipids	Valdiate	177302	134847	105025	39.4	1.73	98.88
2.207	isocoumarans	Citalopram aldehyde	206944	160511	48822	37	2.27	87.48
3.837	Polyketides / flavonoids	Calopogoniumisoflavone A	63941	54121	26091	37.9	0.95	90.78
0.824	Amino acids and derivatives	N-Jasmonoylisoleucine	177663	160025	80830	37	1.24	86.58
4.362	Fatty acyl / octadecanoid	12-hydroxyjasmonic acid 12-O-beta-D-glucoside	852022	796982	863992	36.7	1.08	84.74
1.306	Polyketides	11-Hydroxy-12-methoxydihydrokawain	936173	840565	473929	37.2	3.57	90.34
1.473	Polyketides	11-Hydroxy-12-methoxydihydrokawain	423638	391700	142553	38.5	2.60	95.73
3.190	Fatty acyl / eicosanoids	Lipoxin D4	177437	154168	12059	36.1	3.93	84.96
1.698	Polyketides	10-Deoxymethymycin	123586	134376	96012	39.5	0.76	98.63
2.793	Fatty acyl /fatty acid conjugates	Dethiobiotin	109110	67783	13014	39.2	1.63	97.79
3.053	Glycerophospholipids	PA(12:0/0:0)	940540	329908	73427	37.1	-3.81	90.03
5.133	Glycerophospholipids	PA(14:0/18:1(9Z))	286920	205649	19140	37.5	-0.45	88.19
5.209	Glycerophospholipids	PA(16:0/18:2(9Z,12Z))	436592	59327	13690	36.3	-0.81	82.34
2.107	Glycerophospholipids	PA(22:6(4Z,7Z,10Z,13Z,16Z,19Z)/0:0)	71067	64376	16128	37.5	2.05	90.10
2.100	Glycerophospholipids	1-(18-mercaptooctadecanoyl)-sn-glycerol 3-phosphate	40107	41869	11761	36.4	-0.58	82.88
0.855	Glycerophospholipids	PC(8:0/0:0)	25828	18323	22535	36.9	-2.93	88.03
6.906	carbohydrate and derivatives)	Sedoheptulose 1,7-bisphosphate	32035	26192	34820	38.4	2.89	95.33
2.446	Prenol lipids	Menthol propylene glycol carbonate	11300	7998	41833	37.6	-2.76	91.05
0.864	Fatty acyl /fatty amides	N,N-diethyl-3-hydroxybut-2-enamide	103744	44691	17230	36.2	2.01	83.56
5.133	Fatty acyl /fatty amides	N-oleoyl glutamic acid	54422	49759	26785	37.5	3.88	92.08
2.679	Fatty acyl /fatty amides	Pipericine	170551	167884	47191	37.9	1.80	91.61

2.416	Fatty acyl /fatty amides	N-(4-benzenesulfonamide) arachidonoyl amine	962539	1028563	855250	36.7	3.53	87.74
2.793	Fatty acyl /fatty amides	N-(5-hydroxy-pentyl) arachidonoyl amine	45511	42032	87005	38.9	1.34	96.18
3.503	Fatty acyl /fatty amides	N-stearoyl serine	1922346	2196104	2252120	39.2	2.73	99.24
2.736	Fatty acyl /fatty amides	Anandamide (20:2, n-6)	130785	156711	34340	38.7	2.17	96.25
4.252	N-acyl pyrrolidines	N-(14-Methylhexadecanoyl)pyrrolidine	244741	271588	254391	38.6	3.43	97.06
2.808	Amino acids and derivatives	L-N-(1H-Indol-3-ylacetyl)aspartic acid	105926	107607	38356	38	-2.64	93.12
3.719	Amino acids and derivatives	Methylhippuric acid	104204	96025	40500	38.4	-3.95	96.44
3.205	Amino acids and derivatives	Suberylglycine	245261	293947	204961	37.8	-0.13	89.19
4.457	Amino acids and derivatives	Pentacosanoylglycine	2287474	3144687	5090121	39	2.89	98.57
3.625	Amino acids and derivatives	Tricosanoylglycine	58377	92731	183991	39	1.69	96.98
8.686	Amino acids and derivatives	N-Succinyl-L,L-2,6-diaminopimelate	57987	65949	55062	38.6	0.13	93.12
4.362	N-acyl-piperidines	Pipercitine	352146	377736	372288	39	2.99	98.31
3.766	N-acylpyrrolidines	N-Hexadecanoylpyrrolidine	196359	188926	154160	36.5	3.73	86.79
6.369	Sphingolipids	Cer(d18:0/h17:0)	82683	101699	20851	38.6	2.03	95.37
0.681	nitroimidazole	Metronidazole	177302	134847	105025	39	2.63	98.01
2.534	Fatty acyl / octadecanoids	12R-HOME(9E)	34360	23438	10602	37.1	-2.36	88.55
4.709	Fatty acyl / octadecanoids	7-keto-stearic acid	55945	50083	49245	37.5	3.66	91.66
1.832	Carbohydrates and derivatives	Acaciabiuronic acid	190566	172348	19484	38.7	-0.64	94.51
1.539	Carbohydrates and derivatives	1,2,10-Trihydroxydihydro-trans-linalyl oxide 7-O-beta-D-glucopyranoside	499739	183713	38120	36.7	2.84	86.76
3.719	Carbohydrates and derivatives	1,2,10-Trihydroxydihydro-trans-linalyl oxide 7-O-beta-D-glucopyranoside	884074	818247	129286	38	-0.82	91.05
1.573	Carbohydrates and derivatives	1,2,10-Trihydroxydihydro-trans-linalyl oxide 7-O-beta-D-glucopyranoside	337858	183904	48524	36.4	0.10	81.92
1.786	Carbohydrates and derivatives	1,2,10-Trihydroxydihydro-trans-linalyl oxide 7-O-beta-D-glucopyranoside	119168	65233	25863	36.6	-1.25	84.34
4.364	Carbohydrates and derivatives	2-[4-(3-Hydroxypropyl)-2-methoxyphenoxy]-1,3-propanediol 1-glucoside	275522	258945	31626	37.9	-3.02	93.31
2.923	Carbohydrates and derivatives	Benzyl beta-primeveroside	300302	207019	42060	37.4	-0.61	87.81
5.275	Carbohydrates and derivatives	Phenethyl rutinoside	280440	216462	10036	35.8	-2.92	82.26
4.741	Carbohydrates and derivatives	Verbasoside	140372	82691	2956	38.7	0.49	94.19
3.548	Carbohydrates and derivatives	2,4-Dihydroxy-7,8-dimethoxy-2H-1,4-benzoxazin-3(4H)-one 2-glucoside	117635	187089	22542	37.1	-0.05	85.57
0.609	Benzene and substituted derivatives	4R,5R,6S-Trihydroxy-2-hydroxymethyl-2-cyclohexen-1-one 6-(2-hydroxy-6-methylbenzoate)	64600	101194	24251	35.6	2.50	81.19
0.670	Amino acids and derivatives	Ophthalmic acid	542449	699984	464860	37.2	1.72	87.84
9.396	Amino acids and derivatives	Thyrotropin releasing hormone	959957	1526969	792769	39	-3.27	98.89
2.461	organosulfonic acids	Acrylic acid-2-acrylamido-2-methyl propane sulfonic acid copolymer	1190151	4856141	862682	37.9	-3.82	93.94
6.205	other fatty acyls	N-(3-(hexadecanoyloxy)-heptadecanoyl)-L-ornithine	59738	34277	4024	38.9	0.97	95.74
1.793	Fatty acyl / fatty acids	12-oxo-5E,8E,10Z-heptadecatrienoic acid	64525	62443	39295	36.5	-1.88	84.91
5.793	Carbohydrates and derivatives	Imidazoleacetic acid ribotide	402112	11274	1996	38.4	-0.41	92.35
3.609	Carbohydrates and derivatives	2-Hydroxybenzaldehyde O-[xylosyl-(1->6)-glucoside]	170797	98835	19754	38.7	-1.51	95.51
2.500	Carbohydrates and derivatives	Ptelatoside A	1619243	1666472	135867	38.8	-1.65	95.97
3.795	Benzene and substituted derivatives	Ethopropazine	221349	42023	7771	36.2	3.82	85.58
1.515	Benzene and substituted derivatives	Thioridazine	74017	85508	69998	37.3	3.90	90.96
2.728	Benzene and substituted derivatives	(4-Methylphenyl)acetaldehyde	10847	17887	11185	38.7	3.51	97.73
1.355	Benzene and substituted derivatives	(4-Methylphenyl)acetaldehyde	127513	133856	68493	38.9	3.65	98.62
10.44	Benzene and substituted derivatives	Tropicamide	61806	317460	39644	37.1	-0.73	86.37

2.069	Benzene and substituted derivatives	Musanolone F	161499	176858	24900	38.7	-1.93	96.00
0.925	phenylsulphates (arylsulphates)	Dopamine 4-sulfate	143637	269404	113831	35.2	-3.63	80.48
5.335	Glycerophospolipids	PC(12:0/15:1(9Z))	1479446	219873	6548	38	0.36	90.36
6.009	Glycerophospolipids	PC(12:0/17:1(9Z))	965576	440310	49008	38.9	0.34	94.69
5.571	Glycerophospolipids	PC(14:1(9Z)/14:0)	3365765	338279	30790	39.1	-0.84	96.64
5.674	Glycerophospolipids	PC(14:1(9Z)/14:0)	2695379	594692	44905	39.2	-0.31	96.19
5.765	Glycerophospolipids	PC(17:2(9Z,12Z)/13:0)	1827658	592020	43474	39	-0.42	95.41
6.005	Glycerophospolipids	PC(18:4(6Z,9Z,12Z,15Z)/13:0)	2331754	1373692	243376	38.7	-2.86	96.97
3.214	Glycerophospolipids	PC(11:0/11:0)	3999924	4011575	4314458	39	2.47	98.12
0.538	Glycerophospolipids	PC(22:0/22:4(7Z,10Z,13Z,16Z))	34695	35177	34638	35.4	2.87	80.25
6.372	Glycerophospolipids	PC(17:2(9Z,12Z)/15:0)	572432	210441	4680	38.2	-1.22	92.69
6.076	Glycerophospolipids	PC(20:5(5Z,8Z,11Z,14Z,17Z)/13:0)	815418	339702	84432	38.9	-1.56	96.50
6.597	Glycerophospolipids	PE(16:0/18:1(11Z))	1434589	625781	67493	37.5	-1.29	88.82
5.457	Glycerophospolipids	PE(16:1(9Z)/16:1(9Z))	2640451	874040	174383	39.6	-0.61	98.84
6.327	Glycerophospolipids	PE(16:1(9Z)/17:0)	3003974	1274801	44913	38.7	-0.98	94.93
6.005	Glycerophospolipids	PE(18:1(11Z)/14:0)	8944504	4558794	702319	39.8	-0.48	99.58
6.075	Glycerophospolipids	PE(18:1(11Z)/16:1(9Z))	3138978	1038703	232495	39.7	-0.61	99.40
6.654	Glycerophospolipids	PE(18:1(11Z)/18:1(11Z))	463716	111822	17844	37.9	-1.46	91.47
6.495	Glycerophospolipids	PE(18:2(9Z,12Z)/21:0)	77676	45247	14791	37.1	-1.99	87.86
5.453	Glycerophospolipids	PE(18:4(6Z,9Z,12Z,15Z)/16:1(9Z))	712726	337802	65039	38.1	-3.03	93.89
1.618	Glycerophospolipids	PG(12:0/0:0)	239644	223290	63535	38.6	3.01	96.77
5.685	Glycerophospolipids	PG(12:0/17:0)	115170	111553	72141	36.1	3.98	84.95
4.232	Glycerophospolipids	PG(14:0/16:1(9Z)	513919	51200	0	37	-1.53	87.08
5.076	Glycerophospolipids	PG(14:0/18:0)	37896	17915	231	38.3	-1.05	92.71
5.072	Glycerophospolipids	PG(15:0/18:1(9Z))	1921711	432569	1343	39.4	-0.86	97.81
0.897	Glycerophospolipids	PG(16:0/0:0)	124644	112398	47067	36.7	3.54	87.82
5.369	Glycerophospolipids	PG(16:0/18:1(11Z))	1313785	399743	13038	39.8	-0.44	99.31
4.339	Glycerophospolipids	PG(16:1(9Z)/16:1(9Z))	3147692	500949	30247	38.8	-0.90	95.21
5.163	Glycerophospolipids	PG(17:0/18:2(9Z,12Z))	926186	213602	1255	39.5	-0.75	98.41
4.887	Glycerophospolipids	PG(18:1(11Z)/16:1(9Z))	3518392	888368	78513	39.6	-0.63	98.84
5.666	Glycerophospolipids	PG(18:1(11Z)/17:0)	215505	14725	154	38.9	-1.12	95.84
5.434	Glycerophospolipids	PG(18:1(11Z)/18:1(11Z))	977377	182463	5074	39.7	-0.55	98.95
5.369	Glycerophospolipids	PG(18:4(6Z,9Z,12Z,15Z)/18:0)	131707	63914	508	38.5	-3.24	96.50
5.815	Glycerophospolipids	PG(19:0/18:2(9Z,12Z))	1262	611	264	39.2	-0.70	97.02
4.891	Glycerophospolipids	PG(20:5(5Z,8Z,11Z,14Z,17Z)/16:0)	718847	248038	37143	37.2	-3.37	89.95
2.991	Glycerophospolipids	PG(22:2(13Z,16Z)/0:0)	447525	397747	176618	37	2.73	88.31
0.638	Glycerophospolipids	PG(O-18:0/0:0)	155451	184216	56553	37.7	-1.42	90.21
5.006	Glycerophospolipids	PG(17:0/20:5(5Z,8Z,11Z,14Z,17Z))	612634	683560	717452	39	0.55	95.49
4.709	Glycerophospolipids	PG(18:3(6Z,9Z,12Z)/14:0)	1224975	1262959	1401743	39	-2.44	98.01
1.222	Glycerophospolipids	PG(22:1(11Z)/0:0)	237996	221351	385745	39.1	-1.93	97.58
4.529	Glycerophospolipids	PG(13:0/18:1(9Z))	1156832	226983	7515	38.7	-1.02	94.91

1.809	Glycerophospolipids	PG(22:1(11Z)/0:0)	592610	531525	714769	38.9	-1.55	96.52
0.817	polyclic hydrocarbon	Santene	142168	137275	76400	38.7	3.60	97.67
2.671	polyethylene glycol (ether)	Heptaethylene glycol	43786	38105	162673	38.3	2.30	94.16
2.705	polyethylene glycols	Hexaethylene glycol	54162	57580	197153	36.2	2.72	84.05
2.900	polyethylene glycols (ethers)	Heptaethylene glycol	25912	29038	99161	38.4	2.41	94.74
3.510	Amino acids and derivatives	Ascorbalamic acid	183056	159638	127973	37.8	0.77	89.79
2.759	Fatty acyl / eicosanoids	2-glyceryl-PGD2	95808	89508	47606	36.3	-3.24	85.55
1.657	pteridines and derivatives	7-Hydroxy-6-methyl-8-ribityl lumazine	8063553	3444048	476645	37.3	-3.53	90.59
0.635	purine and derivatives	5'-n-propylthioadenosine	67027	106824	34486	35.6	-2.63	80.88
1.421	purine and derivatives	Adenosine	423360	230015	101169	35.5	3.04	80.85
1.421	purine and derivatives	Adenine	45967	24333	11592	38.8	3.97	98.82
0.757	purine and derivatives	Guanine	369755	150277	81171	39	2.21	97.73
1.440	purine and derivatives	Guanine	142201	98284	39876	39.1	1.83	97.57
2.815	Benzene and substituted derivatives	Isomorellic acid	309793	222635	19174	36.9	-0.24	84.63
2.034	Benzene and substituted derivatives	Isomorellic acid	119964	111282	23062	37.1	1.36	87.18
3.079	Benzene and substituted derivatives	Morellin	241563	185759	8720	37.8	2.88	92.17
2.359	Benzene and substituted derivatives	Morellinol	262025	242473	61172	39.5	1.00	98.69
2.861	Benzene and substituted derivatives	Morellinol	186955	142909	9883	37.5	2.22	90.17
2.347	Benzene and substituted derivatives	Morellinol	132484	102292	12651	36.4	-3.40	85.90
1.493	pyridines and derivatives	4-Pyridoxolactone	141154	477358	95050	36.2	-0.36	81.51
0.898	pyridines and derivatives	4-Pyridoxic acid	301036	280499	148729	35.8	-3.53	83.00
2.070	pyridines and derivatives	Pyridoxamine	2783715	1418880	283218	38.8	2.34	97.02
1.433	Pyrimidine and derivative	Zalcitabine	422159	163209	32279	39	-0.55	95.52
1.862	Pyrimidine and derivative	3'-Azido-3'-deoxy-5'- O-beta-D-glucopyranuronosylthymidine	117217	165291	268079	37.6	-1.92	90.29
3.727	Pyrimidine and derivative	Pentobarbital	2705669	385670	91950	38.6	-2.27	95.73
3.803	Pyrimidine and derivative	Pentobarbital	2380638	343776	54148	39.3	0.27	96.68
2.008	Pyrimidine and derivative	Aprobarbital	1252104	493704	53041	37.1	2.89	88.94
3.171	Pyrimidine and derivative	Aprobarbital	258533	107123	25613	37.8	1.62	90.74
1.330	Pyrimidine and derivative	Thymidine	1243766	757262	218201	36.6	2.18	85.48
1.001	pyrrolotriazines	3-Methylpyrrolo[1,2-a]pyrazine	166290	103992	99193	36.9	-1.12	86.01
8.979	Alcohols and polyols	Chlorogenoquinone	95617	92633	58801	37.9	3.77	94.01
3.065	quinoline derivative	Kynurenic acid	1396249	1083202	28430	38	3.19	93.80
3.171	quinoline derivative	Rufloxacin	199799	140021	261740	38.2	-0.25	91.29
2.766	quinoline derivative	6-Methylquinoline	1403088	387016	90145	38.2	1.53	92.94
1.505	quinoline derivative	8-hydroxyquinoline	1287645	457267	93842	38.5	2.83	95.77
1.360	quinoline derivative	8-hydroxyquinoline	1205226	567732	58225	38.1	2.99	93.97
2.896	quinoline derivative	8-hydroxyquinoline	1097449	685824	270799	38.8	3.03	97.71
2.450	quinoline derivative	8-hydroxyquinoline	846210	288227	38989	37.8	3.31	93.07
4.067	quinoline derivative	8-hydroxyquinoline	343320	159949	49948	38.4	3.06	95.59
4.833	quinoline derivative	8-hydroxyquinoline	65371	34158	13727	39	3.01	98.58
9.571	Benzene and substituted derivatives	Hexylresorcinol	361123	225690	118866	39.4	1.64	99.07

3.614	Retenoid	Etretinate	86074	68632	70277	38.6	1.80	94.95
9.396	Polyketides / flavonoids	12a-Hydroxyisomillettone	436202	604193	361951	36.8	3.77	88.55
4.385	Fatty acyl / fatty acids	Stearic acid	15647029	9467442	4394799	39.9	0.10	99.37
2.831	Prenol lipids	S-Furanopetasitin	266998	158705	31902	36.8	-3.24	87.61
1.866	Prenol lipids	Armillaricin	389706	385461	262232	39.5	0.61	98.17
5.144	Prenol lipids	3-Hydroxy-10'-apo-b,y-carotenal	96747	58610	74570	37.6	-2.51	91.06
5.145	Prenol lipids	3-Hydroxy-10'-apo-b,y-carotenal	163803	164939	187422	39.3	1.76	98.82
10.16	Sphingolipids	Sphinganine	166042	139999	97851	39.3	0.03	96.50
2.374	Sphingolipids	Penaresidin A	2030263	2246993	2212769	38.5	3.05	95.89
9.286	Sphingolipids	C16 Sphinganine	1219588	965155	709133	39.5	0.98	98.78
4.320	Sphingolipids	N-(hexadecanoyl)-deoxysphing-4-enine-1-sulfonate	185847	11160	4462	36.7	-0.48	84.30
1.352	Steroid and derivatives	Eplerenone	22360631	24173083	10561780	39.1	1.65	97.53
3.243	Steroid and derivatives	Dehydroepiandrosterone sulfate	104221	85836	29440	36.3	2.57	84.50
0.946	Steroid and derivatives	(25R)-26,26,26-trifluoro-1alpha,25-dihydroxyvitamin D3	534166	513946	488803	39.1	-2.45	98.41
4.235	Steroid and derivatives	(6RS)-22-oxo-23,24,25,26,27-pentanorcholecalciferol 6,19-sulfur dioxide adduct	345521	170012	131645	38.2	-0.71	91.65
5.925	Fatty acyl / fatty acids	Behenic acid	60818	31900	11979	37.1	-2.20	87.97
1.348	Benzene and substituted derivatives	Styrene	191622	180936	95457	38	2.56	92.84
1.813	sugar acid and derivatives	D-arabinonate	30748	32661	34225	38.3	0.57	92.01
1.881	sugar acids and derivatives	3-Deoxy-D-manno-octulosonate	100785	126413	60453	37.7	-0.31	88.97
0.918	sulfoxides	Camelinin	604976	369243	123231	38.1	0.03	90.32
0.723	sulfoxides	(Z)-[3-(Methylsulfinyl)-1-propenyl] 2-propenyl disulfide	35462	115089	100363	36.6	-0.13	82.98
7.035	sulfoxides	(Z)-[3-(Methylsulfinyl)-1-propenyl] 2-propenyl disulfide	63735	74155	87277	38	3.26	93.72
2.382	Prenol lipids	(-)-trans-Carveol glucoside	58677	51607	104008	36.9	2.86	87.74
3.017	Prenol lipids	Eremosulphoxinolide A	180921	137949	26571	37.2	0.75	86.97
1.352	tetrahydroisoquinolines	1,2,3,4-Tetrahydroisoquinoline	196647	215628	74623	39	3.43	99.07
5.449	Prenol lipids	gamma-tocotrienol	364658	251365	473867	39.5	-1.34	99.20
1.840	Prenol lipids	15-Acetoxyscirpene-3,4-diol 4-O-a-D-glucopyranoside	245825	138119	39426	36.4	-2.91	85.45
6.689	Glycerolipids	TG(18:4(6Z,9Z,12Z,15Z)/18:4(6Z,9Z,12Z,15Z)/18:4(6Z,9Z,12Z,15Z))	79341	65076	69295	37.1	-2.13	88.09
0.681	Amino acid and derivatives	Glycylprolylhydroxyproline	365912	199809	83855	38.3	-2.90	95.15
1.008	Amino acid and derivatives	Glycylprolylhydroxyproline	3053635	3169306	977401	38.9	-2.33	97.07
4.731	Prenol lipids	Lucidenic acid D1	216700	250101	124345	39.5	0.60	98.30
6.609	Prenol lipids	Lucidenic acid D1	117866	119297	116600	38.7	0.67	94.17
0.706	Amino acid and derivatives	Tryptamine	104490	124846	144139	37.4	3.32	90.95
3.438	Fatty acyl / fatty acid	9-heptadecylenic acid	46577	21907	705	39.6	-1.03	99.31
3.758	Fatty acyl / fatty acid	Oleic acid	159246	99299	46371	39.2	-1.19	97.48
4.709	Fatty acyl / fatty acid	7,12-octadecadiynoic acid	86741	172970	169251	39.2	2.67	98.93
4.994	Fatty acyl / fatty acid	7,11-octadecadiynoic acid	103305	106921	126539	38.8	2.04	96.39
5.312	Fatty acyl / fatty acid	17Z-octadecenoic acid	29017	31680	55512	37.7	3.81	93.20
3.397	Steroid and derivatives	(23S)-1alpha-hydroxy-25,27-didehydrovitamin D3 26,23-lactone	62156	64749	62916	36.5	1.56	84.43
7.094	Fatty acyl/fatty esters	Behenyl linoleate	339102	336995	401095	36.5	-3.79	86.69
2.930	Steroid and derivative	Physalolactone	1123838	233096	36775	36	2.83	83.59

1.493	unclassified	Choline bitartrate	328566	312689	98997	36.4	-2.52	85.24
Day 56								
RT (min)	**Chemical class**	**Suggested compound**	**A1**	**A4**	**A8**	**Score**	**Mass Error (ppm)**	**Isotope Similar-ity**
1.275	Prenol lipids	Vomitoxin	842362	919063	903332	38.6	2.86	96.24
1.473	Prenol lipids	Vomitoxin	307176	344151	331075	38.6	2.49	96.05
3.235	(unclassified)	Distichonic acid A	217515	43803	28173	36.3	0.26	81.93
1.637	(unclassified)	5'-(dimethylsulfonio)-5'-deoxyadenosine	50884	59975	63739	38.8	1.68	96.19
6.609	Glycerophospholipids	PI(O-16:0/20:5(5Z,8Z,11Z,14Z,17Z))	199363	193802	207178	38.1	2.30	93.19
12.00	Polyketides	2'-Hydroxy-4',6'-dimethoxy-3'-methyldihydrochalcone	7818522	7702715	7973184	38.8	-3.58	98.26
3.214	Glycerolipids	MG(0:0/22:2(13Z,16Z)/0:0)	55949	48016	54285	39.2	0.93	97.19
2.043	Polyketides	(S)-(E)-2'-(3,6-Dimethyl-2-heptenyl)-3',4',7-trihydroxyflavanone	613740	577665	605393	38.6	0.86	94.18
9.251	Indoles and derivatives	Alkaloid AQC2	172213	153183	131996	37.5	2.93	90.76
0.710	Indoles and derivatives	Indole-3-carbinol	625268	472822	466897	38.3	3.11	95.19
2.873	Polyketides / flavonoids	7-Chloro-3,4',5,6,8-pentamethoxyflavone	84047	133893	140640	37.9	1.41	91.01
0.798	benzene and substituted derivatives	N-Acetylprocainamide	102628	98854	105816	38.5	2.32	95.28
0.799	amino acid and derivatives	(S)-N-(4,5-Dihydro-1-methyl-4-oxo-1H-imidazol-2-yl)alanine	814069	752676	616456	38.1	1.41	92.30
2.290	alcohols and polyols	Pantothenic acid	150008	92356	52693	35.9	0.93	80.45
0.647	alcohols and polyols	D-4-O-Methyl-myo-inositol	223583	44846	26556	37.5	-0.87	88.32
3.495	alkaloids and derivatives	SN-38	206967	213712	184370	36.3	0.93	82.56
7.662	Glycerolipids	DG(P-14:0/18:1(9Z))	99137	84165	85207	37.4	1.51	88.58
1.330	Benzene and substituted derivatives	Hydroxykynurenine	604428	309944	248981	38.5	0.43	93.13
1.386	Benzene and substituted derivatives	N'-Formylkynurenine	313513	266299	109399	36.6	-2.97	86.30
1.505	Benzene and substituted derivatives	N'-Formylkynurenine	477970	277073	152191	38.3	2.90	94.84
1.607	Benzene and substituted derivatives	fluorobenzoylpropionic acid	32405	35467	24329	38.8	1.13	95.22
3.605	amino acid and derivatives	L-cis-Cyclo(aspartylphenylalanyl)	194886	58372	42358	38.5	0.07	92.59
3.025	amino acid and derivatives	L-cis-Cyclo(aspartylphenylalanyl)	125152	40385	25089	36.7	-0.67	84.41
3.193	amino acid and derivatives	L-cis-Cyclo(aspartylphenylalanyl)	92790	57414	43430	35.6	-3.32	81.70
3.084	amino acid and derivatives	Levetiracetam	74983	25248	9583	39.5	1.74	99.39
0.952	aldehyde	1-(3-Aminopropyl)-4-aminobutanal	2935	107297	67531	39.2	2.83	99.14
1.448	amino acid and derivatives	Descarbonyl-lacosamide	438219	266649	146574	38.7	1.31	94.95
2.259	amines (alkyldiarylamines)	Isothipendyl	1077350	576072	158022	38.1	0.89	91.62
2.031	amino acid and derivatives	L-Phenylalanine	236957	145867	76828	37.2	3.25	90.04
3.339	amino acid and derivatives	L-Tryptophan	203362	131334	80466	39	1.95	97.19
2.500	amino acid and derivatives	N-Acetylglutamine	244661	158508	94916	38.7	1.86	95.72
0.666	amino acid and derivatives	N-Acetylhistidine	69241	66073	49702	39.4	0.81	98.06
4.661	amino acid and derivatives	L,L-Cyclo(leucylprolyl)	117976	128202	66311	39.6	1.34	99.83
3.403	amino acid and derivatives	L-alpha-Amino-1H-pyrrole-1-hexanoic acid	346276	362835	219469	39.3	1.76	98.62
0.856	amino acid and derivatives	N-(1-Deoxy-1-fructosyl)valine	132858	94326	80844	38.5	0.83	93.39
0.834	amino acid and derivatives	N-Carbamoyl-2-amino-2-(4-hydroxyphenyl)acetic acid	121682	73495	52715	39.6	0.27	98.28

1.003	amino acid and derivatives	Coutaric acid	81159	103280	132662	37.8	1.28	90.38
0.811	amino acid and derivatives	N-a-Acetyl-L-arginine	538820	165475	174234	38.7	0.33	93.87
1.238	Fatty acyl / amino fatty acid	11-amino-undecanoic acid	4225518	4185391	3536257	39	2.49	98.14
3.254	alcohol and polyol	Paromomycin	113263	125048	102709	35.5	2.31	80.15
1.001	alcohol and polyol	Voglibose	150677	134074	96396	38.2	-3.78	95.32
1.037	Purines and derivative	N1-methyladenine	218294	176229	119250	38.2	2.55	94.16
11.99	benzene and substituted derivatives	Methamphetamine	90363	87566	92259	36.4	0.33	82.27
7.132	Fatty acyl	Cohibin A	534746	161396	184725	38.5	1.86	94.73
6.005	Fatty acyl	Cohibin A	3870353	1922177	1396531	38.9	2.15	97.05
4.827	Fatty acyl	Cohibin A	1018530	497114	263310	38.6	1.72	95.26
1.729	Benzene and substituted derivatives	Sennidin C	53605	46681	47618	36.6	2.25	85.74
2.031	Aralkylamines / amines	Porphobilinogen	178228	56363	38992	38.6	2.44	95.86
2.222	Aralkylamines / amines	Porphobilinogen	174329	120217	70216	38.1	2.91	93.72
0.689	Benzene and substituted derivatives	S-2,5-Dimethyl-3-furanyl 3-methylbutanethioate	138049	97227	73046	38.3	-0.13	91.62
1.863	pyrimidines and derivatives	Aprobarbital	189167	187870	151941	38.3	2.36	94.18
1.985	pyrimidines and derivatives	Metharbital	164196	127156	96217	37.1	2.50	88.44
9.396	Benzene and substituted derivatives	Procarbazine	231775	272507	318735	38.7	0.86	94.57
0.710	Benzene and substituted derivatives	Acidissiminol epoxide	43899	53945	60209	35.9	-1.00	80.78
1.196	Benzene and substituted derivatives	N-Acetylarylamine	213835	153315	51580	38.1	3.33	94.23
3.006	Benzene and substituted derivatives	5-Phenyl-1,3-oxazinane-2,4-dione	17619	47964	17909	39.1	1.73	97.63
10.01	Benzene and substituted derivatives	1,3,5-Triphenylcyclohexane	60958	53593	43179	37.3	-2.33	89.17
2.937	Benzene and substituted derivatives	Udenafil	1317558	968715	203823	36.9	1.14	85.92
1.740	Benzene and substituted derivatives	N-Undecylbenzenesulfonic acid	492767	647926	1454080	38.8	-1.80	96.18
0.677	Benzene and substituted derivatives	Tiapride	81873	40164	22792	38.1	-0.25	90.76
0.737	Benzene and substituted derivatives	Dimethylbenzimidazole	161181	10311	248059	39	2.73	98.03
2.758	Benzene and substituted derivatives	Desloratadine	551301	657121	615164	36.1	3.73	85.07
2.801	beta hydroxy acids and derivatives	2-Hexenoylcarnitine	155540	99980	101700	36.7	0.00	83.45
1.535	beta hydroxy acids and derivatives	Glutarylcarnitine	213466	126149	88440	38.1	1.97	93.08
2.732	beta hydroxy acids and derivatives	Pimelylcarnitine	141794	92075	62256	38.1	3.16	94.31
4.055	biotin and derivatives	Biotin	45625	26482	16879	38.6	1.05	94.33
2.976	Benzene and substituted derivatives	Telmisartan	275891	173731	96407	38.4	0.87	92.90
1.961	Benzene and substituted derivatives	Telmisartan	311148	245257	168904	36.3	-2.06	84.00
2.987	Benzene and substituted derivatives	Telmisartan	209444	133718	79027	38.4	0.84	93.11
1.333	Benzene and substituted derivatives	Telmisartan	60090	57215	54049	35.8	-1.43	80.93
3.517	Benzene and substituted derivatives	Biphenyl	71751	75945	71702	38	-2.51	92.88
1.523	Benzene and substituted derivatives	Olmesartan	16380	24344	24790	36.9	-2.61	87.71
3.256	Fatty acyl / fatty acids	13:0(12Me,12Me)	52014	53086	37061	38.7	-1.90	95.74
3.335	Fatty acyl / fatty acids	13:0(12Me,12Me)	33839	51747	32256	38.6	-1.99	95.42
5.152	Fatty acyl / fatty acids	19:0(11Me)	61785	85321	65096	38.7	-1.52	95.56
1.326	Prenol lipids	Lamioside	361566	142130	89366	36.5	-0.24	82.83
1.759	Prenol lipids	Flakinin A	80058	89151	86750	38.2	3.19	94.62

1.348	Prenol lipids	Flakinin A	126527	124126	128934	38.9	0.71	95.45
1.355	Prenol lipids	Parthenin	65887	72347	79708	35.9	3.55	83.46
3.412	Steroid and derivatives	Estradiol dipropionate	180350	167695	173514	37.7	3.68	92.63
4.909	Prenol lipids	(-)-Jolkinol A	146658	93565	73452	35.7	1.57	80.34
5.032	Prenol lipids	Helvolic acid	81797	74739	73632	38.1	0.86	91.77
3.267	Prenol lipids	7,8,7',8'-Tetradehydroastaxanthin	80035	73792	81451	37.4	-2.53	89.92
1.036	carboxylic acid esters	Ethyl 2-(methyldithio)propionate	224789	490211	207577	37.1	-3.82	90.07
6.735	Prenol lipids / Carotenoid	Ketospirilloxanthin	245740	239457	244653	38.9	3.41	98.72
4.676	Benzene and substituted derivatives	3,4-Dihydroxyphenylvaleric acid	111961	96352	85429	38.7	-3.59	97.51
5.940	Sphingolipids	Cer(t18:0/16:0)	416847	319019	281996	38.7	1.91	95.78
5.937	Sphingolipids	Cer(d14:1/20:0)	180302	152220	144010	37.1	-3.80	89.76
6.575	Sphingolipids	Cer(d18:0/18:0(2OH))	280171	221107	131272	39	1.74	97.27
6.365	Sphingolipids	Cer(d18:1/17:0)	136573	145306	129405	37.2	-0.81	86.75
6.853	Sphingolipids	N-Stearoylsphingosine	236710	316646	453218	38.4	2.03	94.39
1.557	Polyketides / flavonoids	Antiarone J	42815	41882	41085	37.8	2.18	91.66
2.347	Steroid and derivatives	(25S)-5alpha-cholestan-3beta,6alpha, 7beta,8beta,15alpha,16beta,26-heptol	169823	171095	186998	36	0.97	81.41
1.473	Polyketides/phenylpropanoids	(Z)-3-Phenyl-2-propenal	120564	132249	132583	38.9	3.95	98.98
1.406	Carbohydrate and derivatives	D-arabinonate	175456	68476	105863	37.8	1.33	90.55
2.412	coumaric acid and derivatives	Caffeoylmalic acid	76680	69489	48104	36.4	-0.65	82.99
0.919	amino acid and derivatives	Coutaric acid	99529	116364	136052	37.6	1.90	90.39
7.224	Glycerolipids	DG(18:4(6Z,9Z,12Z,15Z)/18:1(9Z)/0:0)[iso2]	420374	158933	88092	36.4	-3.15	85.92
7.658	Glycerolipids	DG(16:0/18:3(9Z,12Z,15Z)/0:0)[iso2]	68236	72304	77381	36.2	-1.42	82.89
8.189	Glycerolipids	DG(14:1(9Z)/22:2(13Z,16Z)/0:0)[iso2]	45031	43845	45201	36.2	-2.63	83.93
0.539	Glycerophospholipids	PA(22:6(4Z,7Z,10Z,13Z,16Z,19Z)/20:5(5Z,8Z,11Z,14Z,17Z))	25270	15743	26432	36.4	-3.01	85.37
4.826	Glycerophospholipids	PG(14:0/18:1(11Z))	1010505	695171	329050	39.3	-0.81	97.59
4.617	Glycerophospholipids	PG(15:0/18:2(9Z,12Z))	284307	200460	19160	39.2	-0.80	96.89
4.903	Glycerophospholipids	PG(12:0/19:0)	26484	33320	20257	35.4	3.63	81.43
5.442	Glycerophospholipids	PG(20:5(5Z,8Z,11Z,14Z,17Z)/18:0)	119531	460262	54064	38.7	-2.72	96.56
0.919	Glycerophospholipids	PI(12:0/12:0)	33025	44974	66819	38.6	-2.88	96.60
5.538	Glycerophospholipids	PI(17:2(9Z,12Z)/0:0)	198310	82004	25978	36.8	0.93	85.29
1.003	Glycerophospholipids	PI(12:0/12:0)	47756	64101	89652	38.7	-2.84	96.62
7.028	dialkyldisulphides	1-(1-Propenylthio)propyl propyl disulfide	100345	71854	22972	36.6	3.20	86.94
3.553	dialkyldisulphides	1-(1-Propenylthio)propyl propyl disulfide	28074	39818	13930	36.6	1.46	84.55
3.057	dialkyldisulphides	1-(1-Propenylthio)propyl propyl disulfide	21334	28567	11129	36.6	1.32	84.48
5.995	Fatty acyl /fatty acids	Genipinic acid	2174048	809557	429105	39.3	0.62	97.40
0.864	Fatty acyl /fatty acids	Tranexamic Acid	89098	47827	34290	36.2	2.01	83.56
1.326	Amino acids and derivatives	Alanyl-Glutamine	1017449	871659	612558	37.1	1.75	87.60
1.497	Amino acids and derivatives	Asparaginyl-Proline	751598	594908	424175	38.5	3.58	96.76
1.547	Amino acids and derivatives	Asparaginyl-Proline	648111	480873	262352	38.1	3.32	94.53
1.216	Amino acids and derivatives	Asparaginyl-Proline	439500	383325	170839	37.8	2.96	92.39
1.086	Amino acids and derivatives	Glutaminyl-Proline	242909	175981	138085	37	0.11	84.99

0.761	Amino acids and derivatives	Glycyl-L-leucine	672949	259790	82518	39.1	1.98	98.08
2.424	Amino acids and derivatives	Glycyl-L-leucine	118670	60169	19083	39.4	1.99	99.52
0.651	Amino acids and derivatives	Glycyl-L-leucine	107145	62397	34985	38.5	2.62	95.65
3.491	Amino acids and derivatives	Glycyl-Methionine	1056577	1051402	988836	38.4	-1.23	93.33
2.812	Amino acids and derivatives	Glycyl-Phenylalanine	233317	162337	81415	36.6	2.18	85.41
0.849	Amino acids and derivatives	Glycylproline	446754	344002	280293	38.2	1.42	92.89
1.615	Amino acids and derivatives	Glycyl-Tyrosine	78052	50173	13980	38.3	-3.62	95.83
1.947	Amino acids and derivatives	Hydroxyprolyl-Isoleucine	328430	265185	146569	38.8	2.75	97.16
1.459	Amino acids and derivatives	Isoleucyl-Lysine	360796	138722	28637	39.4	1.01	98.23
2.435	Amino acids and derivatives	Isoleucyl-Threonine	490328	143511	45497	39.4	0.77	98.14
4.942	Amino acids and derivatives	Leucyl-phenylalanine	130505	23712	16137	37.8	-2.97	92.46
2.827	Amino acids and derivatives	L-gamma-glutamyl-L-valine	437805	307572	221655	35.3	-3.02	80.30
1.326	Amino acids and derivatives	Prolyl-Alanine	160215	83632	54459	38.6	0.17	93.25
2.591	Amino acids and derivatives	Prolyl-Tyrosine	1479505	783260	542450	36.1	2.67	83.66
0.860	Amino acids and derivatives	Arginyl-Valine	128025	162971	44532	36.2	-0.31	81.60
0.677	Amino acids and derivatives	Asparaginyl-Hydroxyproline	259891	328116	292517	38.9	0.38	94.73
2.070	Amino acids and derivatives	Asparaginyl-Isoleucine	337023	541671	527085	38.7	1.89	95.94
2.923	Amino acids and derivatives	Glutaminyl-Glutamate	152801	209116	61418	35.4	-2.94	80.37
0.956	Amino acids and derivatives	Hydroxyprolyl-Glutamine	617477	630122	504713	37.3	2.21	88.93
4.810	Amino acids and derivatives	L,L-Cyclo(leucylprolyl)	28055	29209	5714	39.5	1.25	98.87
2.321	Amino acids and derivatives	Trandolaprilat	58893	64844	57352	39	-0.22	95.04
2.976	Amino acids and derivatives	N5-Acetyl-N2-gamma-L-glutamyl-L-ornithine	386152	101306	66058	36.6	0.03	83.24
3.224	Amino acids and derivatives	Isoleucyl-Valine	423337	204625	41967	39.4	1.53	98.88
2.207	Amino acids and derivatives	N5-Acetyl-N2-gamma-L-glutamyl-L-ornithine	74093	73352	46902	37.5	-2.09	89.75
5.438	Glycerolipids	1-(14-methyl-pentadecanoyl)-2-(8-[3]-ladderane-octanyl)-sn-glycerol	332088	1083266	152347	39.1	1.72	97.45
1.707	Prenol lipids	16,17-Dihydro-16a,17-dihydroxygibberellin A4 17-glucoside	827258	609176	354058	35.7	-3.35	82.55
4.823	Prenol lipids	Narasin	35825	150039	20732	37.3	-3.97	91.27
0.767	Prenol lipids	Persicachrome	77153	76240	83767	35.8	2.59	82.07
4.356	Fatty acyl / Eicosanoid	LTE4	25589	68759	13871	37.1	3.95	90.05
5.948	Fatty acyl / Eicosanoid	Dichotellate A	59123	61357	74299	36.5	-0.97	83.88
3.404	Steroid and derivatives	Norselic acid C	68380	65693	59307	38.9	1.14	95.68
2.496	Benzene and substituted derivatives	Phenethyl 6-galloylglucoside	116365	123980	128210	37.2	-3.70	90.21
5.144	Fatty acyl / Fatty acid	4Z,7Z,10Z,13Z,16Z,19Z,22Z,25Z-octacosaoctaenoic acid	1640674	1960722	1758137	39.5	-0.71	98.38
3.160	Fatty acyl / Fatty acid	cis-9-palmitoleic acid	358189	445058	64907	39.2	-1.67	98.08
3.667	Fatty acyl / Fatty acid	Palmitic acid	4319425	5469861	4791863	39.8	-0.36	99.48
3.037	Fatty acyl / Fatty acid	3R,5S-Dimethyldodecanoic acid	159910	189672	189893	38.9	-2.10	97.00
4.017	Fatty acyl / Fatty acid	Heptadecanoic acid	866459	931009	964079	39.8	-0.55	99.48
1.839	Fatty acyl / Fatty acid	2-Methylacetophenone	76563	87938	80994	36.5	-2.40	85.33
2.648	Fatty acyl carnitines	3-hydroxy-cis-5-octenoylcarnitine	2872747	2017739	1596364	39.4	0.41	97.53
0.554	fatty acyl carnitines	3-hydroxy-cis-5-octenoylcarnitine	297678	316193	264213	37.8	3.76	93.61
2.420	fatty acyl carnitines	(7Z,10Z,13Z,16Z)-docosatetraenoylcarnitine	85272	95246	118200	37.6	1.61	90.11

5.255	fatty acyl carnitines	O-behenoylcarnitine	121092	106073	114164	38.9	1.53	96.51
4.518	fatty acyl carnitines	Arachidyl carnitine	204528	194799	206789	39.4	1.54	98.71
0.855	fatty acyl carnitines	(9Z)-3-hydroxydodecenoylcarnitine	59828	68090	66190	38.9	0.80	95.70
1.184	fatty acyl carnitines	(9Z,12Z,15Z)-3-hydroxyoctadecatrienoylcarnitine	132910	139138	130673	39.5	0.73	98.36
2.378	fatty acyl carnitines	O-(17-carboxyheptadecanoyl)carnitine	114796	118247	118048	39.2	0.67	96.83
4.244	fatty acyl carnitines	Palmitoylcarnitine	1460091	1481976	1511068	38.7	2.01	96.07
1.954	fatty acyl glycosides	Prenyl apiosyl-(1->6)-glucoside	328062	174657	211175	38.3	0.10	91.80
1.303	fatty acyl glycosides	1-(3-Methyl-2-butenoyl)-6-apiosylglucose	158887	124032	84853	37.9	-1.85	91.49
2.923	fatty acyl glycosides	3-Methyl-3-butenyl apiosyl-(1->6)-glucoside	166695	107175	79681	37.9	2.98	93.17
2.945	fatty acyl glycosides	3-Methyl-3-butenyl apiosyl-(1->6)-glucoside	98803	107347	97075	38.3	-0.18	91.75
2.846	fatty acyl glycosides	3-Methyl-3-butenyl apiosyl-(1->6)-glucoside	477012	617000	618941	37.5	-0.31	87.65
0.824	Fatty acyl/fatty amides	N-(3-oxododecanoyl) homoserine lactone	80139	79139	77496	36.5	0.31	82.86
1.599	Fatty acyl/fatty amides	N-(3-oxododecanoyl) homoserine lactone	72030	65221	35344	38	1.05	91.04
6.605	fatty acyl/fatty alcohol	phenolic phthiocerol	387231	202925	154159	38.1	1.76	92.70
5.373	Fatty acyl /fatty alcohol	phenolic phthiocerol	198691	973542	124937	39.3	2.26	99.08
7.708	Fatty acyl /fatty alcohol	phenolic phthiocerol	85686	127845	65444	38.2	1.40	92.72
2.412	Fatty acyl /Fatty aldehyde	9Z,11E,13-Tetradecatrienal	426027	378441	389554	39.1	-2.92	98.88
5.156	Fatty acyl/fatty amides	Docosanamide	77413	78909	86760	38.9	2.02	97.04
4.343	Fatty acyl /fatty ester	Mayolene-17	302438	91700	19993	39.1	1.56	97.37
6.076	Fatty acyl /fatty ester	Mayolene-19	2216421	1032006	632818	39.3	1.99	98.96
4.891	Fatty acyl /fatty ester	Mayolene-19	1289395	1195194	279015	39.2	1.97	98.54
7.213	Fatty acyl /fatty ester	Mayolene-19	451383	176530	105163	37.9	1.44	91.15
6.377	Fatty acyl /fatty ester	Mayolene-20	505214	201572	107783	38.5	-0.46	93.29
6.365	Fatty acyl /fatty ester	Mayolene-19	654433	720933	245111	35.2	1.88	78.31
5.167	Fatty acyl /fatty ester	Mayolene-20	193182	528753	133402	38.4	1.33	93.70
1.432	fatty acyl carnitines	3-hydroxy-cis-5-octenoylcarnitine	217150	229618	247730	35.6	3.20	81.93
4.731	Polyketides / flavonoids	Laxiflorin	110582	106853	112245	39.5	0.81	98.69
6.609	Polyketides / flavonoids	Laxiflorin	204994	221865	280522	38.9	0.85	95.49
0.936	Polyketides / flavonoids	2',4',5,7-Tetramethoxy-8-methylflavanone	276059	187334	201430	38.4	3.68	96.32
0.504	Polyketides / flavonoids	5,7-Dihydroxyflavone 7-benzoate	19982	19466	14216	38.2	2.79	94.12
8.979	Polyketides / flavonoids	Demethyltorosaflavone C	105964	92930	91469	38.1	-2.90	93.81
5.816	Polyketides / flavonoids	Demethyltorosaflavone D	12402	8474	2423	38.7	0.72	94.41
2.030	Polyketides / flavonoids	Epilumaflavanone B	304489	113874	96855	39	1.66	97.04
1.958	Polyketides / flavonoids	Euchrenone a14	88458	64360	44016	36	-2.16	82.71
1.226	Polyketides / flavonoids	Prebarbigerone	47773	60426	60444	38.7	0.70	94.52
0.635	Polyketides / flavonoids	Galangin 5,7-dimethyl ether	88837	74839	66136	36.4	-1.00	83.29
3.780	Polyketides / flavonoids	Lonchocarpenin	103109	67282	63215	38.4	1.32	93.71
1.215	Polyketides / flavonoids	Heteroflavanone B	255047	283437	284812	39	0.30	95.61
3.517	Polyketides / flavonoids	Artocommunol CA	263881	191289	155694	36.4	-0.63	82.89
4.425	Polyketides / flavonoids	Isochamanetin	81102	60082	56807	36.6	-2.26	85.87
1.470	Polyketides / flavonoids	Heteroflavanone B	30688	52070	41625	38.8	1.14	95.18

2.050	Polyketides / flavonoids	Quercetol B	38187	39563	36841	38.2	3.04	94.46
2.416	Benzene and substituted derivatives	Fluconazole	729851	733945	834624	38.9	-2.86	97.92
1.355	furopyrans	Cyclocalopin F	152454	153344	172731	38.5	2.53	95.62
8.979	amino acid and derivatives	Avenic acid A	1155164	1082845	1025130	39.2	0.91	97.35
0.647	amino acid and derivatives	4-Guanidinobutanoic acid	354145	763917	985754	38.3	3.17	95.44
0.670	amino acid and derivatives	(S)-4-Amino-5-oxopentanoate	105879	79496	50352	36	3.45	83.82
4.404	sugar acids and derivatives	Alginic acid	16541	20514	17029	36.9	-0.77	85.24
1.269	amino acid and derivatives	gamma-Glutamyl-beta-aminopropiononitrile	665789	722096	531450	37.4	1.66	88.86
0.670	amino acid and derivatives	gamma-glutamyl-ethylamide	99580	149293	75053	37.8	-1.42	90.76
2.564	amino acid and derivatives	(2S,4S)-Pinnatanine	48470	45446	44528	36.7	1.95	85.67
6.609	Glycerophospholipids	PI(O-20:0/20:5(5Z,8Z,11Z,14Z,17Z))	176595	194726	192685	36.9	2.40	87.51
1.599	Glycerophospholipids	PI(13:0/12:0)	961815	975849	969786	38.8	-1.91	96.49
4.537	Glycerophospholipids	PS(O-16:0/14:1(9Z))	22664	23295	191	36.7	0.09	83.56
4.826	Glycerophospholipids	PS(P-16:0/16:1(9Z))	137398	75899	47320	39.2	0.31	96.61
4.268	amino acid and derivatives	N-[(3a,5b,7b)-7-hydroxy-24-oxo-3-(sulfoxy)cholan-24-yl]-Glycine	111518	61218	26154	36.3	1.64	83.41
6.365	Glycerolipids	MGDG(18:2(9Z,12Z)/18:3(9Z,12Z,15Z))	2763542	4385295	1520964	39.3	-2.46	99.27
0.623	alkaloids and derivatives	Flazine methyl ether	123902	143965	66576	36.2	-1.77	83.02
0.651	Benzene and substituted derivatives	4-Aminohippuric acid	272316	59458	41885	38.1	-3.68	94.93
1.638	Benzene and substituted derivatives	4-Aminohippuric acid	182555	89736	57669	39.1	0.11	95.77
1.033	Amino acids and derivatives	N-Ribosylhistidine	1146625	1710265	954778	37.2	2.17	88.64
5.769	Prenol lipids / hopanoid	2-methylbacteriohopane-32,33,34,35-tetrol	759294	273801	103852	38.9	2.20	97.29
5.369	Prenol lipids / hopanoid	bacteriohopane-,32,33,34-triol-35-cyclitol	120141	103688	160369	39.2	1.88	98.29
4.366	Prenol lipids / hopanoid	adenosylhopane	205004	66249	41760	37.1	2.21	88.35
0.862	Hydroxycoumarin	Mammea E/BB	134392	893285	997506	35.9	2.24	81.93
1.001	hypoxanthines	7-Methylguanine	70072	81613	168761	39	2.21	97.73
3.095	Benzene and substituted derivatives	Sulindac sulfide	50451	55730	29867	37.5	-0.45	88.15
5.995	Indoles	Indoleacetic acid	1883921	1251683	465211	39.1	2.40	98.16
6.887	Indoles	Cyclobrassinone	71971	74481	87182	37.6	-2.72	91.32
1.950	Amino acids and derivatives	5-Hydroxy-L-tryptophan	49548	29976	21076	38.8	-3.32	97.93
4.932	Indoles	2-Indolecarboxylic acid	726321	790063	254035	39	2.27	97.88
3.065	Indoles	2-Indolecarboxylic acid	22814	173617	16798	38.6	2.35	95.96
3.609	Indoles	1H-Indole-3-carboxaldehyde	458071	354991	130852	36.6	3.52	86.90
2.766	Indoles	Indoleacrylic acid	422193	402204	69470	38.4	2.84	95.54
3.323	Amino acid and derivatives	5-Methoxytryptophan	143891	54841	42806	37.5	2.00	90.04
9.533	Prenol lipids	Valdiate	123665	119643	102270	39.4	1.73	98.88
2.207	isocoumarans (antidepressant)	Citalopram aldehyde	122380	102694	81843	37	2.27	87.48
3.837	Polyketides / flavonoids	Calopogoniumisoflavone A	40616	40749	34465	37.9	0.95	90.78
0.824	Amino acid and derivatives	N-Jasmonoylisoleucine	56911	56613	58738	37	1.24	86.58
4.362	Fatty acyl / octadecanoid	12-hydroxyjasmonic acid 12-O-beta-D-glucoside	995648	898312	988790	36.7	1.08	84.74
1.306	Polyketides	11-Hydroxy-12-methoxydihydrokawain	514910	496025	504550	37.2	3.57	90.34
1.473	Polyketides	11-Hydroxy-12-methoxydihydrokawain	140545	167545	162695	38.5	2.60	95.73

3.190	Fatty acyl / octadecanoid	Lipoxin D4	80296	54793	41750	36.1	3.93	84.96
1.698	Polyketides	10-Deoxymethymycin	99239	96254	87943	39.5	0.76	98.63
3.053	Glycerophospholipids	PA(12:0/0:0)	682584	174801	119600	37.1	-3.81	90.03
5.133	Glycerophospholipids	PA(14:0/18:1(9Z))	566168	61099	32566	37.5	-0.45	88.19
5.209	Glycerophospholipids	PA(16:0/18:2(9Z,12Z))	853807	67466	15232	36.3	-0.81	82.34
2.107	Glycerophospholipids	PA(22:6(4Z,7Z,10Z,13Z,16Z,19Z)/0:0)	48012	131784	23542	37.5	2.05	90.10
0.855	Glycerophospholipids	PC(8:0/0:0)	18468	24055	22741	36.9	-2.93	88.03
6.906	Carbohydrate and derivatives	Sedoheptulose 1,7-bisphosphate	22659	18582	23376	38.4	2.89	95.33
2.416	Fatty acyl / fatty amides	N-(4-benzenesulfonamide) arachidonoyl amine	732642	957451	799641	36.7	3.53	87.74
2.793	Fatty acyl / fatty amides	N-(5-hydroxy-pentyl) arachidonoyl amine	84319	89971	73220	38.9	1.34	96.18
5.133	Fatty acyl / fatty amides	N-oleoyl glutamic acid	32166	39665	30946	37.5	3.88	92.08
3.503	Fatty acyl / fatty amides	N-stearoyl serine	1895778	1931633	1934677	39.2	2.73	99.24
2.679	Fatty acyl / fatty amides	Pipericine	62663	72426	73917	37.9	1.80	91.61
2.736	Fatty acyl / fatty amides	Anandamide (20:2, n-6)	86470	83746	79901	38.7	2.17	96.25
4.252	N-acyl pyrrolidines	N-(14-Methylhexadecanoyl)pyrrolidine	233766	230871	246405	38.6	3.43	97.06
2.808	Amino acid and derivatives	L-N-(1H-Indol-3-ylacetyl)aspartic acid	101064	112130	85635	38	-2.64	93.12
3.625	Amino acid and derivatives	Tricosanoylglycine	163637	156545	159903	39	1.69	96.98
3.719	Amino acid and derivatives	Methylhippuric acid	76314	309563	118302	38.4	-3.95	96.44
4.457	Amino acid and derivatives	Pentacosanoylglycine	4493381	4589077	4626582	39	2.89	98.57
3.205	Amino acid and derivatives	Suberylglycine	125544	180127	181548	37.8	-0.13	89.19
8.686	Amino acid and derivatives	N-Succinyl-L,L-2,6-diaminopimelate	62193	62604	59097	38.6	0.13	93.12
4.362	N-acyl-piperidines	Pipercitine	322145	324269	326640	39	2.99	98.31
3.766	N-acylpyrrolidines	N-Hexadecanoylpyrrolidine	135779	143036	158946	36.5	3.73	86.79
6.369	Sphingolipids	Cer(d18:0/h17:0)	213747	236345	157058	38.6	2.03	95.37
0.681	nitroimidazole	Metronidazole	308110	253113	228459	39	2.63	98.01
2.534	Fatty acyl / octadecanoids	12R-HOME(9E)	7615	18747	15715	37.1	-2.36	88.55
4.709	Fatty acyl / octadecanoids	7-keto-stearic acid	55847	57600	60162	37.5	3.66	91.66
1.832	Carbohydrates and derivatives	Acaciabiuronic acid	110822	56037	31205	38.7	-0.64	94.51
1.539	Carbohydrates and derivatives	1,2,10-Trihydroxydihydro-trans-linalyl oxide 7-O-beta-D-glucopyranoside	164193	63199	100446	36.7	2.84	86.76
3.719	Carbohydrates and derivatives	1,2,10-Trihydroxydihydro-trans-linalyl oxide 7-O-beta-D-glucopyranoside	234550	384699	310017	38	-0.82	91.05
1.573	Carbohydrates and derivatives	1,2,10-Trihydroxydihydro-trans-linalyl oxide 7-O-beta-D-glucopyranoside	126801	95184	95449	36.4	0.10	81.92
3.548	Carbohydrates and derivatives	2,4-Dihydroxy-7,8-dimethoxy-2H-1,4-benzoxazin-3(4H)-one 2-glucoside	86131	39116	21227	37.1	-0.05	85.57
4.364	Carbohydrates and derivatives	2-[4-(3-Hydroxypropyl)-2-methoxyphenoxy]-1,3-propanediol 1-glucoside	108654	60679	67145	37.9	-3.02	93.31
2.923	Carbohydrates and derivatives	Benzyl beta-primeveroside	139023	111080	82611	37.4	-0.61	87.81
5.275	Carbohydrates and derivatives	Phenethyl rutinoside	247571	69095	56394	35.8	-2.92	82.26
4.741	Carbohydrates and derivatives	Verbasoside	46758	40109	16836	38.7	0.49	94.19
1.786	Carbohydrates and derivatives	1,2,10-Trihydroxydihydro-trans-linalyl oxide 7-O-beta-D-glucopyranoside	41663	32424	51709	36.6	-1.25	84.34
0.609	Benzene and substituted derivatives	4R,5R,6S-Trihydroxy-2-hydroxymethyl-2-cyclohexen-1-one 6-(2-hydroxy-6-methylbenzoate)	72482	52539	19116	35.6	2.50	81.19
0.670	Amino acids and derivatives	Ophthalmic acid	766667	1168115	984977	37.2	1.72	87.84
9.396	Amino acids and derivatives	Thyrotropin releasing hormone	289505	334664	394101	39	-3.27	98.89

2.461	organosulfonic acids	Acrylic acid-2-acrylamido-2-methyl propane sulfonic acid copolymer	598507	872537	853012	37.9	-3.82	93.94
6.205	other fatty acyls	N-(3-(hexadecanoyloxy)-heptadecanoyl)-L-ornithine	138417	49988	79649	38.9	0.97	95.74
1.793	Fatty acyl / fatty acids	12-oxo-5E,8E,10Z-heptadecatrienoic acid	38134	42877	45123	36.5	-1.88	84.91
5.793	Carbohydrates and derivatives	Imidazoleacetic acid ribotide	1177	708	878	38.4	-0.41	92.35
3.609	Carbohydrates and derivatives	2-Hydroxybenzaldehyde O-[xylosyl-(1->6)-glucoside]	73590	49829	42682	38.7	-1.51	95.51
2.500	Carbohydrates and derivatives	Ptelatoside A	759231	430847	275568	38.8	-1.65	95.97
3.795	Benzene and substituted derivatives	Ethopropazine	70967	36571	17853	36.2	3.82	85.58
1.515	Benzene and substituted derivatives	Thioridazine	66666	75064	72674	37.3	3.90	90.96
1.355	Benzene and substituted derivatives	(4-Methylphenyl)acetaldehyde	54383	52688	50844	38.9	3.65	98.62
10.44	Benzene and substituted derivatives	Tropicamide	32214	31057	35212	37.1	-0.73	86.37
2.069	Benzene and substituted derivatives	Musanolone F	102069	62435	48179	38.7	-1.93	96.00
0.925	Benzene and substituted derivatives	Dopamine 4-sulfate	126452	103585	93849	35.2	-3.63	80.48
5.335	Glycerophospholipids	PC(12:0/15:1(9Z))	211234	88696	48112	38	0.36	90.36
6.009	Glycerophospholipids	PC(12:0/17:1(9Z))	270463	136578	85830	38.9	0.34	94.69
5.674	Glycerophospholipids	PC(14:1(9Z)/14:0)	544342	223997	68250	39.2	-0.31	96.19
5.571	Glycerophospholipids	PC(14:1(9Z)/14:0)	357584	156374	18193	39.1	-0.84	96.64
5.765	Glycerophospholipids	PC(17:2(9Z,12Z)/13:0)	497380	183656	53472	39	-0.42	95.41
6.005	Glycerophospholipids	PC(18:4(6Z,9Z,12Z,15Z)/13:0)	887023	449648	356496	38.7	-2.86	96.97
3.214	Glycerophospholipids	PC(11:0/11:0)	4161744	4053544	4233925	39	2.47	98.12
6.372	Glycerophospholipids	PC(17:2(9Z,12Z)/15:0)	254012	74654	37077	38.2	-1.22	92.69
6.076	Glycerophospholipids	PC(20:5(5Z,8Z,11Z,14Z,17Z)/13:0)	503976	262883	221203	38.9	-1.56	96.50
6.597	Glycerophospholipids	PE(16:0/18:1(11Z))	259236	120895	65407	37.5	-1.29	88.82
5.457	Glycerophospholipids	PE(16:1(9Z)/16:1(9Z))	740403	244908	144780	39.6	-0.61	98.84
6.327	Glycerophospholipids	PE(16:1(9Z)/17:0)	630059	323878	131324	38.7	-0.98	94.93
6.005	Glycerophospholipids	PE(18:1(11Z)/14:0)	2670510	1600752	1041711	39.8	-0.48	99.58
6.075	Glycerophospholipids	PE(18:1(11Z)/16:1(9Z))	1804823	883123	482489	39.7	-0.61	99.40
6.654	Glycerophospholipids	PE(18:1(11Z)/18:1(11Z))	199372	87117	76757	37.9	-1.46	91.47
6.495	Glycerophospholipids	PE(18:2(9Z,12Z)/21:0)	218027	138953	31245	37.1	-1.99	87.86
5.453	Glycerophospholipids	PE(18:4(6Z,9Z,12Z,15Z)/16:1(9Z))	306900	104350	69218	38.1	-3.03	93.89
4.339	Glycerophospholipids	PG(16:1(9Z)/16:1(9Z))	434173	129797	15335	38.8	-0.90	95.21
4.709	Glycerophospholipids	PG(18:3(6Z,9Z,12Z)/14:0)	1318919	1266108	1311935	39	-2.44	98.01
1.618	Glycerophospholipids	PG(12:0/0:0)	48322	64908	51294	38.6	3.01	96.77
5.685	Glycerophospholipids	PG(12:0/17:0)	69179	77922	68844	36.1	3.98	84.95
4.232	Glycerophospholipids	PG(14:0/16:1(9Z)	19449	33113	5648	37	-1.53	87.08
5.076	Glycerophospholipids	PG(14:0/18:0)	49184	67805	11442	38.3	-1.05	92.71
5.072	Glycerophospholipids	PG(15:0/18:1(9Z))	248809	586701	108389	39.4	-0.86	97.81
5.369	Glycerophospholipids	PG(16:0/18:1(11Z))	320938	2281661	251154	39.8	-0.44	99.31
5.163	Glycerophospholipids	PG(17:0/18:2(9Z,12Z))	209207	939892	137931	39.5	-0.75	98.41
5.006	Glycerophospholipids	PG(17:0/20:5(5Z,8Z,11Z,14Z,17Z))	609202	746810	711747	39	0.55	95.49
4.887	Glycerophospholipids	PG(18:1(11Z)/16:1(9Z))	1410180	2172499	397386	39.6	-0.63	98.84
5.666	Glycerophospholipids	PG(18:1(11Z)/17:0)	17403	237729	29310	38.9	-1.12	95.84

5.434	Glycerophospholipids	PG(18:1(11Z)/18:1(11Z))	667916	2522175	270566	39.7	-0.55	98.95
5.369	Glycerophospholipids	PG(18:4(6Z,9Z,12Z,15Z)/18:0)	52154	445956	46675	38.5	-3.24	96.50
4.891	Glycerophospholipids	PG(20:5(5Z,8Z,11Z,14Z,17Z)/16:0)	403749	528516	127723	37.2	-3.37	89.95
0.897	Glycerophospholipids	PG(16:0/0:0)	30474	34461	44623	36.7	3.54	87.82
1.222	Glycerophospholipids	PG(22:1(11Z)/0:0)	293581	287028	318167	39.1	-1.93	97.58
2.991	Glycerophospholipids	PG(22:2(13Z,16Z)/0:0)	141842	161856	180111	37	2.73	88.31
0.638	Glycerophospholipids	PG(O-18:0/0:0)	40619	45462	47869	37.7	-1.42	90.21
4.529	Glycerophospholipids	PG(13:0/18:1(9Z))	98682	205801	25776	38.7	-1.02	94.91
1.809	Glycerophospholipids	PG(22:1(11Z)/0:0)	586301	604707	632776	38.9	-1.55	96.52
0.817	polyclic hydrocarbon	Santene	53456	54425	58884	38.7	3.60	97.67
2.671	polyethylene glycol	Heptaethylene glycol	176038	158954	148439	38.3	2.30	94.16
2.705	polyethylene glycols	Hexaethylene glycol	186416	185733	181773	36.2	2.72	84.05
2.900	polyethylene glycols	Heptaethylene glycol	97749	92185	87595	38.4	2.41	94.74
3.510	Amino acids and derivatives	Ascorbalamic acid	137345	148399	133474	37.8	0.77	89.79
2.759	Fatty acyl / eicosanoids	2-glyceryl-PGD2	42643	38968	41695	36.3	-3.24	85.55
1.657	pteridines and derivatives	7-Hydroxy-6-methyl-8-ribityl lumazine	3830224	1020005	658700	37.3	-3.53	90.59
0.635	purine and derivatives	5'-n-propylthioadenosine	92521	66391	50628	35.6	-2.63	80.88
1.440	purine and derivatives	Guanine	953409	1035538	524615	39.1	1.83	97.57
0.757	purine and derivatives	Guanine	260900	317257	189702	39	2.21	97.73
1.421	purine and derivatives	Adenosine	512745	769190	539351	35.5	3.04	80.85
2.815	Benzene and substituted derivatives	Isomorellic acid	200309	110052	78300	36.9	-0.24	84.63
2.034	Benzene and substituted derivatives	Isomorellic acid	125408	57822	42560	37.1	1.36	87.18
3.079	Benzene and substituted derivatives	Morellin	89698	39048	30190	37.8	2.88	92.17
2.861	Benzene and substituted derivatives	Morellinol	130226	48572	32075	37.5	2.22	90.17
2.347	Benzene and substituted derivatives	Morellinol	76125	40823	28697	36.4	-3.40	85.90
2.359	Benzene and substituted derivatives	Morellinol	47798	45659	42160	39.5	1.00	98.69
1.493	pyridines and derivatives	4-Pyridoxolactone	244536	90571	72056	36.2	-0.36	81.51
0.898	pyridines and derivatives	4-Pyridoxic acid	401456	332356	256635	35.8	-3.53	83.00
2.070	pyridoxamine	Pyridoxamine	1145467	141488	53541	38.8	2.34	97.02
1.433	pyrimidine derivative	Zalcitabine	182816	45022	39492	39	-0.55	95.52
1.862	pyrimidine derivative	3'-Azido-3'-deoxy-5'- O-beta-D-glucopyranuronosylthymidine	405836	520711	806784	37.6	-1.92	90.29
3.727	pyrimidine derivative	Pentobarbital	1022943	159984	113383	38.6	-2.27	95.73
3.803	pyrimidine derivative	Pentobarbital	943615	134995	77414	39.3	0.27	96.68
2.008	pyrimidine derivative	Aprobarbital	923937	149126	68636	37.1	2.89	88.94
3.171	pyrimidine derivative	Aprobarbital	294980	72085	41700	37.8	1.62	90.74
1.330	pyrimidine nucleoside	Thymidine	1052156	331493	268686	36.6	2.18	85.48
1.001	pyrimidine derivative	3-Methylpyrrolo[1,2-a]pyrazine	137765	102429	138165	36.9	-1.12	86.01
8.979	alcohols and polyols	Chlorogenoquinone	73207	66545	62911	37.9	3.77	94.01
3.065	quinoline derivative	Kynurenic acid	53449	536115	38031	38	3.19	93.80
3.171	quinoline derivative	Rufloxacin	416848	415710	513244	38.2	-0.25	91.29
2.896	quinoline derivative	8-hydroxyquinoline	600137	529599	330506	38.8	3.03	97.71

4.067	quinoline derivative	8-hydroxyquinoline	516652	222513	185135	38.4	3.06	95.59
1.505	quinoline derivative	8-hydroxyquinoline	508090	271131	125100	38.5	2.83	95.77
2.450	quinoline derivative	8-hydroxyquinoline	469094	292762	93279	37.8	3.31	93.07
1.360	quinoline derivative	8-hydroxyquinoline	327192	175299	94998	38.1	2.99	93.97
2.766	quinoline derivative	6-Methylquinoline	122182	153171	33386	38.2	1.53	92.94
9.571	Benzene and substituted derivatives	Hexylresorcinol	204363	210980	140026	39.4	1.64	99.07
3.614	Retenoid	Etretinate	75679	70604	56964	38.6	1.80	94.95
9.396	Polyketides / flavonoids	12a-Hydroxyisomillettone	115795	135134	161441	36.8	3.77	88.55
4.385	Fatty acyl / fatty acids	Stearic acid	5322992	7070848	6012220	39.9	0.10	99.37
2.831	Prenol lipids	S-Furanopetasitin	145226	82908	56546	36.8	-3.24	87.61
1.866	Prenol lipids	Armillaricin	212766	198418	181427	39.5	0.61	98.17
5.144	Prenol lipids	3-Hydroxy-10'-apo-b,y-carotenal	60854	64028	48599	37.6	-2.51	91.06
5.145	Prenol lipids	3-Hydroxy-10'-apo-b,y-carotenal	156308	198969	175568	39.3	1.76	98.82
10.16	Sphingolipids	Sphinganine	128784	114765	98103	39.3	0.03	96.50
2.374	Sphingolipids	Penaresidin A	1913792	1958719	1980387	38.5	3.05	95.89
9.286	Sphingolipids	C16 Sphinganine	926275	831838	736137	39.5	0.98	98.78
4.320	Sphingolipids	N-(hexadecanoyl)-deoxysphing-4-enine-1-sulfonate	223035	77583	287934	36.7	-0.48	84.30
1.352	Steroid and derivatives	Eplerenone	8383789	7866280	8387617	39.1	1.65	97.53
3.243	Steroid and derivatives	Dehydroepiandrosterone sulfate	33506	55989	49148	36.3	2.57	84.50
0.946	Steroid and derivatives	(25R)-26,26,26-trifluoro-1alpha,25-dihydroxyvitamin D3	457695	433170	372389	39.1	-2.45	98.41
4.235	Steroid and derivatives	(6RS)-22-oxo-23,24,25,26,27-pentanorcholecalciferol 6,19-sulfur dioxide adduct	279226	205643	168042	38.2	-0.71	91.65
5.925	Fatty acyl / fatty acids	Behenic acid	11246	23447	12111	37.1	-2.20	87.97
1.348	benzene and substituted derivatives	Styrene	84299	86457	87699	38	2.56	92.84
1.881	sugar acids and derivatives	3-Deoxy-D-manno-octulosonate	191925	365444	135072	37.7	-0.31	88.97
0.918	sulfoxides	Camelinin	631214	300984	218893	38.1	0.03	90.32
7.035	sulfoxides	(Z)-[3-(Methylsulfinyl)-1-propenyl] 2-propenyl disulfide	79737	48985	15555	38	3.26	93.72
0.723	sulfoxides	(Z)-[3-(Methylsulfinyl)-1-propenyl] 2-propenyl disulfide	86852	143073	132257	36.6	-0.13	82.98
2.382	Prenol lipids	(-)-trans-Carveol glucoside	101003	102765	87680	36.9	2.86	87.74
1.352	tetrahydroisoquinolines	1,2,3,4-Tetrahydroisoquinoline	59093	55403	60098	39	3.43	99.07
5.449	Prenol lipids	gamma-tocotrienol	288790	364844	338673	39.5	-1.34	99.20
1.840	Prenol lipids	15-Acetoxyscirpene-3,4-diol 4-O-a-D-glucopyranoside	118757	95708	66970	36.4	-2.91	85.45
6.689	Glycerolipids	TG(18:4(6Z,9Z,12Z,15Z)/18:4(6Z,9Z,12Z,15Z)/18:4(6Z,9Z,12Z,15Z))	71112	84993	78505	37.1	-2.13	88.09
0.681	Amino acids and derivatives	Glycylprolylhydroxyproline	183939	129241	87117	38.3	-2.90	95.15
1.008	Amino acids and derivatives	Glycylprolylhydroxyproline	912394	714067	615349	38.9	-2.33	97.07
4.731	Prenol lipids/tripterpenoids	Lucidenic acid D1	105026	98635	111286	39.5	0.60	98.30
6.609	Prenol lipids/triterpenoids	Lucidenic acid D1	110717	117373	126947	38.7	0.67	94.17
0.706	Amino acids and derivatives	Tryptamine	301933	132179	129899	37.4	3.32	90.95
3.438	Fatty acyl / fatty acid	9-heptadecylenic acid	70191	189155	35294	39.6	-1.03	99.31
3.758	Fatty acyl / fatty acid	Oleic acid	345089	1258260	175980	39.2	-1.19	97.48
4.709	Fatty acyl / fatty acid	7,12-octadecadiynoic acid	136748	145514	182455	39.2	2.67	98.93
4.994	Fatty acyl / fatty acid	7,11-octadecadiynoic acid	102798	136999	134798	38.8	2.04	96.39

5.312	Fatty acyl / fatty acids	17Z-octadecenoic acid	54070	58960	57570	37.7	3.81	93.20
3.397	Steroid and derivatives	(23S)-1alpha-hydroxy-25,27-didehydrovitamin D3 26,23-lactone	71662	61768	57389	36.5	1.56	84.43
7.094	Fatty acyl/fatty ester	Behenyl linoleate	336740	394076	416702	36.5	-3.79	86.69
2.930	Steroid and derivatives	Physalolactone	262325	177735	58413	36	2.83	83.59
0.796	Fatty acyl / fatty acid	2R-aminoheptanoic acid	43917	28111	23692	38.3	2.98	94.95
1.806	Purines and derivatives	6-Dimethylaminopurine	395065	123440	107150	38.9	1.70	96.38
1.493	(unclassified)	Choline bitartrate	302715	246837	191114	36.4	-2.52	85.24
2.984	Indoles	Indolepyruvate	20800	20184	16643	38.8	2.69	97.42
2.728	Tetrapyrroles and derivatives	Mono(glucosyluronic acid)bilirubin	73677	41788	27336	35.1	3.97	80.20
2.279	Fatty acyl / eicosanoids	PGA3	38581	36476	35183	36.5	1.79	84.57
2.793	Amino acids and derivatives	Prolyl-Valine	57585	26056	18477	39.2	1.63	97.79
1.505	benzene and substituted derivatives	Sildenafil	676524	599387	244734	38.5	2.89	96.06
0.942	Prenol lipids/sesterterpenoids	25-Cinnamoyl-vulgaroside	15895	20696	14438	37.3	-3.94	91.07
1.599	Amino acids and derivatives	Hydroxyprolyl-Isoleucine	37229	40616	40233	36.9	3.07	88.00
6.335	Fatty acyl / fatty amide	IC202A	41896	46733	31593	36.9	-2.47	87.29
1.260	Glycerophospholipid	PI(O-20:0/0:0)	31379	31686	28558	38.6	-2.47	95.87
1.477	Benzene and substituted derivatives	Styrene	29726	33523	29519	38.6	3.37	96.95
3.659	Fatty acyl / fatty acid	Tricosanedioic acid	113447	129650	127958	39.2	2.17	98.70
4.716	Fatty acyl / fatty acid	13:0(12Me,12Me)	16559	17023	17209	37.7	-2.00	91.09
2.412	Fatty acyl / glycosides	3-O-(beta-D-glucopyranosyl-(1->6)-beta-D-glucopyranosyl) ethyl 3-hydroxyoctanoate	26105	33230	33611	35.9	-2.12	81.79
1.561	Prenol lipids	7'-hydroxyabscisic acid	68856	72206	77711	36.8	2.70	87.43
2.412	Indoles	Cyclobrassinone	36116	39630	47446	37.5	-2.65	90.49
2.500	Glycerolipids	Glycerol tributanoate	198	11745	14677	39.4	-1.10	98.54
2.283	Amino acids and derivatives	Hydroxyprolyl-Isoleucine	34769	38956	41928	37.8	3.69	93.26
1.592	Polyketides /phenylpropanoids	Linalyl cinnamate	36517	43114	44822	38.1	-1.80	92.85
0.596	Fatty acyl / fatty amide	pentanamide	46417	45360	46759	38.8	3.74	98.21
1.809	Glycerophospholipids	PG(16:0/0:0)	38463	39051	46408	38.2	-1.46	92.68
4.777	Prenol lipids / diterpenoids	Pristanic acid	11294	13793	14123	37.5	-1.53	89.13
1.348	benzene and substituted derivatives	p-Xylene	48697	48482	48890	38.8	3.06	97.61

Day 96

RT (min)	Chemical class	Suggested compound	A1	A4	A8	Score	Mass Error (ppm)	Isotope Similarity
1.275	Prenol lipids	Vomitoxin	296245	627926	923409	38.6	2.86	96.24
1.473	Prenol lipids	Vomitoxin	123315	282272	471794	38.6	2.49	96.05
3.235	(unclassified)	Distichonic acid A	36403	21296	13125	36.3	0.26	81.93
1.637	(unclassified)	5'-(dimethylsulfonio)-5'-deoxyadenosine	19123	45056	68328	38.8	1.68	96.19
3.673	(unclassified)	Dukunolide C	31530	22400	15466	37.1	-1.73	87.44
0.744	(unclassified)	S-adenosyl-1,8-diamino-3-thiooctane	65821	139042	162778	34.5	-0.83	73.33
6.609	glycerophosphoinositols	PI(O-16:0/20:5(5Z,8Z,11Z,14Z,17Z))	207015	236869	217772	38.1	2.30	93.19

12.00	Polyketides	2'-Hydroxy-4',6'-dimethoxy-3'-methyldihydrochalcone	7712502	9022106	9056355	38.8	-3.58	98.26
3.214	Glycerolipids	MG(0:0/22:2(13Z,16Z)/0:0)	47553	54969	57540	39.2	0.93	97.19
2.043	Polyketides	(S)-(E)-2'-(3,6-Dimethyl-2-heptenyl)-3',4',7-trihydroxyflavanone	401267	947707	1007894	38.6	0.86	94.18
9.251	Indoles	Alkaloid AQC2	155321	142189	109802	37.5	2.93	90.76
0.710	Indoles	Indole-3-carbinol	427495	212491	145061	38.3	3.11	95.19
2.873	Polyketides / flavonoids	7-Chloro-3,4',5,6,8-pentamethoxyflavone	95427	93438	73970	37.9	1.41	91.01
0.798	Benzene and substituted derivatives	N-Acetylprocainamide	74977	117444	240449	38.5	2.32	95.28
0.799	Amino acids and derivatives	(S)-N-(4,5-Dihydro-1-methyl-4-oxo-1H-imidazol-2-yl)alanine	430571	477477	475044	38.1	1.41	92.30
2.290	alcohols and polyols	Pantothenic acid	58914	41737	35383	35.9	0.93	80.45
0.647	alcohols and polyols	D-4-O-Methyl-myo-inositol	68714	64064	18391	37.5	-0.87	88.32
3.495	alkaloids and derivatives	SN-38	141467	176468	173048	36.3	0.93	82.56
7.662	Glycerolipids	DG(P-14:0/18:1(9Z))	77927	92497	85440	37.4	1.51	88.58
1.330	Benzene and substituted derivatives	Hydroxykynurenine	316981	274260	177045	38.5	0.43	93.13
1.386	Benzene and substituted derivatives	N'-Formylkynurenine	216606	156558	90267	36.6	-2.97	86.30
1.806	Purine and derivatives	1-ethyladenine	155124	117544	72395	38.9	1.70	96.38
1.505	Benzene and substituted derivatives	N'-Formylkynurenine	242671	202501	139159	38.3	2.90	94.84
1.607	Benzene and substituted derivatives	fluorobenzoylpropionic acid	41175	28472	22110	38.8	1.13	95.22
3.605	amino acids and derivatives	L-cis-Cyclo(aspartylphenylalanyl)	101222	70523	49487	38.5	0.07	92.59
3.025	amino acids and derivatives	L-cis-Cyclo(aspartylphenylalanyl)	56128	10908	8765	36.7	-0.67	84.41
3.193	amino acids and derivatives	L-cis-Cyclo(aspartylphenylalanyl)	32916	28974	23976	35.6	-3.32	81.70
3.084	amino acids and derivatives	Levetiracetam	37040	25067	11500	39.5	1.74	99.39
0.952	aldehyde	1-(3-Aminopropyl)-4-aminobutanal	1038	75614	0	39.2	2.83	99.14
1.448	amino acids and derivatives	Descarbonyl-lacosamide	195875	216046	96899	38.7	1.31	94.95
2.259	amino acids and derivatives	Isothipendyl	209906	127499	102694	38.1	0.89	91.62
2.031	amino acids and derivatives	L-Phenylalanine	133041	51595	41937	37.2	3.25	90.04
3.339	amino acids and derivatives	L-Tryptophan	118054	110742	58112	39	1.95	97.19
4.661	amino acids and derivatives	L,L-Cyclo(leucylprolyl)	29475	116453	38713	39.6	1.34	99.83
3.403	amino acids and derivatives	L-alpha-Amino-1H-pyrrole-1-hexanoic acid	127370	270741	81851	39.3	1.76	98.62
2.500	amino acids and derivatives	N-Acetylglutamine	82186	133348	113355	38.7	1.86	95.72
0.666	amino acids and derivatives	N-Acetylhistidine	65058	537798	43338	39.4	0.81	98.06
0.856	amino acids and derivatives	N-(1-Deoxy-1-fructosyl)valine	57875	72280	59438	38.5	0.83	93.39
0.834	amino acids and derivatives	N-Carbamoyl-2-amino-2-(4-hydroxyphenyl)acetic acid	64232	57120	44287	39.6	0.27	98.28
1.003	amino acids and derivatives	Coutaric acid	46894	123124	241979	37.8	1.28	90.38
3.002	amino acids and derivatives	Leukotriene C4	28690	23179	14825	36.2	-2.45	84.10
4.653	amino acids and derivatives	Trypanothione	27702	18916	7157	38.1	1.03	91.72
2.165	amino acids and derivatives	3-Methylcrotonylglycine	41310	49173	42747	37.8	3.21	92.78
2.614	amino acids and derivatives	5-Aminolevulinic acid	49442	56916	46557	38.4	3.84	96.35
2.039	amino acids and derivatives	Indicaxanthin	47566	61155	54112	38.8	-2.33	96.54
0.811	amino acids and derivatives	N-a-Acetyl-L-arginine	144337	690172	73096	38.7	0.33	93.87
1.238	Fatty acyl / fatty acid	11-amino-undecanoic acid	4086020	3928061	2864304	39	2.49	98.14
3.254	Alcohol and polyols	Paromomycin	47801	126332	94213	35.5	2.31	80.15

1.001	Alcohol and polyols	Voglibose	76734	75056	76453	38.2	-3.78	95.32
1.037	Purine and derivatives	N1-methyladenine	279699	120809	74896	38.2	2.55	94.16
11.99	Benzene and substituted derivatives	Methamphetamine	92761	108087	92736	36.4	0.33	82.27
6.005	annonaceous acetogenins	Cohibin A	729674	1006377	435856	38.9	2.15	97.05
4.827	annonaceous acetogenins	Cohibin A	167576	231840	275609	38.6	1.72	95.26
7.132	annonaceous acetogenins	Cohibin A	107533	101665	155186	38.5	1.86	94.73
1.729	Benzene and substituted derivatives	Sennidin C	41203	32213	43138	36.6	2.25	85.74
2.031	Aralkylamines / amines	Porphobilinogen	88001	70331	43444	38.6	2.44	95.86
2.222	Aralkylamines / amines	Porphobilinogen	110852	143791	54131	38.1	2.91	93.72
0.689	Benzene and substituted derivatives	S-2,5-Dimethyl-3-furanyl 3-methylbutanethioate	112079	86419	73572	38.3	-0.13	91.62
1.863	pyrimidines and derivatives	Aprobarbital	84830	107998	96039	38.3	2.36	94.18
1.985	pyrimidines and derivatives	Metharbital	56703	76337	61105	37.1	2.50	88.44
9.396	Benzene and substituted derivatives	Procarbazine	215914	247379	257758	38.7	0.86	94.57
0.710	Benzene and substituted derivatives	Acidissiminol epoxide	44737	75130	56772	35.9	-1.00	80.78
7.101	Benzene and substituted derivatives	10,11-Dihydroxycarbamazepine	35591	29312	24513	38.6	2.25	95.44
7.303	Benzene and substituted derivatives	Fluvoxamine	12789	11283	10926	38.8	2.05	96.64
7.185	Benzene and substituted derivatives	alpha-(Methoxyimino)-N-methyl-2-[[[1-[3-(trifluoromethyl)phenyl] ethoxy]imino]methyl]benzeneacetamide	23075	25495	3804	37.4	2.28	89.78
1.505	Benzene and substituted derivatives	Sildenafil	672511	1571412	767291	38.5	2.89	96.06
1.196	Benzene and substituted derivatives	N-Acetylarylamine	120846	39322	32522	38.1	3.33	94.23
3.006	Benzene and substituted derivatives	5-Phenyl-1,3-oxazinane-2,4-dione	47432	59496	16223	39.1	1.73	97.63
10.009	Benzene and substituted derivatives	1,3,5-Triphenylcyclohexane	51251	46978	42626	37.3	-2.33	89.17
2.937	Benzene and substituted derivatives	Udenafil	296470	2044419	461569	36.9	1.14	85.92
1.740	Benzene and substituted derivatives	N-Undecylbenzenesulfonic acid	632317	1367952	1005720	38.8	-1.80	96.18
0.677	Benzene and substituted derivatives	Tiapride	47662	44279	23371	38.1	-0.25	90.76
0.737	Benzene and substituted derivatives	Dimethylbenzimidazole	17012	5271	59199	39	2.73	98.03
2.758	Benzene and substituted derivatives	Desloratadine	318831	339994	294902	36.1	3.73	85.07
2.873	Benzene and substituted derivatives	Morellin	33349	36557	29889	36.7	2.45	86.55
2.801	beta hydroxy acids and derivatives	2-Hexenoylcarnitine	141833	124654	129621	36.7	0.00	83.45
1.535	beta hydroxy acids and derivatives	Glutarylcarnitine	107795	89147	59590	38.1	1.97	93.08
2.732	beta hydroxy acids and derivatives	Pimelylcarnitine	49177	57663	47980	38.1	3.16	94.31
4.055	biotin and derivatives	Biotin	13831	28980	8383	38.6	1.05	94.33
2.976	Benzene and substituted derivatives	Telmisartan	115877	147769	105657	38.4	0.87	92.90
2.987	Benzene and substituted derivatives	Telmisartan	137364	119585	78475	38.4	0.84	93.11
3.517	Benzene and substituted derivatives	Biphenyl	70359	73419	66926	38	-2.51	92.88
1.961	Benzene and substituted derivatives	Telmisartan	246437	247315	238655	36.3	-2.06	84.00
1.333	Benzene and substituted derivatives	Telmisartan	62058	128865	36895	35.8	-1.43	80.93
1.523	Benzene and substituted derivatives	Olmesartan	2451	12398	29644	36.9	-2.61	87.71
3.256	Fatty acyl / fatty acids	13:0(12Me,12Me)	49836	53692	44954	38.7	-1.90	95.74
3.335	Fatty acyl / fatty acids	13:0(12Me,12Me)	4675	36872	43120	38.6	-1.99	95.42
5.152	Fatty acyl / fatty acids	19:0(11Me)	59211	123041	125733	38.7	-1.52	95.56

1.326	Prenol lipids	Lamioside	175819	121553	125644	36.5	-0.24	82.83
1.348	Prenol lipids	Flakinin A	99610	157365	171097	38.9	0.71	95.45
1.759	Prenol lipids	Flakinin A	48987	109326	136637	38.2	3.19	94.62
1.355	Prenol lipids	Parthenin	59677	91398	102028	35.9	3.55	83.46
3.412	Prenol lipids	Estradiol dipropionate	125962	230510	218299	37.7	3.68	92.63
4.909	Prenol lipids	(-)-Jolkinol A	91185	100553	77755	35.7	1.57	80.34
5.032	Prenol lipids	Helvolic acid	82552	98831	97855	38.1	0.86	91.77
3.267	Prenol lipids	7,8,7',8'-Tetradehydroastaxanthin	24718	48354	83315	37.4	-2.53	89.92
4.653	carbohydrate and derivatives	Chitin	16906	13705	6032	37.6	0.19	88.31
2.450	carbohydrate and derivatives	5-Phosphoribosylamine	13542	57654	11269	37.5	2.97	91.01
4.958	carbohydrate and derivatives	Chitin	12064	21483	5918	36.5	-1.25	84.13
9.399	carbohydrate and derivatives	2-(Arabinosylamino)-3-(glucosylamino)propanenitrile	36656	40206	43749	39.2	0.02	95.99
4.794	carbohydrate and derivatives	Verbasoside	22857	32339	42013	38.8	-0.24	94.26
1.036	carboxylic acid esters	Ethyl 2-(methyldithio)propionate	2236058	766142	814937	37.1	-3.82	90.07
6.735	Prenol lipids / Carotenoid	Ketospirilloxanthin	236411	663962	666251	38.9	3.41	98.72
4.676	Benzene and substituted derivatives	3,4-Dihydroxyphenylvaleric acid	50201	28228	26598	38.7	-3.59	97.51
5.940	Sphingolipids	Cer(t18:0/16:0)	210486	226063	285205	38.7	1.91	95.78
5.937	Sphingolipids	Cer(d14:1/20:0)	88262	58413	97894	37.1	-3.80	89.76
6.575	Sphingolipids	Cer(d18:0/18:0(2OH))	151620	126739	160818	39	1.74	97.27
6.365	Sphingolipids	Cer(d18:1/17:0)	77736	84688	117984	37.2	-0.81	86.75
6.853	Sphingolipids	N-Stearoylsphingosine	61883	42296	77162	38.4	2.03	94.39
1.557	Polyketides / flavonoids	Antiarone J	15709	47720	69470	37.8	2.18	91.66
2.347	Steroid and derivatives	(25S)-5alpha-cholestan-3beta,6alpha,7beta,8beta,15alpha,16beta,26-heptol	85704	233394	385371	36	0.97	81.41
1.473	Polyketides	(Z)-3-Phenyl-2-propenal	57074	144285	263530	38.9	3.95	98.98
1.406	Carbohydrates and derivatives	D-arabinonate	237283	38984	38267	37.8	1.33	90.55
2.412	coumaric acid and derivatives	Caffeoylmalic acid	39544	42767	23764	36.4	-0.65	82.99
1.189	coumarin	Coumarin	58904	31717	26275	36.2	3.76	85.29
0.919	Amino acids and derivatives	Coutaric acid	49648	106160	268818	37.6	1.90	90.39
7.658	Glycerolipids	DG(16:0/18:3(9Z,12Z,15Z)/0:0)[iso2]	62105	74828	76369	36.2	-1.42	82.89
7.224	Glycerolipids	DG(18:4(6Z,9Z,12Z,15Z)/18:1(9Z)/0:0)[iso2]	47798	59043	73341	36.4	-3.15	85.92
8.189	Glycerolipids	DG(14:1(9Z)/22:2(13Z,16Z)/0:0)[iso2]	35793	50256	70560	36.2	-2.63	83.93
0.539	Glycerophospholipids	PA(22:6(4Z,7Z,10Z,13Z,16Z,19Z)/20:5(5Z,8Z,11Z,14Z,17Z))	54405	46627	38746	36.4	-3.01	85.37
4.826	Glycerophospholipids	PG(14:0/18:1(11Z))	267429	430513	347201	39.3	-0.81	97.59
4.617	Glycerophospholipids	PG(17:2(9Z,12Z)/16:0)	55385	71658	6400	39.2	-0.80	96.89
5.442	Glycerophospholipids	PG(20:5(5Z,8Z,11Z,14Z,17Z)/18:0)	30163	13867	77606	38.7	-2.72	96.56
0.919	Glycerophospholipids	PI(12:0/12:0)	16194	64482	145411	38.6	-2.88	96.60
5.538	Glycerophospholipids	PI(17:2(9Z,12Z)/0:0)	96733	96303	58230	36.8	0.93	85.29
1.003	Glycerophospholipids	PI(12:0/12:0)	29136	101992	190006	38.7	-2.84	96.62
3.553	dialkyldisulphides	1-(1-Propenylthio)propyl propyl disulfide	54014	234349	150488	36.6	1.46	84.55
7.028	dialkyldisulphides	1-(1-Propenylthio)propyl propyl disulfide	81466	200547	155609	36.6	3.20	86.94
3.057	dialkyldisulphides	1-(1-Propenylthio)propyl propyl disulfide	42775	185601	139338	36.6	1.32	84.48

5.995	Fatty acyl/fatty acids	Genipinic acid	960683	360059	104874	39.3	0.62	97.40
3.659	Fatty acyl/fatty acids	Tricosanedioic acid	29054	121339	183990	39.2	2.17	98.70
0.860	Amino acids and derivatives	Arginyl-Valine	188455	49463	41850	36.2	-0.31	81.60
1.216	Amino acids and derivatives	Asparaginyl-Proline	515206	458215	200103	37.8	2.96	92.39
1.497	Amino acids and derivatives	Asparaginyl-Proline	249133	242329	177173	38.5	3.58	96.76
1.547	Amino acids and derivatives	Asparaginyl-Proline	234992	212199	164342	38.1	3.32	94.53
2.812	Amino acids and derivatives	Glycyl-Phenylalanine	105632	99641	45426	36.6	2.18	85.41
1.615	Amino acids and derivatives	Glycyl-Tyrosine	50072	18451	9434	38.3	-3.62	95.83
1.459	Amino acids and derivatives	Isoleucyl-Lysine	168056	33271	12453	39.4	1.01	98.23
2.435	Amino acids and derivatives	Isoleucyl-Threonine	138406	20889	8979	39.4	0.77	98.14
4.942	Amino acids and derivatives	Leucyl-phenylalanine	51245	10673	6304	37.8	-2.97	92.46
2.827	Amino acids and derivatives	L-gamma-glutamyl-L-valine	209938	203044	162925	35.3	-3.02	80.30
2.591	Amino acids and derivatives	Prolyl-Tyrosine	511959	487785	357080	36.1	2.67	83.66
2.923	Amino acids and derivatives	Glutaminyl-Glutamate	98034	186553	129892	35.4	-2.94	80.37
1.086	Amino acids and derivatives	Glutaminyl-Proline	91632	162901	118158	37	0.11	84.99
0.761	Amino acids and derivatives	Glycyl-L-leucine	239989	485867	208916	39.1	1.98	98.08
0.651	Amino acids and derivatives	Glycyl-L-leucine	33784	69550	11252	38.5	2.62	95.65
0.849	Amino acids and derivatives	Glycylproline	228246	399224	186714	38.2	1.42	92.89
0.956	Amino acids and derivatives	Hydroxyprolyl-Glutamine	406286	961793	374343	37.3	2.21	88.93
1.947	Amino acids and derivatives	Hydroxyprolyl-Isoleucine	110357	149436	105343	38.8	2.75	97.16
4.810	Amino acids and derivatives	L,L-Cyclo(leucylprolyl)	5928	67575	2985	39.5	1.25	98.87
1.326	Amino acids and derivatives	Prolyl-Alanine	77833	159649	57795	38.6	0.17	93.25
1.326	Amino acids and derivatives	Alanyl-Glutamine	317263	342239	402417	37.1	1.75	87.60
0.677	Amino acids and derivatives	Asparaginyl-Hydroxyproline	170493	154518	176736	38.9	0.38	94.73
2.070	Amino acids and derivatives	Asparaginyl-Isoleucine	126961	221871	264402	38.7	1.89	95.94
3.491	Amino acids and derivatives	Glycyl-Methionine	871427	962508	1008373	38.4	-1.23	93.33
2.321	Amino acids and derivatives	Trandolaprilat	51273	64741	78877	39	-0.22	95.04
8.180	Amino acids and derivatives	Arginyl-Histidine	27523	21325	12979	37.8	-3.87	93.49
1.269	Amino acids and derivatives	Aspartyl-L-proline	66625	50177	32823	38.2	1.90	93.33
2.424	Amino acids and derivatives	Glycyl-L-leucine	63540	30820	13043	39.4	1.99	99.52
3.415	Amino acids and derivatives	Tryptophyl-Glycine	35619	27274	25699	38.3	0.63	92.14
1.315	Amino acids and derivatives	Aspartyl-Tryptophan	30299	42102	36364	36.7	0.73	84.26
0.674	Amino acids and derivatives	Glycyl-Phenylalanine	46006	96302	93320	38	2.58	93.13
4.459	Amino acids and derivatives	L,L-Cyclo(leucylprolyl)	36785	51062	22303	39.2	1.23	97.73
1.954	Amino acids and derivatives	L-glycyl-L-hydroxyproline	32561	72297	57615	37.2	2.16	88.81
2.191	Amino acids and derivatives	Prolyl-Valine	22964	24274	16274	38.1	-0.41	91.04
0.780	Amino acids and derivatives	L-gamma-glutamyl-L-isoleucine	35473	28319	43382	39.4	0.25	97.39
2.976	Amino acids and derivatives	N5-Acetyl-N2-gamma-L-glutamyl-L-ornithine	94321	266840	51081	36.6	0.03	83.24
2.766	Amino acids and derivatives	N5-Acetyl-N2-gamma-L-glutamyl-L-ornithine	85404	169379	63830	36.1	1.71	82.69
3.224	Amino acids and derivatives	Isoleucyl-Valine	163973	28368	19143	39.4	1.53	98.88
2.207	Amino acids and derivatives	N5-Acetyl-N2-gamma-L-glutamyl-L-ornithine	38385	141034	31576	37.5	-2.09	89.75

5.438	Glycerolipids	1-(14-methyl-pentadecanoyl)-2-(8-[3]-ladderane-octanyl)-sn-glycerol	98053	42946	212866	39.1	1.72	97.45
1.707	Prenol lipids	16,17-Dihydro-16a,17-dihydroxygibberellin A4 17-glucoside	343305	489305	482480	35.7	-3.35	82.55
4.823	Prenol lipids	Narasin	11350	9835	95156	37.3	-3.97	91.27
0.767	Prenol lipids	Persicachrome	65319	126542	221596	35.8	2.59	82.07
4.356	Fatty acyl /Eicosanoids	LTE4	11438	129786	42884	37.1	3.95	90.05
5.948	Fatty acyl /Eicosanoids	Dichotellate A	55255	143542	97613	36.5	-0.97	83.88
3.404	Steroid and derivatives	Norselic acid C	43111	89550	93720	38.9	1.14	95.68
2.496	Benzene and substituted derivatives	Phenethyl 6-galloylglucoside	111943	145084	167189	37.2	-3.70	90.21
3.160	Fatty acyl / fatty acid	cis-9-palmitoleic acid	104642	135835	59894	39.2	-1.67	98.08
5.144	Fatty acyl / fatty acid	4Z,7Z,10Z,13Z,16Z,19Z,22Z,25Z-octacosaoctaenoic acid	1166974	3340167	3357449	39.5	-0.71	98.38
3.667	Fatty acyl / fatty acid	Palmitic acid	4086023	9250195	10517624	39.8	-0.36	99.48
3.037	Fatty acyl / fatty acid	3R,5S-Dimethyldodecanoic acid	138778	254265	286753	38.9	-2.10	97.00
4.017	Fatty acyl / fatty acid	Heptadecanoic acid	938557	1184376	1214313	39.8	-0.55	99.48
1.839	fatty acyl / fatty esters	2-Methylacetophenone	88354	142445	132194	36.5	-2.40	85.33
2.648	fatty acyl / fatty esters	3-hydroxy-cis-5-octenoylcarnitine	2041217	1990546	1714358	39.4	0.41	97.53
2.420	fatty acyl / fatty esters	(7Z,10Z,13Z,16Z)-docosatetraenoylcarnitine	43747	90088	171061	37.6	1.61	90.11
0.554	fatty acyl / fatty esters	3-hydroxy-cis-5-octenoylcarnitine	284896	327994	760692	37.8	3.76	93.61
4.518	fatty acyl / fatty esters	Arachidyl carnitine	116640	319956	272230	39.4	1.54	98.71
5.255	fatty acyl / fatty esters	O-behenoylcarnitine	64063	182862	146378	38.9	1.53	96.51
0.855	fatty acyl / fatty esters	(9Z)-3-hydroxydodecenoylcarnitine	99931	124864	69326	38.9	0.80	95.70
1.184	fatty acyl / fatty esters	(9Z,12Z,15Z)-3-hydroxyoctadecatrienoylcarnitine	56662	161739	221014	39.5	0.73	98.36
2.378	fatty acyl / fatty esters	O-(17-carboxyheptadecanoyl)carnitine	55148	159499	208876	39.2	0.67	96.83
4.244	fatty acyl / fatty esters	Palmitoylcarnitine	1499061	1694356	1729224	38.7	2.01	96.07
1.954	fatty acyl glycosides	Prenyl apiosyl-(1->6)-glucoside	76100	125102	91695	38.3	0.10	91.80
4.962	fatty acyl glycosides	Corchoionoside B	27952	27847	21324	35.5	-2.77	80.91
2.923	fatty acyl glycosides	3-Methyl-3-butenyl apiosyl-(1->6)-glucoside	60266	67903	62106	37.9	2.98	93.17
2.846	fatty acyl glycosides	3-Methyl-3-butenyl apiosyl-(1->6)-glucoside	429498	437112	367621	37.5	-0.31	87.65
1.303	fatty acyl glycosides	1-(3-Methyl-2-butenoyl)-6-apiosylglucose	79824	89264	90367	37.9	-1.85	91.49
2.945	fatty acyl glycosides	3-Methyl-3-butenyl apiosyl-(1->6)-glucoside	64177	69683	127890	38.3	-0.18	91.75
0.824	fatty acyl / fatty amides	N-(3-oxododecanoyl) homoserine lactone	66298	114107	125560	36.5	0.31	82.86
1.599	fatty acyl / fatty amides	N-(3-oxododecanoyl) homoserine lactone	22803	48198	66703	38	1.05	91.04
6.605	fatty acyl/fatty alcohol	phenolic phthiocerol	83323	117413	64203	38.1	1.76	92.70
3.399	fatty acyls/eicosanoids	LTF4	65794	78670	43420	34.6	0.89	74.33
6.487	fatty acyls/eicosanoids	LTF4	8181	8671	1358	35.8	2.12	81.35
7.190	fatty acyls/fatty alcohols	(R)-2-Hydroxysterculic acid	19691	16998	20717	37.9	3.17	93.31
4.617	fatty acyls/fatty esters	Mayolene-18	30761	32047	10182	39.2	1.24	97.31
7.498	fatty acyls/fatty esters	Mayolene-20	13951	23576	21297	37.9	0.77	90.34
5.373	fatty acyl/fatty alcohol	phenolic phthiocerol	110356	52276	193293	39.3	2.26	99.08
7.708	fatty acyl/fatty alcohol	phenolic phthiocerol	43866	43587	66219	38.2	1.40	92.72
2.412	fatty acyl/Fatty aldehyde	9Z,11E,13-Tetradecatrienal	228791	550359	404399	39.1	-2.92	98.88
5.156	fatty acyl/fatty amides	Docosanamide	52772	91980	72816	38.9	2.02	97.04

4.343	fatty acyls/fatty esters	Mayolene-17	65174	64443	32257	39.1	1.56	97.37
6.076	fatty acyls/fatty esters	Mayolene-19	402361	587097	200702	39.3	1.99	98.96
6.377	fatty acyls/fatty esters	Mayolene-20	38132	145301	48112	38.5	-0.46	93.29
4.891	fatty acyls/fatty esters	Mayolene-19	199000	238717	251251	39.2	1.97	98.54
7.213	fatty acyls/fatty esters	Mayolene-19	61311	85569	98186	37.9	1.44	91.15
5.167	fatty acyls/fatty esters	Mayolene-20	89276	64807	164052	38.4	1.33	93.70
1.432	fatty acyls/fatty esters	3-hydroxy-cis-5-octenoylcarnitine	180826	307142	412155	35.6	3.20	81.93
4.731	Polyketides / flavonoids	Laxiflorin	107843	123332	216451	39.5	0.81	98.69
6.609	Polyketides / flavonoids	Laxiflorin	181484	252589	191213	38.9	0.85	95.49
0.936	Polyketides / flavonoids	2',4',5,7-Tetramethoxy-8-methylflavanone	117666	118023	106498	38.4	3.68	96.32
8.979	Polyketides / flavonoids	Demethyltorosaflavone C	98446	102956	95943	38.1	-2.90	93.81
0.504	Polyketides / flavonoids	5,7-Dihydroxyflavone 7-benzoate	29622	35161	77385	38.2	2.79	94.12
5.816	Polyketides / flavonoids	Demethyltorosaflavone D	8406	1506	2769	38.7	0.72	94.41
2.030	Polyketides / flavonoids	Epilumaflavanone B	177190	103790	83059	39	1.66	97.04
1.958	Polyketides / flavonoids	Euchrenone a14	73969	72848	45797	36	-2.16	82.71
1.226	Polyketides / flavonoids	Prebarbigerone	18908	41572	102693	38.7	0.70	94.52
0.635	Polyketides / flavonoids	Galangin 5,7-dimethyl ether	56538	57548	38903	36.4	-1.00	83.29
3.780	Polyketides / flavonoids	Lonchocarpenin	47123	41914	23394	38.4	1.32	93.71
1.215	Polyketides / flavonoids	Heteroflavanone B	87784	220392	394764	39	0.30	95.61
3.517	Polyketides / flavonoids	Artocommunol CA	147469	142236	119854	36.4	-0.63	82.89
4.425	Polyketides / flavonoids	Isochamanetin	41244	43710	29426	36.6	-2.26	85.87
1.470	Polyketides / flavonoids	Heteroflavanone B	17067	39913	56062	38.8	1.14	95.18
2.050	Polyketides / flavonoids	Quercetol B	20963	61506	68078	38.2	3.04	94.46
2.416	Benzene and substituted derivatives	Fluconazole	514489	846173	1151938	38.9	-2.86	97.92
1.355	furopyrans	Cyclocalopin F	126004	228645	246654	38.5	2.53	95.62
8.979	amino acid and derivatives	Avenic acid A	1076459	1092476	985787	39.2	0.91	97.35
0.647	amino acid and derivatives	4-Guanidinobutanoic acid	365505	390645	731339	38.3	3.17	95.44
0.670	amino acid and derivatives	(S)-4-Amino-5-oxopentanoate	76002	59441	47463	36	3.45	83.82
4.404	sugar acids and derivatives	Alginic acid	20359	29892	29457	36.9	-0.77	85.24
1.269	amino acid and derivatives	gamma-Glutamyl-beta-aminopropiononitrile	400311	290498	352531	37.4	1.66	88.86
0.670	amino acid and derivatives	gamma-glutamyl-ethylamide	99566	54215	17746	37.8	-1.42	90.76
2.564	amino acid and derivatives	(2S,4S)-Pinnatanine	32619	28237	20935	36.7	1.95	85.67
7.434	Glycerolipids	DG(13:0/22:4(7Z,10Z,13Z,16Z)/0:0)[iso2]	27540	39615	39299	35.7	2.03	81.04
6.655	Glycerolipids	1-(14-methyl-pentadecanoyl)-2-(8-[3]-ladderane-octanyl)-sn-glycerol	33339	48843	49470	38.8	-2.06	96.31
7.753	Glycerolipids	1-(14-methyl-pentadecanoyl)-2-(8-[3]-ladderane-octanyl)-sn-glycerol	24164	27867	40017	38.6	0.59	93.76
6.609	Glycerophospholipids	PI(O-20:0/20:5(5Z,8Z,11Z,14Z,17Z))	177949	204591	194172	36.9	2.40	87.51
5.453	Glycerophospholipids	PC(12:0/17:2(9Z,12Z))	22167	20145	7258	38.8	1.33	95.49
5.201	Glycerophospholipids	PG(18:0/18:2(9Z,12Z))	110	12	0	37.9	1.10	90.79
1.599	Glycerophospholipids	PI(13:0/12:0)	474767	1531637	2006121	38.8	-1.91	96.49
4.537	Glycerophospholipids	PS(O-16:0/14:1(9Z))	5917	1766	315	36.7	0.09	83.56
4.826	Glycerophospholipids	PS(P-16:0/16:1(9Z))	21819	18928	33840	39.2	0.31	96.61

4.268	glycine conjugates	N-[(3a,5b,7b)-7-hydroxy-24-oxo-3-(sulfoxy)cholan-24-yl]-Glycine	68465	43677	22679	36.3	1.64	83.41
6.365	Glycerolipids	MGDG(18:2(9Z,12Z)/18:3(9Z,12Z,15Z))	377482	352972	831270	39.3	-2.46	99.27
0.623	alkaloids and derivatives	Flazine methyl ether	87625	62501	42639	36.2	-1.77	83.02
1.638	Benzene and substituted derivatives	4-Aminohippuric acid	106540	78679	49601	39.1	0.11	95.77
0.651	Benzene and substituted derivatives	4-Aminohippuric acid	56889	143172	52493	38.1	-3.68	94.93
1.033	Amino acids and derivatives	N-Ribosylhistidine	867766	1811355	545457	37.2	2.17	88.64
5.769	Prenol lipids / hopanoids	2-methylbacteriohopane-32,33,34,35-tetrol	82535	156284	25418	38.9	2.20	97.29
5.369	Prenol lipids / hopanoids	bacteriohopane-,32,33,34-triol-35-cyclitol	148081	182386	242891	39.2	1.88	98.29
0.862	Hydroxycoumarin	Mammea E/BB	645367	831429	1855292	35.9	2.24	81.93
1.001	hypoxanthines	7-Methylguanine	107391	18385	96623	39	2.21	97.73
3.095	Benzene and substituted derivatives	Sulindac sulfide	152705	30027	35855	37.5	-0.45	88.15
5.995	Indoles	Indoleacetic acid	7647	324479	39611	39.1	2.40	98.16
6.887	Indoles	Cyclobrassinone	66583	159510	165186	37.6	-2.72	91.32
2.766	Indoles	1H-Indole-3-carboxaldehyde	60758	30931	21646	38.5	2.82	95.91
4.406	Indoles	alpha-Hydroxy-1-methyl-1H-indole-3-propanoic acid	39713	26541	15314	37.3	0.58	87.14
1.950	Amino acids and derivatives	5-Hydroxy-L-tryptophan	30094	22858	15670	38.8	-3.32	97.93
4.932	Indoles	2-Indolecarboxylic acid	51699	225391	41160	39	2.27	97.88
3.065	Indoles	2-Indolecarboxylic acid	8737	9033	21686	38.6	2.35	95.96
2.766	Indoles	Indoleacrylic acid	177815	64391	37667	38.4	2.84	95.54
3.609	Indoles	1H-Indole-3-carboxaldehyde	115190	125107	37539	36.6	3.52	86.90
7.235	Indoles	3-Methylene-indolenine	88286	10395	10955	39	3.96	99.50
3.548	Indoles	L-1,2,3,4-Tetrahydro-beta-carboline-3-carboxylic acid	57766	63133	32186	38.3	3.19	95.46
3.323	Indoles	Melatonin	27348	32185	30745	35.2	-3.56	80.00
3.323	Amino acids and derivatives	5-Methoxytryptophan	71024	53344	28800	37.5	2.00	90.04
9.533	Prenol lipids	Valdiate	95396	97419	118440	39.4	1.73	98.88
2.207	isocoumarans (antidepressant)	Citalopram aldehyde	60819	66547	50618	37	2.27	87.48
3.837	Polyketides / flavonoids	Calopogoniumisoflavone A	33296	28583	23743	37.9	0.95	90.78
0.824	Amino acids and derivatives	N-Jasmonoylisoleucine	40105	81046	153438	37	1.24	86.58
4.362	Fatty acyl / octadecanoid	12-hydroxyjasmonic acid 12-O-beta-D-glucoside	895954	1109705	922756	36.7	1.08	84.74
1.306	Polyketides	11-Hydroxy-12-methoxydihydrokawain	299338	454390	709427	37.2	3.57	90.34
1.473	Polyketides	11-Hydroxy-12-methoxydihydrokawain	69758	165481	328108	38.5	2.60	95.73
3.190	Fatty acyl / eicosanoid	Lipoxin D4	53209	72118	101623	36.1	3.93	84.96
1.698	Polyketides	10-Deoxymethymycin	29413	117094	144021	39.5	0.76	98.63
2.793	Fattyl acyl / fatty acid	Dethiobiotin	25518	54980	11676	39.2	1.63	97.79
3.053	Glycerophospholipids	PA(12:0/0:0)	137033	91945	67320	37.1	-3.81	90.03
5.209	Glycerophospholipids	PA(16:0/18:2(9Z,12Z))	35118	16322	18619	36.3	-0.81	82.34
5.133	Glycerophospholipids	PA(14:0/18:1(9Z))	18675	20795	24214	37.5	-0.45	88.19
2.107	Glycerophospholipids	PA(22:6(4Z,7Z,10Z,13Z,16Z,19Z)/0:0)	34222	28826	20902	37.5	2.05	90.10
0.855	Glycerophospholipids	PC(8:0/0:0)	20634	32117	25791	36.9	-2.93	88.03
6.906	Carbohydrate and derivatives	Sedoheptulose 1,7-bisphosphate	25867	40072	34901	38.4	2.89	95.33
2.793	Fetty acyl / Fatty amides	N-(5-hydroxy-pentyl) arachidonoyl amine	39599	114472	102788	38.9	1.34	96.18

0.864	Fetty acyl / Fatty amides	N,N-diethyl-3-hydroxybut-2-enamide	42234	43241	35849	36.2	2.01	83.56
5.133	Fetty acyl / Fatty amides	N-oleoyl glutamic acid	13062	54398	48923	37.5	3.88	92.08
3.503	Fetty acyl / Fatty amides	N-stearoyl serine	1872958	2164150	2131484	39.2	2.73	99.24
2.416	Fetty acyl / Fatty amides	N-(4-benzenesulfonamide) arachidonoyl amine	536577	818434	1017053	36.7	3.53	87.74
2.679	Fetty acyl / Fatty amides	Pipericine	6714	50269	59942	37.9	1.80	91.61
2.736	Fetty acyl / Fatty amides	Anandamide (20:2, n-6)	8673	56262	63220	38.7	2.17	96.25
4.252	N-acyl pyrrolidines	N-(14-Methylhexadecanoyl)pyrrolidine	226410	272943	294086	38.6	3.43	97.06
2.808	Amino acids and derivatives	L-N-(1H-Indol-3-ylacetyl)aspartic acid	73232	65521	44655	38	-2.64	93.12
3.719	Amino acids and derivatives	Methylhippuric acid	102322	56150	100444	38.4	-3.95	96.44
4.457	Amino acids and derivatives	Pentacosanoylglycine	2990699	6219735	4891343	39	2.89	98.57
3.205	Amino acids and derivatives	Suberylglycine	80395	118210	115892	37.8	-0.13	89.19
3.625	Amino acids and derivatives	Tricosanoylglycine	87634	192241	147665	39	1.69	96.98
8.686	Amino acids and derivatives	N-Succinyl-L,L-2,6-diaminopimelate	57761	49472	47970	38.6	0.13	93.12
4.362	N-acyl-piperidines	Pipercitine	316056	373852	384293	39	2.99	98.31
3.766	N-acylpyrrolidines	N-Hexadecanoylpyrrolidine	82553	195037	181722	36.5	3.73	86.79
6.369	Sphingolipids	Cer(d18:0/h17:0)	169889	167095	232635	38.6	2.03	95.37
0.681	nitroimidazole	Metronidazole	192298	186815	201305	39	2.63	98.01
2.534	Fatty acyl / octadecanoids	12R-HOME(9E)	11554	33494	34213	37.1	-2.36	88.55
4.709	Fatty acyl / octadecanoids	7-keto-stearic acid	54475	60980	61263	37.5	3.66	91.66
1.832	Carbohydrates and derivatives	Acaciabiuronic acid	46602	25937	17312	38.7	-0.64	94.51
1.539	Carbohydrates and derivatives	1,2,10-Trihydroxydihydro-trans-linalyl oxide 7-O-beta-D-glucopyranoside	64999	58495	47758	36.7	2.84	86.76
3.719	Carbohydrates and derivatives	1,2,10-Trihydroxydihydro-trans-linalyl oxide 7-O-beta-D-glucopyranoside	165453	210165	131583	38	-0.82	91.05
1.786	Carbohydrates and derivatives	1,2,10-Trihydroxydihydro-trans-linalyl oxide 7-O-beta-D-glucopyranoside	69661	26511	31481	36.6	-1.25	84.34
3.548	Carbohydrates and derivatives	2,4-Dihydroxy-7,8-dimethoxy-2H-1,4-benzoxazin-3(4H)-one 2-glucoside	52632	9916	10001	37.1	-0.05	85.57
5.275	Carbohydrates and derivatives	Phenethyl rutinoside	54400	31799	13768	35.8	-2.92	82.26
1.573	Carbohydrates and derivatives	1,2,10-Trihydroxydihydro-trans-linalyl oxide 7-O-beta-D-glucopyranoside	72482	101784	66875	36.4	0.10	81.92
4.364	Carbohydrates and derivatives	2-[4-(3-Hydroxypropyl)-2-methoxyphenoxy]-1,3-propanediol 1-glucoside	74108	114389	106168	37.9	-3.02	93.31
2.923	Carbohydrates and derivatives	Benzyl beta-primeveroside	56803	72286	68943	37.4	-0.61	87.81
4.741	Carbohydrates and derivatives	Verbasoside	21515	29444	22660	38.7	0.49	94.19
0.609	Benzene and substituted derivatives	4R,5R,6S-Trihydroxy-2-hydroxymethyl-2-cyclohexen-1-one 6-(2-hydroxy-6-methylbenzoate)	55958	23495	13333	35.6	2.50	81.19
0.670	Amino acids and derivatives	Ophthalmic acid	418506	459409	596073	37.2	1.72	87.84
9.396	Amino acids and derivatives	Thyrotropin releasing hormone	266672	301200	308226	39	-3.27	98.89
2.461	organosulfonic acids	Acrylic acid-2-acrylamido-2-methyl propane sulfonic acid copolymer	297639	413665	455159	37.9	-3.82	93.94
6.205	other fatty acyls	N-(3-(hexadecanoyloxy)-heptadecanoyl)-L-ornithine	80062	11546	30364	38.9	0.97	95.74
1.793	Fatty acyl / fatty acids	12-oxo-5E,8E,10Z-heptadecatrienoic acid	34710	54901	49276	36.5	-1.88	84.91
5.793	Carbohydrates and derivatives	Imidazoleacetic acid ribotide	551	379	331	38.4	-0.41	92.35
3.609	Carbohydrates and derivatives	2-Hydroxybenzaldehyde O-[xylosyl-(1->6)-glucoside]	64156	35895	27885	38.7	-1.51	95.51
2.500	Carbohydrates and derivatives	Ptelatoside A	193500	286108	220853	38.8	-1.65	95.97
3.795	Benzene and substituted derivatives	Ethopropazine	30250	9968	7015	36.2	3.82	85.58
1.515	Benzene and substituted derivatives	Thioridazine	32390	49086	64992	37.3	3.90	90.96
1.355	Benzene and substituted derivatives	(4-Methylphenyl)acetaldehyde	41030	70098	74840	38.9	3.65	98.62

10.44	Benzene and substituted derivatives	Tropicamide	68608	48357	24372	37.1	-0.73	86.37
2.069	Benzene and substituted derivatives	Musanolone F	67113	49988	33123	38.7	-1.93	96.00
3.472	Polyketides / phenylpropanoids	Rifaximin	16015	12633	3594	38.4	1.67	93.92
1.425	Polyketides / phenylpropanoids	Di-4-coumaroylputrescine	27207	34692	23163	36.4	1.83	84.18
0.925	Benzene and substituted derivatives	Dopamine 4-sulfate	64140	64781	53495	35.2	-3.63	80.48
5.335	Glycerophospholipids	PC(12:0/15:1(9Z))	44205	18535	2356	38	0.36	90.36
3.214	Glycerophospholipids	PC(11:0/11:0)	4101147	4688132	4607816	39	2.47	98.12
6.009	Glycerophospholipids	PC(12:0/17:1(9Z))	37991	54197	15470	38.9	0.34	94.69
5.674	Glycerophospholipids	PC(14:1(9Z)/14:0)	23743	44438	4337	39.2	-0.31	96.19
5.571	Glycerophospholipids	PC(14:1(9Z)/14:0)	9484	20072	1209	39.1	-0.84	96.64
5.765	Glycerophospholipids	PC(17:2(9Z,12Z)/13:0)	46871	115734	9590	39	-0.42	95.41
6.005	Glycerophospholipids	PC(18:4(6Z,9Z,12Z,15Z)/13:0)	177119	224740	81109	38.7	-2.86	96.97
6.372	Glycerophospholipids	PC(17:2(9Z,12Z)/15:0)	7108	71427	0	38.2	-1.22	92.69
6.076	Glycerophospholipids	PC(20:5(5Z,8Z,11Z,14Z,17Z)/13:0)	110696	176769	53712	38.9	-1.56	96.50
6.597	Glycerophospholipids	PE(16:0/18:1(11Z))	35824	72218	16064	37.5	-1.29	88.82
5.457	Glycerophospholipids	PE(16:1(9Z)/16:1(9Z))	164419	217625	33559	39.6	-0.61	98.84
6.327	Glycerophospholipids	PE(16:1(9Z)/17:0)	33030	97898	5656	38.7	-0.98	94.93
6.005	Glycerophospholipids	PE(18:1(11Z)/14:0)	484705	709132	238757	39.8	-0.48	99.58
6.075	Glycerophospholipids	PE(18:1(11Z)/16:1(9Z))	305971	508483	135689	39.7	-0.61	99.40
6.654	Glycerophospholipids	PE(18:1(11Z)/18:1(11Z))	17821	29224	19353	37.9	-1.46	91.47
5.453	Glycerophospholipids	PE(18:4(6Z,9Z,12Z,15Z)/16:1(9Z))	71727	85229	20593	38.1	-3.03	93.89
6.495	Glycerophospholipids	PE(18:2(9Z,12Z)/21:0)	28770	10486	69589	37.1	-1.99	87.86
4.339	Glycerophospholipids	PG(16:1(9Z)/16:1(9Z))	97820	109699	19936	38.8	-0.90	95.21
5.006	Glycerophospholipids	PG(17:0/20:5(5Z,8Z,11Z,14Z,17Z))	399264	660586	638675	39	0.55	95.49
4.887	Glycerophospholipids	PG(18:1(11Z)/16:1(9Z))	366736	491719	380056	39.6	-0.63	98.84
4.709	Glycerophospholipids	PG(18:3(6Z,9Z,12Z)/14:0)	1328505	1481477	1463920	39	-2.44	98.01
4.891	Glycerophospholipids	PG(20:5(5Z,8Z,11Z,14Z,17Z)/16:0)	92970	170003	157926	37.2	-3.37	89.95
1.618	Glycerophospholipids	PG(12:0/0:0)	26255	64387	90335	38.6	3.01	96.77
5.685	Glycerophospholipids	PG(12:0/17:0)	22723	93689	96714	36.1	3.98	84.95
4.232	Glycerophospholipids	PG(14:0/16:1(9Z)	3723	18611	28190	37	-1.53	87.08
5.076	Glycerophospholipids	PG(14:0/18:0)	20558	52168	282429	38.3	-1.05	92.71
5.072	Glycerophospholipids	PG(15:0/18:1(9Z))	54591	79403	117291	39.4	-0.86	97.81
0.897	Glycerophospholipids	PG(16:0/0:0)	10561	50276	77729	36.7	3.54	87.82
5.369	Glycerophospholipids	PG(16:0/18:1(11Z))	249174	151719	491955	39.8	-0.44	99.31
5.163	Glycerophospholipids	PG(17:0/18:2(9Z,12Z))	98957	83024	212458	39.5	-0.75	98.41
5.666	Glycerophospholipids	PG(18:1(11Z)/17:0)	43680	2111	92350	38.9	-1.12	95.84
5.434	Glycerophospholipids	PG(18:1(11Z)/18:1(11Z))	185862	77317	395326	39.7	-0.55	98.95
5.369	Glycerophospholipids	PG(18:4(6Z,9Z,12Z,15Z)/18:0)	39586	16268	82937	38.5	-3.24	96.50
1.222	Glycerophospholipids	PG(22:1(11Z)/0:0)	149824	445768	541566	39.1	-1.93	97.58
2.991	Glycerophospholipids	PG(22:2(13Z,16Z)/0:0)	34330	118394	207743	37	2.73	88.31
0.638	Glycerophospholipids	PG(O-18:0/0:0)	29299	60785	102351	37.7	-1.42	90.21

4.529	Glycerophospholipids	PG(13:0/18:1(9Z))	12969	60897	113966	38.7	-1.02	94.91
1.809	Glycerophospholipids	PG(22:1(11Z)/0:0)	369925	1057980	1220743	38.9	-1.55	96.52
6.320	Glycerophospholipids	PE(18:4(6Z,9Z,12Z,15Z)/17:0)	14223	33857	4618	38.1	-0.72	91.47
5.121	Glycerophospholipids	PS(O-16:0/17:2(9Z,12Z))	0	117	0	39.1	0.23	95.70
4.903	Glycerophospholipids	PG(17:0/14:0)	2040	6276	58955	35.4	3.63	81.43
2.252	Glycerophospholipids	PG(18:1(9Z)/0:0)	3924	1970	12940	39.1	-1.56	97.27
3.979	Glycerophospholipids	PG(18:4(6Z,9Z,12Z,15Z)/15:1(9Z))	3834	26556	44481	38	-0.76	90.76
5.076	Glycerophospholipids	PG(18:4(6Z,9Z,12Z,15Z)/17:0)	12529	12841	22250	37.9	-3.38	93.25
1.200	Glycerophospholipids	PS(20:5(5Z,8Z,11Z,14Z,17Z)/0:0)	28267	38694	46884	37.7	1.09	90.05
0.676	piperazines	Vilazodone	22679	47049	47311	38.3	-1.61	93.33
4.901	piperidines	Reduced haloperidol	29708	48748	20577	35.8	1.05	80.40
0.817	polyclic hydrocarbon	Santene	30106	71603	113820	38.7	3.60	97.67
1.330	polyethylene glycols	Heptaethylene glycol	19379	16171	11490	37.2	3.14	89.83
2.671	polyethylene glycols	Heptaethylene glycol	81393	191609	251302	38.3	2.30	94.16
2.705	polyethylene glycols	Hexaethylene glycol	103999	272432	304413	36.2	2.72	84.05
2.900	polyethylene glycols	Heptaethylene glycol	52512	129920	144970	38.4	2.41	94.74
2.336	Polyketides	Zaragozic acid A	31854	30543	19530	36.7	3.32	87.35
3.780	Polyketides / flavonones	alpha,4,2'-Trihydroxy-4-O-geranyldihydrochalcone	24218	21613	14364	37.8	1.45	90.95
9.399	Polyketides / flavonoids	Sinaticin	30444	38674	40988	37.1	-1.63	87.43
1.561	Prenol lipids /sesquiterpenoids	7'-hydroxyabscisic acid	47225	92813	119023	36.8	2.70	87.43
6.860	Prenol lipids /sesquiterpenoids	15-Acetoxyscirpene-3,4-diol 4-O-a-D-glucopyranoside	12962	15867	3846	37.5	1.50	89.12
4.366	prenol lipids/hopanoids	adenosylhopane	11003	6532	34067	37.1	2.21	88.35
6.639	prenol lipids/hopanoids	bacteriohopane-32,33,34,35-tetrol	28626	35261	43426	37.7	2.51	91.28
2.104	prenol lipids	(-)-trans-Carveol glucoside	9800	14250	14427	38.9	3.58	98.49
3.510	Amino acids and derivatives)	Ascorbalamic acid	126348	120367	133383	37.8	0.77	89.79
2.759	Fatty acyl / eicosanoids	2-glyceryl-PGD2	28873	58460	64934	36.3	-3.24	85.55
1.657	pteridines and derivatives	7-Hydroxy-6-methyl-8-ribityl lumazine	1015890	506308	323188	37.3	-3.53	90.59
0.635	purine and derivatives	5'-n-propylthioadenosine	49875	42065	24010	35.6	-2.63	80.88
1.421	purine and derivatives	Adenosine	1194734	207494	184354	35.5	3.04	80.85
1.440	purine and derivatives	Guanine	1365520	390686	357415	39.1	1.83	97.57
0.757	purine and derivatives	Guanine	126438	126969	162548	39	2.21	97.73
4.314	purine and derivatives	Penciclovir	25959	35707	17876	38.8	0.49	94.82
2.815	Benzene and substituted derivatives	Isomorellic acid	96471	83068	57989	36.9	-0.24	84.63
2.034	Benzene and substituted derivatives	Isomorellic acid	50475	47465	40350	37.1	1.36	87.18
2.861	Benzene and substituted derivatives	Morellinol	70975	37209	18691	37.5	2.22	90.17
2.347	Benzene and substituted derivatives	Morellinol	44764	34757	22473	36.4	-3.40	85.90
3.079	Benzene and substituted derivatives	Morellin	31954	32066	17028	37.8	2.88	92.17
2.359	Benzene and substituted derivatives	Morellinol	11258	59671	79308	39.5	1.00	98.69
1.493	pyridines and derivatives	4-Pyridoxolactone	226721	149201	42030	36.2	-0.36	81.51
0.898	pyridinecarboxylic acids	4-Pyridoxic acid	189212	189536	159106	35.8	-3.53	83.00
2.070	pyridoxamine	Pyridoxamine	31495	599783	128864	38.8	2.34	97.02

1.433	Pyrimidine and derivatives	Zalcitabine	43076	58018	39907	39	-0.55	95.52
1.862	Pyrimidine and derivatives	3'-Azido-3'-deoxy-5'- O-beta-D-glucopyranuronosylthymidine	63504	59618	548190	37.6	-1.92	90.29
3.727	Pyrimidine and derivatives	Pentobarbital	509611	395252	187812	38.6	-2.27	95.73
3.803	Pyrimidine and derivatives	Pentobarbital	508921	373677	153992	39.3	0.27	96.68
2.008	Pyrimidine and derivatives	Aprobarbital	465567	331456	103624	37.1	2.89	88.94
3.171	Pyrimidine and derivatives	Aprobarbital	127795	92288	54956	37.8	1.62	90.74
1.330	Pyrimidine and derivatives	Thymidine	553087	434487	284401	36.6	2.18	85.48
0.784	Pyrimidine and derivatives	Butalbital	64306	58131	46792	36.1	0.35	80.90
1.001	pyrrolotriazines	3-Methylpyrrolo[1,2-a]pyrazine	100046	75249	72599	36.9	-1.12	86.01
8.979	Alcohols and polyols	Chlorogenoquinone	69204	70420	61188	37.9	3.77	94.01
3.065	quinolines and derivatives	Kynurenic acid	30527	25320	60571	38	3.19	93.80
3.171	quinolines and derivatives	Rufloxacin	140486	115775	969606	38.2	-0.25	91.29
2.766	quinolines and derivatives	6-Methylquinoline	94632	93798	14058	38.2	1.53	92.94
4.067	quinolines and derivatives	8-hydroxyquinoline	582492	96069	96385	38.4	3.06	95.59
1.505	quinolines and derivatives	8-hydroxyquinoline	218794	190964	119104	38.5	2.83	95.77
2.896	quinolines and derivatives	8-hydroxyquinoline	209619	218113	161490	38.8	3.03	97.71
1.360	quinolines and derivatives	8-hydroxyquinoline	161289	186675	97469	38.1	2.99	93.97
2.450	quinolines and derivatives	8-hydroxyquinoline	71565	106031	31301	37.8	3.31	93.07
1.520	quinolines and derivatives	Margrapine A	53332	53802	39111	38.6	-2.13	95.32
1.452	quinolines and derivatives	Quinaldic acid	79235	85657	77227	38.7	1.52	95.28
9.571	Benzene and substituted derivatives	Hexylresorcinol	124375	151231	208555	39.4	1.64	99.07
3.614	Retenoid	Etretinate	38609	126213	117419	38.6	1.80	94.95
9.396	Polyketides / flavonoids	12a-Hydroxyisomillettone	95172	111578	123084	36.8	3.77	88.55
3.560	Fatty acyl	Nomilinic acid 17-glucoside	0	2634	4535	38.5	1.86	94.68
4.385	Fatty acyl / fatty acids	Stearic acid	4883505	10272801	11229662	39.9	0.10	99.37
2.831	Prenol lipids / sesquiterpenoids	S-Furanopetasitin	55412	50728	46714	36.8	-3.24	87.61
1.866	Prenol lipids / sesquiterpenoids	Armillaricin	62663	239937	286574	39.5	0.61	98.17
5.144	Prenol lipids / sesterpenoids	3-Hydroxy-10'-apo-b,y-carotenal	29086	102455	108735	37.6	-2.51	91.06
5.145	Prenol lipids / sesterpenoids	3-Hydroxy-10'-apo-b,y-carotenal	123270	219756	214033	39.3	1.76	98.82
10.16	sphingolipids	Sphinganine	107439	98157	104190	39.3	0.03	96.50
2.374	sphingolipids	Penaresidin A	1916429	2240135	2232213	38.5	3.05	95.89
9.286	sphingolipids	C16 Sphinganine	768396	706464	728247	39.5	0.98	98.78
4.320	sphingolipids	N-(hexadecanoyl)-deoxysphing-4-enine-1-sulfonate	53163	191434	37729	36.7	-0.48	84.30
0.538	sphingolipids	LacCer(d18:1/20:0)	53342	72447	62192	32.9	0.45	64.91
5.263	sphingolipids	Cer(d14:1/20:0)	43127	16592	18534	35.9	0.58	80.41
6.563	sphingolipids	Cer(d15:1/20:0)	25591	37453	38985	37.7	-2.55	91.29
5.476	sphingolipids	SM(d18:0/12:0)	4719	321	4988	35.9	1.28	81.12
1.352	sphingolipids	Eplerenone	6022200	11213354	12506965	39.1	1.65	97.53
3.243	steroids and derivatives	Dehydroepiandrosterone sulfate	27567	77621	34910	36.3	2.57	84.50
9.190	steroids and derivatives	3a,7a,12b-Trihydroxy-5b-cholanoic acid	248	0	0	37.8	-3.31	92.81
2.892	steroids and derivatives	Physagulin E	23178	21395	9457	36.1	2.07	83.17

4.432	steroids and derivatives	pregnenolone sulfate	13316	33424	11406	36.7	3.96	88.34
4.235	steroids and derivatives	(6RS)-22-oxo-23,24,25,26,27-pentanorvitamin D3 6,19-sulfur dioxide adduct	201652	223003	151893	38.2	-0.71	91.65
0.946	steroids and derivatives	(25R)-26,26,26-trifluoro-1alpha,25-dihydroxyvitamin D3	128390	387289	568759	39.1	-2.45	98.41
5.925	Fatty acyl /fatty acid	Behenic acid	11170	17241	25040	37.1	-2.20	87.97
1.348	Benzene and substituted derivatives	Styrene	40927	84579	115175	38	2.56	92.84
1.881	sugar acids and derivatives	3-Deoxy-D-manno-octulosonate	116106	33579	30203	37.7	-0.31	88.97
0.918	sulfoxides	Camelinin	140675	180296	119548	38.1	0.03	90.32
0.723	sulfoxides	(Z)-[3-(Methylsulfinyl)-1-propenyl] 2-propenyl disulfide	121403	112299	111719	36.6	-0.13	82.98
7.035	sulfoxides	(Z)-[3-(Methylsulfinyl)-1-propenyl] 2-propenyl disulfide	78321	248659	152333	38	3.26	93.72
2.382	Prenol lipids	(-)-trans-Carveol glucoside	51975	140625	155590	36.9	2.86	87.74
1.352	tetrahydroisoquinolines	1,2,3,4-Tetrahydroisoquinoline	40774	78571	91635	39	3.43	99.07
2.728	Tetrapyrroles and derivatives	Mono(glucosyluronic acid)bilirubin	33600	23932	13902	35.1	3.97	80.20
5.449	Prenol lipids	gamma-tocotrienol	276390	723449	728484	39.5	-1.34	99.20
1.840	Prenol lipids	15-Acetoxyscirpene-3,4-diol 4-O-a-D-glucopyranoside	43169	58467	56155	36.4	-2.91	85.45
6.689	Glycerolipids	TG(18:4(6Z,9Z,12Z,15Z)/18:4(6Z,9Z,12Z,15Z)/18:4(6Z,9Z,12Z,15Z))	72368	114037	104091	37.1	-2.13	88.09
0.681	Amino acids and derivatives	Glycylprolylhydroxyproline	100192	95323	103701	38.3	-2.90	95.15
1.008	Amino acids and derivatives	Glycylprolylhydroxyproline	605435	802384	473985	38.9	-2.33	97.07
4.731	Prenol lipids / tripterpenoids	Lucidenic acid D1	100768	116453	204084	39.5	0.60	98.30
6.609	Prenol lipids / tripterpenoids	Lucidenic acid D1	119926	134643	134397	38.7	0.67	94.17
0.706	Amino acids and derivatives	Tryptamine	226145	92817	104322	37.4	3.32	90.95
1.493	(unclassified)	Choline bitartrate	107585	116181	93550	36.4	-2.52	85.24
1.977	(unclassified)	1,6-anhMurNAc	58075	55205	49746	37.5	0.84	88.31
3.438	Fatty acyl / fatty acid	9-heptadecylenic acid	44842	70114	43449	39.6	-1.03	99.31
4.709	Fatty acyl / fatty acid	7,12-octadecadiynoic acid	41827	131795	151644	39.2	2.67	98.93
3.758	Fatty acyl / fatty acid	Oleic acid	142503	170951	188674	39.2	-1.19	97.48
4.994	Fatty acyl / fatty acid	7,11-octadecadiynoic acid	83910	119079	112330	38.8	2.04	96.39
5.312	Fatty acyl / fatty acid	17Z-octadecenoic acid	36175	77328	65132	37.7	3.81	93.20
3.397	Steroid and derivatives	(23S)-1alpha-hydroxy-25,27-didehydrovitamin D3 26,23-lactone	45802	70063	70445	36.5	1.56	84.43
7.094	fatty acyls/fatty esters	Behenyl linoleate	367718	389992	349265	36.5	-3.79	86.69
2.930	steroids and derivatives	Physalolactone	49368	251457	84686	36	2.83	83.59

Day 120

RT (min)	Chemical class	Suggested compound	A1	A4	A8	Score	Mass Error (ppm)	Isotope Similarity
1.473	Prenol lipids	Vomitoxin	654307	741459	438062	38.6	2.49	96.05
1.275	Prenol lipids	Vomitoxin	1291159	1280195	1014956	38.6	2.86	96.24
3.235	(unclassified)	Distichonic acid A	83400	76407	37013	36.3	0.26	81.93
1.637	(unclassified)	5'-(dimethylsulfonio)-5'-deoxyadenosine	45862	30163	47945	38.8	1.68	96.19
1.493	(unclassified)	Choline bitartrate	1357215	622108	399796	36.4	-2.52	85.24
6.609	Glycerophospholipids	PI(O-16:0/20:5(5Z,8Z,11Z,14Z,17Z))	175791	249539	197681	38.1	2.30	93.19
12.00	Polyketides / phenylpropanoids	2'-Hydroxy-4',6'-dimethoxy-3'-methyldihydrochalcone	8170288	9488023	8038979	38.8	-3.58	98.26

3.214	Glycerolipids	MG(0:0/22:2(13Z,16Z)/0:0)	46773	53124	51950	39.2	0.93	97.19
2.043	Polyketides / phenylpropanoids	(S)-(E)-2'-(3,6-Dimethyl-2-heptenyl)-3',4',7-trihydroxyflavanone	1026465	862683	581443	38.6	0.86	94.18
9.251	Indoles	Alkaloid AQC2	332296	342920	189127	37.5	2.93	90.76
0.710	Indoles	Indole-3-carbinol	309509	537312	1184042	38.3	3.11	95.19
2.873	Polyketides / flavonoids	7-Chloro-3,4',5,6,8-pentamethoxyflavone	290865	175770	166442	37.9	1.41	91.01
0.798	Benzene and substituted derivatives	N-Acetylprocainamide	382291	335504	199585	38.5	2.32	95.28
0.799	Amino acids and derivatives	(S)-N-(4,5-Dihydro-1-methyl-4-oxo-1H-imidazol-2-yl)alanine	3744680	2286700	1213241	38.1	1.41	92.30
2.290	Alcohols and polyols	Pantothenic acid	1353440	2968650	220676	35.9	0.93	80.45
0.647	Alcohols and polyols	D-4-O-Methyl-myo-inositol	887900	378475	279400	37.5	-0.87	88.32
3.495	alkaloids and derivatives	SN-38	1061767	554635	310691	36.3	0.93	82.56
7.662	Glycerolipids	DG(P-14:0/18:1(9Z))	106394	95940	78769	37.4	1.51	88.58
1.330	Benzene and substituted derivatives	Hydroxykynurenine	7204808	2596854	1132854	38.5	0.43	93.13
1.386	Benzene and substituted derivatives	N'-Formylkynurenine	988097	274473	196135	36.6	-2.97	86.30
1.806	Purine and derivatives	1-ethyladenine	409000	476979	44058	38.9	1.70	96.38
1.505	Benzene and substituted derivatives	N'-Formylkynurenine	2606451	631571	339920	38.3	2.90	94.84
1.607	Benzene and substituted derivatives	fluorobenzoylpropionic acid	69878	49063	47106	38.8	1.13	95.22
3.025	Amino acids and derivatives	L-cis-Cyclo(aspartylphenylalanyl)	286183	100375	70030	36.7	-0.67	84.41
3.605	Amino acids and derivatives	L-cis-Cyclo(aspartylphenylalanyl)	963530	346850	184068	38.5	0.07	92.59
3.193	Amino acids and derivatives	L-cis-Cyclo(aspartylphenylalanyl)	579098	101944	100804	35.6	-3.32	81.70
3.084	Amino acids and derivatives	Levetiracetam	2144037	563267	387365	39.5	1.74	99.39
0.952	Aldehydes	1-(3-Aminopropyl)-4-aminobutanal	1016	454212	5276	39.2	2.83	99.14
1.448	Amino acids and derivatives	Descarbonyl-lacosamide	8781774	1448020	807910	38.7	1.31	94.95
2.259	amines (alkyldiarylamines)	Isothipendyl	1887370	723546	90991	38.1	0.89	91.62
4.661	Amino acids and derivatives	L,L-Cyclo(leucylprolyl)	2252421	645854	320389	39.6	1.34	99.83
3.403	Amino acids and derivatives	L-alpha-Amino-1H-pyrrole-1-hexanoic acid	4184527	1586332	1060220	39.3	1.76	98.62
2.031	Amino acids and derivatives	L-Phenylalanine	2919467	934054	247518	37.2	3.25	90.04
3.339	Amino acids and derivatives	L-Tryptophan	3162953	868576	449905	39	1.95	97.19
2.500	Amino acids and derivatives	N-Acetylglutamine	1908859	545982	313332	38.7	1.86	95.72
0.666	Amino acids and derivatives	N-Acetylhistidine	213705	330915	89590	39.4	0.81	98.06
0.856	Amino acids and derivatives	N-(1-Deoxy-1-fructosyl)valine	953369	770930	271904	38.5	0.83	93.39
0.681	Amino acids and derivatives	6-diazo-5-oxo-L-norleucine	162280	422444	271263	39	2.63	98.01
0.834	Amino acids and derivatives	N-Carbamoyl-2-amino-2-(4-hydroxyphenyl)acetic acid	736676	630127	264268	39.6	0.27	98.28
1.003	Amino acids and derivatives	Coutaric acid	607940	600366	251724	37.8	1.28	90.38
0.811	Amino acids and derivatives	N-a-Acetyl-L-arginine	18710110	1275305	433856	38.7	0.33	93.87
1.238	Fatty acyl / fatty acid	11-amino-undecanoic acid	12797595	11277050	6194991	39	2.49	98.14
3.254	Alcohols and polyols	Paromomycin	469519	502146	253755	35.5	2.31	80.15
1.001	Alcohols and polyols	Voglibose	2047679	727194	371512	38.2	-3.78	95.32
1.037	Purine and derivatives	N1-methyladenine	437436	677574	65448	38.2	2.55	94.16
11.99	Benzene and substituted derivatives	Methamphetamine	95532	115529	96891	36.4	0.33	82.27
4.827	annonaceous acetogenins	Cohibin A	1561880	1289206	130286	38.6	1.72	95.26
7.132	annonaceous acetogenins	Cohibin A	629027	293558	80932	38.5	1.86	94.73

6.005	annonaceous acetogenins	Cohibin A	2657704	2785161	299140	38.9	2.15	97.05
1.729	Benzene and substituted derivatives	Sennidin C	208365	88250	38955	36.6	2.25	85.74
2.222	Aralkylamines / amines	Porphobilinogen	9278453	753621	265695	38.1	2.91	93.72
2.031	Aralkylamines / amines	Porphobilinogen	681047	233617	95320	38.6	2.44	95.86
0.689	Benzene and substituted derivatives	S-2,5-Dimethyl-3-furanyl 3-methylbutanethioate	266501	208453	158610	38.3	-0.13	91.62
1.863	Pyrimidines and derivatives	Aprobarbital	613062	517107	369443	38.3	2.36	94.18
1.985	Pyrimidines and derivatives	Metharbital	571243	363013	196873	37.1	2.50	88.44
9.396	Benzene and substituted derivatives	Procarbazine	1292045	858160	866073	38.7	0.86	94.57
0.710	Benzene and substituted derivatives	Acidissiminol epoxide	195836	172416	106647	35.9	-1.00	80.78
1.505	Benzene and substituted derivatives	Sildenafil	18181255	3989420	871121	38.5	2.89	96.06
3.006	Benzene and substituted derivatives	5-Phenyl-1,3-oxazinane-2,4-dione	1473178	110844	30212	39.1	1.73	97.63
1.196	Benzene and substituted derivatives	N-Acetylarylamine	11971807	1487998	263272	38.1	3.33	94.23
10.01	Benzene and substituted derivatives	1,3,5-Triphenylcyclohexane	100802	84838	61416	37.3	-2.33	89.17
2.937	Benzene and substituted derivatives	Udenafil	2919296	2452570	1138031	36.9	1.14	85.92
1.740	Benzene and substituted derivatives	N-Undecylbenzenesulfonic acid	1232748	1307134	1054254	38.8	-1.80	96.18
0.677	Benzene and substituted derivatives	Tiapride	1073029	166514	77120	38.1	-0.25	90.76
0.737	Benzene and substituted derivatives	Dimethylbenzimidazole	7941	28443	55824	39	2.73	98.03
2.758	Benzene and substituted derivatives	Desloratadine	2632670	1115537	1042163	36.1	3.73	85.07
1.535	beta hydroxy acids and derivatives	Glutarylcarnitine	3249201	943638	374031	38.1	1.97	93.08
2.732	beta hydroxy acids and derivatives	Pimelylcarnitine	1395219	378601	234880	38.1	3.16	94.31
2.801	beta hydroxy acids and derivatives	2-Hexenoylcarnitine	1033332	661562	461511	36.7	0.00	83.45
4.055	biotin and derivatives	Biotin	196481	48590	87292	38.6	1.05	94.33
2.976	Benzene and substituted derivatives	Telmisartan	3292203	5227101	997550	38.4	0.87	92.90
3.517	Benzene and substituted derivatives	Biphenyl	116618	95091	83644	38	-2.51	92.88
1.961	Benzene and substituted derivatives	Telmisartan	2770669	1920349	1288107	36.3	-2.06	84.00
1.333	Benzene and substituted derivatives	Telmisartan	405882	793020	341678	35.8	-1.43	80.93
2.987	Benzene and substituted derivatives	Telmisartan	2108946	4039484	924731	38.4	0.84	93.11
1.523	Benzene and substituted derivatives	Olmesartan	60240	67221	41977	36.9	-2.61	87.71
3.256	Fatty acyl / fatty acids	13:0(12Me,12Me)	56315	47502	34825	38.7	-1.90	95.74
5.152	Fatty acyl / fatty acids	19:0(11Me)	202082	169142	66995	38.7	-1.52	95.56
3.335	Fatty acyl / fatty acids	13:0(12Me,12Me)	88866	117968	20317	38.6	-1.99	95.42
1.326	Prenol lipids	Lamioside	2550488	1023127	296474	36.5	-0.24	82.83
1.348	Prenol lipids	Flakinin A	294914	340560	199218	38.9	0.71	95.45
1.759	Prenol lipids	Flakinin A	181236	181560	95072	38.2	3.19	94.62
1.355	Prenol lipids	Parthenin	383484	429056	131765	35.9	3.55	83.46
3.412	Steroid and derivatives	Estradiol dipropionate	241857	225967	146772	37.7	3.68	92.63
4.909	Prenol lipids	(-)-Jolkinol A	1077380	746410	200608	35.7	1.57	80.34
5.032	Prenol lipids	Helvolic acid	98458	92836	75930	38.1	0.86	91.77
3.267	Prenol lipids	7,8,7',8'-Tetradehydroastaxanthin	102179	127234	73536	37.4	-2.53	89.92
1.036	Carboxylic acid esters	Ethyl 2-(methyldithio)propionate	500126	230990	239649	37.1	-3.82	90.07
6.735	Prenol lipids / Carotenoid	Ketospirilloxanthin	810513	779805	340762	38.9	3.41	98.72

4.676	Benzene and substituted derivatives	3,4-Dihydroxyphenylvaleric acid	122128	89925	121494	38.7	-3.59	97.51
5.940	Sphingolipids	Cer(t18:0/16:0)	232618	478557	616898	38.7	1.91	95.78
5.937	Sphingolipids	Cer(d14:1/20:0)	97408	193225	233102	37.1	-3.80	89.76
6.575	Sphingolipids	Cer(d18:0/18:0(2OH))	113418	215777	263467	39	1.74	97.27
6.365	Sphingolipids	Cer(d18:1/17:0)	85716	171535	198737	37.2	-0.81	86.75
6.853	Sphingolipids	N-Stearoylsphingosine	21241	64683	139794	38.4	2.03	94.39
1.557	Polyketide / flavonoids	Antiarone J	147966	142416	58496	37.8	2.18	91.66
2.347	Steroid and derivatives	(25S)-5alpha-cholestan-3beta,6alpha,7beta,8beta,15alpha,16beta,26-heptol	412779	328937	215690	36	0.97	81.41
1.473	Polyketides / phenylpropanoids	(Z)-3-Phenyl-2-propenal	413888	472326	204880	38.9	3.95	98.98
1.406	Carbohydrate and derivatives	D-arabinonate	58483	61013	129265	37.8	1.33	90.55
2.412	coumaric acid and derivatives	Caffeoylmalic acid	189377	78985	77796	36.4	-0.65	82.99
0.919	Amino acids and derivatives	Coutaric acid	662028	695356	303358	37.6	1.90	90.39
7.658	Glycerolipids	DG(16:0/18:3(9Z,12Z,15Z)/0:0)[iso2]	93679	80816	62451	36.2	-1.42	82.89
7.224	Glycerolipids	DG(18:4(6Z,9Z,12Z,15Z)/18:1(9Z)/0:0)[iso2]	158582	22879	13271	36.4	-3.15	85.92
8.189	Glycerolipids	DG(14:1(9Z)/22:2(13Z,16Z)/0:0)[iso2]	57491	76360	42476	36.2	-2.63	83.93
0.539	Glycerophospholipids	PA(22:6(4Z,7Z,10Z,13Z,16Z,19Z)/20:5(5Z,8Z,11Z,14Z,17Z))	124697	84446	41961	36.4	-3.01	85.37
4.826	Glycerophospholipids	PG(14:0/18:1(11Z))	2296126	1110512	164909	39.3	-0.81	97.59
4.617	Glycerophospholipids	PG(17:2(9Z,12Z)/16:0)	543719	982938	4963	39.2	-0.80	96.89
4.903	Glycerophospholipids	PG(17:0/14:0)	59445	23290	17248	35.4	3.63	81.43
5.442	Glycerophospholipids	PG(20:5(5Z,8Z,11Z,14Z,17Z)/18:0)	1648506	62080	886	38.7	-2.72	96.56
0.919	Glycerophospholipids	PI(12:0/12:0)	528538	477348	176966	38.6	-2.88	96.60
1.003	Glycerophospholipids	PI(12:0/12:0)	729886	627079	207564	38.7	-2.84	96.62
5.538	Glycerophospholipids	PI(17:2(9Z,12Z)/0:0)	1161869	1101773	461972	36.8	0.93	85.29
7.028	dialkyldisulphides	1-(1-Propenylthio)propyl propyl disulfide	164724	91164	31836	36.6	3.20	86.94
3.057	dialkyldisulphides	1-(1-Propenylthio)propyl propyl disulfide	180660	66235	31434	36.6	1.32	84.48
3.553	dialkyldisulphides	1-(1-Propenylthio)propyl propyl disulfide	116376	69355	29469	36.6	1.46	84.55
5.995	Fatty acyl / fatty acids	Genipinic acid	185014	313099	81321	39.3	0.62	97.40
3.659	Fatty acyl / fatty acids	Tricosanedioic acid	241829	271028	123486	39.2	2.17	98.70
2.923	Amino acids and derivatives	Glutaminyl-Glutamate	1361025	801093	487240	35.4	-2.94	80.37
0.860	Amino acids and derivatives	Arginyl-Valine	898745	282843	157278	36.2	-0.31	81.60
1.216	Amino acids and derivatives	Asparaginyl-Proline	7532203	1828766	803791	37.8	2.96	92.39
1.497	Amino acids and derivatives	Asparaginyl-Proline	2761772	864666	485646	38.5	3.58	96.76
1.547	Amino acids and derivatives	Asparaginyl-Proline	2534112	623078	230418	38.1	3.32	94.53
0.761	Amino acids and derivatives	Glycyl-L-leucine	1132576	509418	159082	39.1	1.98	98.08
0.849	Amino acids and derivatives	Glycylproline	5753799	1529253	910895	38.2	1.42	92.89
4.810	Amino acids and derivatives	L,L-Cyclo(leucylprolyl)	1451937	337463	122871	39.5	1.25	98.87
2.827	Amino acids and derivatives	L-gamma-glutamyl-L-valine	9849748	1574082	746604	35.3	-3.02	80.30
1.326	Amino acids and derivatives	Prolyl-Alanine	2371106	1094396	363222	38.6	0.17	93.25
1.615	Amino acids and derivatives	Glycyl-Tyrosine	198720	55501	93546	38.3	-3.62	95.83
2.435	Amino acids and derivatives	Isoleucyl-Threonine	317499	115040	172978	39.4	0.77	98.14
4.942	Amino acids and derivatives	Leucyl-phenylalanine	81943	23346	43181	37.8	-2.97	92.46

2.424	Amino acids and derivatives	Glycyl-L-leucine	513106	127454	186342	39.4	1.99	99.52
3.491	Amino acids and derivatives	Glycyl-Methionine	1948659	1182549	1114255	38.4	-1.23	93.33
2.812	Amino acids and derivatives	Glycyl-Phenylalanine	1997007	641810	596635	36.6	2.18	85.41
0.956	Amino acids and derivatives	Hydroxyprolyl-Glutamine	14410530	2403676	1726306	37.3	2.21	88.93
1.947	Amino acids and derivatives	Hydroxyprolyl-Isoleucine	87253662	3158393	827904	38.8	2.75	97.16
1.459	Amino acids and derivatives	Isoleucyl-Lysine	2438209	506923	337969	39.4	1.01	98.23
2.591	Amino acids and derivatives	Prolyl-Tyrosine	97501772	5106059	2790906	36.1	2.67	83.66
2.321	Amino acids and derivatives	Trandolaprilat	127876	122384	60429	39	-0.22	95.04
1.086	Amino acids and derivatives	Glutaminyl-Proline	4791125	2279423	575978	37	0.11	84.99
0.677	Amino acids and derivatives	Asparaginyl-Hydroxyproline	406664	349747	285110	38.9	0.38	94.73
1.326	Amino acids and derivatives	Alanyl-Glutamine	1650433	954389	579714	37.1	1.75	87.60
0.651	Amino acids and derivatives	Glycyl-L-leucine	107811	324157	58149	38.5	2.62	95.65
2.070	Amino acids and derivatives	Asparaginyl-Isoleucine	1153349	2132096	1276979	38.7	1.89	95.94
2.976	Amino acids and derivatives	N5-Acetyl-N2-gamma-L-glutamyl-L-ornithine	5918868	1060604	399036	36.6	0.03	83.24
2.766	Amino acids and derivatives	N5-Acetyl-N2-gamma-L-glutamyl-L-ornithine	5634788	1164202	326463	36.1	1.71	82.69
3.224	Amino acids and derivatives	Isoleucyl-Valine	285700	102327	176313	39.4	1.53	98.88
2.207	Amino acids and derivatives	N5-Acetyl-N2-gamma-L-glutamyl-L-ornithine	2169527	229016	118393	37.5	-2.09	89.75
5.438	Glycerolipids	1-(14-methyl-pentadecanoyl)-2-(8-[3]-ladderane-octanyl)-sn-glycerol	4212872	173953	27644	39.1	1.72	97.45
1.707	Prenol lipids	16,17-Dihydro-16a,17-dihydroxygibberellin A4 17-glucoside	100697280	18799217	4103682	35.7	-3.35	82.55
4.823	Prenol lipids	Narasin	595146	61744	951	37.3	-3.97	91.27
0.767	Prenol lipids	Persicachrome	840735	911842	363173	35.8	2.59	82.07
4.356	Fatty acyls / Eicosanoids	LTE4	460102	302311	306953	37.1	3.95	90.05
5.948	Fatty acyls / Eicosanoids	Dichotellate A	95230	88154	70424	36.5	-0.97	83.88
3.404	Steroid and derivatives	Norselic acid C	99802	87748	55405	38.9	1.14	95.68
2.496	Benzene and substituted derivatives	Phenethyl 6-galloylglucoside	230915	150625	132659	37.2	-3.70	90.21
5.144	Fatty acyl / fatty acids	4Z,7Z,10Z,13Z,16Z,19Z,22Z,25Z-octacosaoctaenoic acid	4543137	3358620	2449444	39.5	-0.71	98.38
3.667	Fatty acyl / fatty acids	Palmitic acid	14542822	12907202	4659195	39.8	-0.36	99.48
3.160	Fatty acyl / fatty acids	cis-9-palmitoleic acid	898111	1017624	23314	39.2	-1.67	98.08
3.037	Fatty acyl / fatty acids	3R,5S-Dimethyldodecanoic acid	332418	315574	171985	38.9	-2.10	97.00
4.017	Fatty acyl / fatty acids	Heptadecanoic acid	1206823	1387117	1239398	39.8	-0.55	99.48
1.839	Fatty acyl / fatty esters	2-Methylacetophenone	185438	269508	129642	36.5	-2.40	85.33
2.648	Fatty acyl / fatty esters	3-hydroxy-cis-5-octenoylcarnitine	16069266	9707724	6875857	39.4	0.41	97.53
2.420	Fatty acyl / fatty esters	(7Z,10Z,13Z,16Z)-docosatetraenoyl carnitine	427143	460566	185658	37.6	1.61	90.11
0.554	Fatty acyl / fatty esters	3-hydroxy-cis-5-octenoylcarnitine	448068	950040	580084	37.8	3.76	93.61
4.518	Fatty acyl / fatty esters	Arachidyl carnitine	244289	208090	161975	39.4	1.54	98.71
5.255	Fatty acyl / fatty esters	O-behenoylcarnitine	132753	120775	97367	38.9	1.53	96.51
2.378	Fatty acyl / fatty esters	O-(17-carboxyheptadecanoyl) carnitine	244599	198276	114232	39.2	0.67	96.83
1.184	Fatty acyl / fatty esters	(9Z,12Z,15Z)-3-hydroxyoctadecatrienoylcarnitine	238704	239605	152641	39.5	0.73	98.36
4.244	Fatty acyl / fatty esters	Palmitoylcarnitine	1652358	1760730	1480903	38.7	2.01	96.07
0.855	Fatty acyl / fatty esters	(9Z)-3-hydroxydodecenoylcarnitine	26113	19193	27843	38.9	0.80	95.70
1.954	fatty acyl glycosides	Prenyl apiosyl-(1->6)-glucoside	1200392	593255	325979	38.3	0.10	91.80

2.945	fatty acyl glycosides	3-Methyl-3-butenyl apiosyl-(1->6)-glucoside	7074820	514113	153803	38.3	-0.18	91.75
2.923	fatty acyl glycosides	3-Methyl-3-butenyl apiosyl-(1->6)-glucoside	6757606	988967	348702	37.9	2.98	93.17
2.846	fatty acyl glycosides	3-Methyl-3-butenyl apiosyl-(1->6)-glucoside	1181402	647592	600703	37.5	-0.31	87.65
1.303	fatty acyl glycosides	1-(3-Methyl-2-butenoyl)-6-apiosylglucose	3479050	1759281	471646	37.9	-1.85	91.49
0.824	fatty acyl / fatty amides	N-(3-oxododecanoyl) homoserine lactone	151320	162380	106915	36.5	0.31	82.86
1.599	fatty acyl / fatty amides	N-(3-oxododecanoyl) homoserine lactone	85410	84682	49010	38	1.05	91.04
6.605	fatty acyl / fatty alcohol	phenolic phthiocerol	157249	343474	47636	38.1	1.76	92.70
4.354	fatty acyl / fatty aldehydes	4,10-undecadiynal	14537	35935	44866	38.3	3.87	96.15
5.373	fatty acyl / fatty alcohol	phenolic phthiocerol	5038422	140242	10120	39.3	2.26	99.08
7.708	fatty acyl / fatty alcohol	phenolic phthiocerol	363258	42469	26857	38.2	1.40	92.72
2.412	fatty acyl / fatty aldehydes	9Z,11E,13-Tetradecatrienal	451195	418285	487131	39.1	-2.92	98.88
5.156	fatty acyl / fatty amides	Docosanamide	75532	64614	49828	38.9	2.02	97.04
4.891	Fatty acyl / fatty esters	Mayolene-19	4595476	1465870	51037	39.2	1.97	98.54
7.213	Fatty acyl / fatty esters	Mayolene-19	304184	284395	33262	37.9	1.44	91.15
5.167	Fatty acyl / fatty esters	Mayolene-20	1321456	391493	29040	38.4	1.33	93.70
4.343	Fatty acyl / fatty esters	Mayolene-17	322891	386125	12244	39.1	1.56	97.37
6.076	Fatty acyl / fatty esters	Mayolene-19	620523	2505944	61302	39.3	1.99	98.96
6.377	Fatty acyl / fatty esters	Mayolene-20	125091	896028	23301	38.5	-0.46	93.29
1.432	Fatty acyl / fatty esters	3-hydroxy-cis-5-octenoylcarnitine	922127	1077237	569753	35.6	3.20	81.93
4.731	Polyketides / flavonoids	Laxiflorin	185260	292761	175894	39.5	0.81	98.69
6.609	Polyketides / flavonoids	Laxiflorin	150883	200299	165590	38.9	0.85	95.49
0.936	Polyketides / flavonoids	2',4',5,7-Tetramethoxy-8-methylflavanone	1956634	827472	625644	38.4	3.68	96.32
0.504	Polyketides / flavonoids	5,7-Dihydroxyflavone 7-benzoate	103640	111690	57082	38.2	2.79	94.12
8.979	Polyketides / flavonoids	Demethyltorosaflavone C	237032	183428	129403	38.1	-2.90	93.81
5.816	Polyketides / flavonoids	Demethyltorosaflavone D	1360775	1577672	1845888	38.7	0.72	94.41
1.958	Polyketides / flavonoids	Euchrenone a14	524432	476390	129442	36	-2.16	82.71
2.030	Polyketides / flavonoids	Epilumaflavanone B	1072128	4704935	274698	39	1.66	97.04
1.226	Polyketides / flavonoids	Prebarbigerone	198298	225211	104527	38.7	0.70	94.52
0.635	Polyketides / flavonoids	Galangin 5,7-dimethyl ether	504275	101079	75379	36.4	-1.00	83.29
3.780	Polyketides / flavonoids	Lonchocarpenin	550120	404346	208266	38.4	1.32	93.71
1.215	Polyketides / flavonoids	Heteroflavanone B	652413	749605	429651	39	0.30	95.61
3.517	Polyketides / flavonoids	Artocommunol CA	1190764	665709	393673	36.4	-0.63	82.89
1.470	Polyketides / flavonoids	Heteroflavanone B	87865	97465	52639	38.8	1.14	95.18
4.425	Polyketides / flavonoids	Isochamanetin	347310	241892	192519	36.6	-2.26	85.87
2.050	Polyketides / flavonoids	Quercetol B	89900	74320	38920	38.2	3.04	94.46
2.416	Benzene and substituted derivatives	Fluconazole	1690995	2031513	1066427	38.9	-2.86	97.92
1.355	furopyrans	Cyclocalopin F	571604	641434	284063	38.5	2.53	95.62
8.979	amino acid and derivatives	Avenic acid A	2328297	1988849	1461303	39.2	0.91	97.35
0.647	amino acid and derivatives	4-Guanidinobutanoic acid	752974	719460	593530	38.3	3.17	95.44
0.670	amino acid and derivatives	(S)-4-Amino-5-oxopentanoate	2447433	581858	262062	36	3.45	83.82
4.404	sugar acids and derivatives	Alginic acid	31394	30864	26320	36.9	-0.77	85.24

1.269	amino acid and derivatives	gamma-Glutamyl-beta-aminopropiononitrile	2152931	857173	410357	37.4	1.66	88.86
0.670	amino acid and derivatives	gamma-glutamyl-ethylamide	717213	374513	99426	37.8	-1.42	90.76
2.564	amino acid and derivatives	(2S,4S)-Pinnatanine	482353	82876	77813	36.7	1.95	85.67
6.609	Glycerophospholipids	PI(O-20:0/20:5(5Z,8Z,11Z,14Z,17Z))	243334	213377	183595	36.9	2.40	87.51
1.599	Glycerophospholipids	PI(13:0/12:0)	2902879	2439637	1250883	38.8	-1.91	96.49
4.537	Glycerophospholipids	PS(O-16:0/14:1(9Z))	16311	1546	5164	36.7	0.09	83.56
4.826	Glycerophospholipids	PS(P-16:0/16:1(9Z))	351015	214798	19856	39.2	0.31	96.61
4.268	Amino acids and derivatives	N-[(3a,5b,7b)-7-hydroxy-24-oxo-3-(sulfoxy)cholan-24-yl]-Glycine	1397010	1254134	252062	36.3	1.64	83.41
6.365	Glycerolipids	MGDG(18:2(9Z,12Z)/18:3(9Z,12Z,15Z))	10446010	201689	19850	39.3	-2.46	99.27
0.623	Alkaloids and derivatives	Flazine methyl ether	478811	227013	101907	36.2	-1.77	83.02
1.638	Benzene and substituted derivatives	4-Aminohippuric acid	1038459	286842	175138	39.1	0.11	95.77
0.651	Benzene and substituted derivatives	4-Aminohippuric acid	1044481	803572	307191	38.1	-3.68	94.93
1.033	Amino acids and derivatives	N-Ribosylhistidine	2924072	2575413	1345290	37.2	2.17	88.64
5.769	Prenol lipids/hopanoids	2-methylbacteriohopane-32,33,34,35-tetrol	194105	1955175	26025	38.9	2.20	97.29
5.369	Prenol lipids/hopanoids	bacteriohopane-,32,33,34-triol-35-cyclitol	768099	1704981	799151	39.2	1.88	98.29
4.366	Prenol lipids/hopanoids	adenosylhopane	106730	224861	258903	37.1	2.21	88.35
0.862	Hydroxycoumarin	Mammea E/BB	1960500	1620734	1142381	35.9	2.24	81.93
1.001	hypoxanthines	7-Methylguanine	1433187	1867948	91056	39	2.21	97.73
3.095	Benzene and substituted derivatives	Sulindac sulfide	293371	126641	76425	37.5	-0.45	88.15
6.887	Indoles	Cyclobrassinone	220978	161040	82817	37.6	-2.72	91.32
5.995	Indoles	Indoleacetic acid	245373	191355	650735	39.1	2.40	98.16
1.950	Amino acids and derivatives	5-Hydroxy-L-tryptophan	162084	126493	124226	38.8	-3.32	97.93
4.932	Indoles	2-Indolecarboxylic acid	174474	151868	263821	39	2.27	97.88
3.065	Indoles	2-Indolecarboxylic acid	502801	411149	185518	38.6	2.35	95.96
3.609	Indoles	1H-Indole-3-carboxaldehyde	881821	401379	268525	36.6	3.52	86.90
2.766	Indoles	Indoleacrylic acid	8811161	921434	285273	38.4	2.84	95.54
3.323	Amino acids and derivatives	5-Methoxytryptophan	1234015	514032	292288	37.5	2.00	90.04
9.533	Prenol lipids	Valdiate	606151	370475	190443	39.4	1.73	98.88
2.207	isocoumarans (antidepressant)	Citalopram aldehyde	866920	1040088	203635	37	2.27	87.48
3.837	Polyketides / flavonoids	Calopogoniumisoflavone A	134853	75107	76858	37.9	0.95	90.78
0.824	Amino acids and derivatives	N-Jasmonoylisoleucine	265650	264332	134721	37	1.24	86.58
4.362	Fatty acyl / octadecanoid	12-hydroxyjasmonic acid 12-O-beta-D-glucoside	956269	1001665	745546	36.7	1.08	84.74
1.473	Polyketides / phenylpropanoids	11-Hydroxy-12-methoxydihydrokawain	539275	616832	271526	38.5	2.60	95.73
1.306	Polyketides / phenylpropanoids	11-Hydroxy-12-methoxydihydrokawain	1082837	1206734	679712	37.2	3.57	90.34
3.190	Fatty acyl / eicosanoids	Lipoxin D4	635059	821883	1109650	36.1	3.93	84.96
1.698	Polyketides	10-Deoxymethymycin	206359	206892	94878	39.5	0.76	98.63
2.793	Fatty acyl / fatty acid	Dethiobiotin	3221168	1213637	948640	39.2	1.63	97.79
3.053	Glycerophospholipids	PA(12:0/0:0)	2361302	1613698	561662	37.1	-3.81	90.03
5.133	Glycerophospholipids	PA(14:0/18:1(9Z))	43680	185745	10837	37.5	-0.45	88.19
5.209	Glycerophospholipids	PA(16:0/18:2(9Z,12Z))	57097	366318	14185	36.3	-0.81	82.34
2.107	Glycerophospholipids	PA(22:6(4Z,7Z,10Z,13Z,16Z,19Z)/0:0)	211529	252527	136922	37.5	2.05	90.10

0.855	Glycerophospholipids	PC(8:0/0:0)	25932	28695	29579	36.9	-2.93	88.03
6.906	Carbohydrate and derivatives	Sedoheptulose 1,7-bisphosphate	37218	35874	35804	38.4	2.89	95.33
2.416	Fatty acyl / fatty amides	N-(4-benzenesulfonamide) arachidonoyl amine	1464560	1459388	879335	36.7	3.53	87.74
2.679	Fatty acyl / fatty amides	Pipericine	51578	33480	23105	37.9	1.80	91.61
2.793	Fatty acyl / fatty amides	N-(5-hydroxy-pentyl) arachidonoyl amine	112472	108753	71417	38.9	1.34	96.18
5.133	Fatty acyl / fatty amides	N-oleoyl glutamic acid	100653	122543	48656	37.5	3.88	92.08
3.503	Fatty acyl / fatty amides	N-stearoyl serine	2070128	2174954	1874509	39.2	2.73	99.24
0.864	Fatty acyl / fatty amides	N,N-diethyl-3-hydroxybut-2-enamide	640662	310068	160553	36.2	2.01	83.56
2.736	Fatty acyl / fatty amides	Anandamide (20:2, n-6)	59649	26358	25847	38.7	2.17	96.25
4.252	N-acyl pyrrolidines	N-(14-Methylhexadecanoyl)pyrrolidine	263016	273717	217050	38.6	3.43	97.06
2.808	Amino acids and derivatives	L-N-(1H-Indol-3-ylacetyl)aspartic acid	275303	183789	181825	38	-2.64	93.12
3.205	Amino acids and derivatives	Suberylglycine	927528	320209	256170	37.8	-0.13	89.19
3.719	Amino acids and derivatives	Methylhippuric acid	197110	96652	122008	38.4	-3.95	96.44
3.625	Amino acids and derivatives	Tricosanoylglycine	134902	126896	131287	39	1.69	96.98
4.457	Amino acids and derivatives	Pentacosanoylglycine	4529498	4609714	3812731	39	2.89	98.57
8.686	Amino acids and derivatives	N-Succinyl-L,L-2,6-diaminopimelate	115307	109172	80619	38.6	0.13	93.12
4.362	N-acyl-piperidines	Pipercitine	371755	389089	301366	39	2.99	98.31
3.766	N-acylpyrrolidines	N-Hexadecanoylpyrrolidine	187447	135904	101765	36.5	3.73	86.79
6.369	Sphingolipids	Cer(d18:0/h17:0)	169164	347668	399953	38.6	2.03	95.37
2.534	Fatty acyl / octadecanoids	12R-HOME(9E)	55320	48337	22983	37.1	-2.36	88.55
4.709	Fatty acyl / octadecanoids	7-keto-stearic acid	60487	64614	55616	37.5	3.66	91.66
1.832	Carbohydrates and derivatives	Acaciabiuronic acid	88906	55832	30430	38.7	-0.64	94.51
1.539	Carbohydrates and derivatives	1,2,10-Trihydroxydihydro-trans-linalyl oxide 7-O-beta-D-glucopyranoside	12531564	813866	241436	36.7	2.84	86.76
3.719	Carbohydrates and derivatives	1,2,10-Trihydroxydihydro-trans-linalyl oxide 7-O-beta-D-glucopyranoside	1152242	1126207	927350	38	-0.82	91.05
1.573	Carbohydrates and derivatives	1,2,10-Trihydroxydihydro-trans-linalyl oxide 7-O-beta-D-glucopyranoside	3657262	299118	206724	36.4	0.10	81.92
1.786	Carbohydrates and derivatives	1,2,10-Trihydroxydihydro-trans-linalyl oxide 7-O-beta-D-glucopyranoside	2958602	171584	116149	36.6	-1.25	84.34
2.923	Carbohydrates and derivatives	Benzyl beta-primeveroside	13334267	1214612	374899	37.4	-0.61	87.81
4.741	Carbohydrates and derivatives	Verbasoside	1324089	272221	129076	38.7	0.49	94.19
3.548	Carbohydrates and derivatives	2,4-Dihydroxy-7,8-dimethoxy-2H-1,4-benzoxazin-3(4H)-one 2-glucoside	66908	30148	21372	37.1	-0.05	85.57
5.275	Carbohydrates and derivatives	Phenethyl rutinoside	1141263	1791623	580640	35.8	-2.92	82.26
4.364	Carbohydrates and derivatives	2-[4-(3-Hydroxypropyl)-2-methoxyphenoxy]-1,3-propanediol 1-glucoside	717771	510606	761689	37.9	-3.02	93.31
0.609	Benzene and substituted derivatives	4R,5R,6S-Trihydroxy-2-hydroxymethyl-2-cyclohexen-1-one 6-(2-hydroxy-6-methylbenzoate)	122852	262300	28089	35.6	2.50	81.19
0.670	Amino acids and derivatives	Ophthalmic acid	900599	614596	652325	37.2	1.72	87.84
9.396	Amino acids and derivatives	Thyrotropin releasing hormone	1276625	963501	966017	39	-3.27	98.89
2.461	organosulfonic acids	Acrylic acid-2-acrylamido-2-methyl propane sulfonic acid copolymer	1905570	2970744	2634269	37.9	-3.82	93.94
6.205	other fatty acyls	N-(3-(hexadecanoyloxy)-heptadecanoyl)-L-ornithine	173984	434291	328996	38.9	0.97	95.74
1.793	Fatty acyl / fatty acid	12-oxo-5E,8E,10Z-heptadecatrienoic acid	59335	88004	53212	36.5	-1.88	84.91
5.793	Carbohydrates and derivatives	Imidazoleacetic acid ribotide	475091	319815	389281	38.4	-0.41	92.35
3.609	Carbohydrates and derivatives	2-Hydroxybenzaldehyde O-[xylosyl-(1->6)-glucoside]	409695	148338	106972	38.7	-1.51	95.51
2.500	Carbohydrates and derivatives	Ptelatoside A	1809298	753012	722061	38.8	-1.65	95.97
3.795	Benzene and substituted derivatives	Ethopropazine	202642	114846	54502	36.2	3.82	85.58

1.515	Benzene and substituted derivatives	Thioridazine	65127	73701	61857	37.3	3.90	90.96
1.355	Benzene and substituted derivatives	(4-Methylphenyl)acetaldehyde	137681	166597	84849	38.9	3.65	98.62
10.44	Benzene and substituted derivatives	Tropicamide	57379	63832	37954	37.1	-0.73	86.37
2.069	Benzene and substituted derivatives	Musanolone F	429489	172085	185763	38.7	-1.93	96.00
0.925	Benzene and substituted derivatives	Dopamine 4-sulfate	312641	311982	302840	35.2	-3.63	80.48
6.009	Glycerophospholipids	PC(12:0/17:1(9Z))	194453	196006	8810	38.9	0.34	94.69
5.571	Glycerophospholipids	PC(14:1(9Z)/14:0)	4097	8027	536	39.1	-0.84	96.64
6.005	Glycerophospholipids	PC(18:4(6Z,9Z,12Z,15Z)/13:0)	550584	637802	58756	38.7	-2.86	96.97
3.214	Glycerophospholipids	PC(11:0/11:0)	3920349	4525127	4033033	39	2.47	98.12
5.335	Glycerophospholipids	PC(12:0/15:1(9Z))	53371	108237	4652	38	0.36	90.36
5.674	Glycerophospholipids	PC(14:1(9Z)/14:0)	235827	1100673	10159	39.2	-0.31	96.19
5.765	Glycerophospholipids	PC(17:2(9Z,12Z)/13:0)	134032	1742724	15822	39	-0.42	95.41
6.076	Glycerophospholipids	PC(20:5(5Z,8Z,11Z,14Z,17Z)/13:0)	132719	633644	30906	38.9	-1.56	96.50
6.372	Glycerophospholipids	PC(17:2(9Z,12Z)/15:0)	11854	714048	0	38.2	-1.22	92.69
6.005	Glycerophospholipids	PE(18:1(11Z)/14:0)	2358465	2441589	135997	39.8	-0.48	99.58
5.453	Glycerophospholipids	PE(18:4(6Z,9Z,12Z,15Z)/16:1(9Z))	157021	347689	29308	38.1	-3.03	93.89
6.597	Glycerophospholipids	PE(16:0/18:1(11Z))	112208	227532	9639	37.5	-1.29	88.82
5.457	Glycerophospholipids	PE(16:1(9Z)/16:1(9Z))	291610	899482	21137	39.6	-0.61	98.84
6.327	Glycerophospholipids	PE(16:1(9Z)/17:0)	152475	1027422	4095	38.7	-0.98	94.93
6.654	Glycerophospholipids	PE(18:1(11Z)/18:1(11Z))	45048	273341	569	37.9	-1.46	91.47
6.075	Glycerophospholipids	PE(18:1(11Z)/16:1(9Z))	546520	2294822	32103	39.7	-0.61	99.40
6.495	Glycerophospholipids	PE(18:2(9Z,12Z)/21:0)	17379	65629	8743	37.1	-1.99	87.86
5.076	Glycerophospholipids	PG(16:0/16:0)	22508	1667	447	38.3	-1.05	92.71
1.618	Glycerophospholipids	PG(12:0/0:0)	235389	231756	81723	38.6	3.01	96.77
0.897	Glycerophospholipids	PG(16:0/0:0)	265391	232691	93590	36.7	3.54	87.82
5.369	Glycerophospholipids	PG(16:0/18:1(11Z))	12236350	380541	22547	39.8	-0.44	99.31
5.072	Glycerophospholipids	PG(16:1(9Z)/17:0)	2135152	630240	8906	39.4	-0.86	97.81
5.163	Glycerophospholipids	PG(17:0/18:2(9Z,12Z))	2571378	676633	449	39.5	-0.75	98.41
4.887	Glycerophospholipids	PG(18:1(11Z)/16:1(9Z))	8868764	1688789	45525	39.6	-0.63	98.84
5.434	Glycerophospholipids	PG(18:1(11Z)/18:1(11Z))	9743951	431150	3941	39.7	-0.55	98.95
5.369	Glycerophospholipids	PG(18:4(6Z,9Z,12Z,15Z)/18:0)	1959405	45283	552	38.5	-3.24	96.50
4.891	Glycerophospholipids	PG(20:5(5Z,8Z,11Z,14Z,17Z)/16:0)	1756615	484324	38790	37.2	-3.37	89.95
2.991	Glycerophospholipids	PG(22:2(13Z,16Z)/0:0)	409600	342596	166928	37	2.73	88.31
5.666	Glycerophospholipids	PG(18:1(11Z)/17:0)	746407	23289	5518	38.9	-1.12	95.84
1.222	Glycerophospholipids	PG(22:1(11Z)/0:0)	581753	479096	354962	39.1	-1.93	97.58
4.232	Glycerophospholipids	PG(14:0/16:1(9Z)	30054	38941	1994	37	-1.53	87.08
4.339	Glycerophospholipids	PG(16:1(9Z)/16:1(9Z))	368506	519356	13765	38.8	-0.90	95.21
0.638	Glycerophospholipids	PG(O-18:0/0:0)	237245	251823	120756	37.7	-1.42	90.21
5.006	Glycerophospholipids	PG(17:0/20:5(5Z,8Z,11Z,14Z,17Z))	506939	623536	552612	39	0.55	95.49
4.709	Glycerophospholipids	PG(18:3(6Z,9Z,12Z)/14:0)	1228753	1432225	1311023	39	-2.44	98.01
5.685	Glycerophospholipids	PG(12:0/17:0)	171447	182573	84782	36.1	3.98	84.95

4.529	Glycerophospholipids	PG(13:0/18:1(9Z))	124984	294123	7682	38.7	-1.02	94.91
4.442	Glycerophospholipids	PG(13:0/18:1(9Z))	4077	2924	0	38.5	-1.47	94.35
1.809	Glycerophospholipids	PG(22:1(11Z)/0:0)	1424062	1146165	740461	38.9	-1.55	96.52
0.817	polyclic hydrocarbon	Santene	187002	216254	106982	38.7	3.60	97.67
2.671	polyethylene glycols	Heptaethylene glycol	325364	278814	136366	38.3	2.30	94.16
2.705	polyethylene glycols	Hexaethylene glycol	382538	306912	178633	36.2	2.72	84.05
2.900	polyethylene glycols	Heptaethylene glycol	187002	164178	86448	38.4	2.41	94.74
1.561	Prenol lipids / sesquiterpenes	7'-hydroxyabscisic acid	149305	152920	93208	36.8	2.70	87.43
3.510	Amino acids and derivatives)	Ascorbalamic acid	421302	244768	187517	37.8	0.77	89.79
2.759	Fatty acyl / eicosanoids	2-glyceryl-PGD2	158853	165499	76705	36.3	-3.24	85.55
1.657	pteridines and derivatives	7-Hydroxy-6-methyl-8-ribityl lumazine	2580903	1318775	299808	37.3	-3.53	90.59
0.635	purine and derivatives	5'-n-propylthioadenosine	155807	103031	60578	35.6	-2.63	80.88
1.421	purine and derivatives	Adenosine	2801138	2795375	439567	35.5	3.04	80.85
0.757	purine and derivatives	Guanine	22425032	952598	1221981	39	2.21	97.73
1.440	purine and derivatives	Guanine	2019441	1672106	195075	39.1	1.83	97.57
2.347	Benzene and substituted derivatives	Morellinol	1138231	412997	133835	36.4	-3.40	85.90
2.359	Benzene and substituted derivatives	Morellinol	183503	169500	67955	39.5	1.00	98.69
3.079	Benzene and substituted derivatives	Morellin	2831899	2318412	606212	37.8	2.88	92.17
2.815	Benzene and substituted derivatives	Isomorellic acid	1094153	901138	329932	36.9	-0.24	84.63
2.861	Benzene and substituted derivatives	Morellinol	3678146	2323117	241445	37.5	2.22	90.17
2.034	Benzene and substituted derivatives	Isomorellic acid	1040727	1362547	211504	37.1	1.36	87.18
1.493	pyridines and derivatives	4-Pyridoxolactone	229721	166904	115580	36.2	-0.36	81.51
0.898	pyridines and derivatives	4-Pyridoxic acid	919336	1051973	354966	35.8	-3.53	83.00
2.070	pyridoxamine	Pyridoxamine	5306243	2881877	2217509	38.8	2.34	97.02
1.433	Pyrimidines and derivative	Zalcitabine	791992	261296	126038	39	-0.55	95.52
1.862	Pyrimidines and derivative	3'-Azido-3'-deoxy-5'- O-beta-D-glucopyranuronosylthymidine	284955	159585	142429	37.6	-1.92	90.29
3.727	Pyrimidines and derivative	Pentobarbital	14929240	3229363	627536	38.6	-2.27	95.73
3.803	Pyrimidines and derivative	Pentobarbital	9374814	1745502	179969	39.3	0.27	96.68
2.008	Pyrimidines and derivative	Aprobarbital	3095661	1233125	241936	37.1	2.89	88.94
3.171	Pyrimidines and derivative	Aprobarbital	1695058	428610	191527	37.8	1.62	90.74
1.330	Pyrimidines and derivative	Thymidine	4157030	2621008	1110376	36.6	2.18	85.48
1.001	pyrrolotriazines	3-Methylpyrrolo[1,2-a]pyrazine	386353	453898	240007	36.9	-1.12	86.01
8.979	Alcohols and polyols	Chlorogenoquinone	156297	127336	88946	37.9	3.77	94.01
3.065	quinoline and derivatives	Kynurenic acid	1023884	849065	488392	38	3.19	93.80
3.171	quinoline and derivatives	Rufloxacin	478041	229066	143935	38.2	-0.25	91.29
2.766	quinoline and derivatives	6-Methylquinoline	2325199	300551	98700	38.2	1.53	92.94
1.505	quinoline and derivatives	8-hydroxyquinoline	4938591	925292	408395	38.5	2.83	95.77
2.896	quinoline and derivatives	8-hydroxyquinoline	1373045	803247	553046	38.8	3.03	97.71
2.450	quinoline and derivatives	8-hydroxyquinoline	731690	329747	354985	37.8	3.31	93.07
1.360	quinoline and derivatives	8-hydroxyquinoline	2936202	787063	526402	38.1	2.99	93.97
4.067	quinoline and derivatives	8-hydroxyquinoline	749534	505951	681715	38.4	3.06	95.59

9.571	Benzene and substituted derivatives	Hexylresorcinol	826259	716838	281804	39.4	1.64	99.07
3.614	Retenoid	Etretinate	124703	111849	57795	38.6	1.80	94.95
9.396	Polyketides / flavonoids	12a-Hydroxyisomillettone	604672	428653	411115	36.8	3.77	88.55
4.385	Fatty acyl / fatty acids	Stearic acid	15125963	15347948	5519662	39.9	0.10	99.37
2.831	Prenol lipids / sesquiterpenoids	S-Furanopetasitin	5844263	968555	293932	36.8	-3.24	87.61
1.866	Prenol lipids / sesquiterpenoids	Armillaricin	535286	488169	242442	39.5	0.61	98.17
5.144	Prenol lipids / Sesterpenoids	3-Hydroxy-10'-apo-b,y-carotenal	145816	109639	65402	37.6	-2.51	91.06
5.145	Prenol lipids / Sesterpenoids	3-Hydroxy-10'-apo-b,y-carotenal	185777	208525	143260	39.3	1.76	98.82
10.16	Sphingolipids	Sphinganine	618334	348951	179880	39.3	0.03	96.50
2.374	Sphingolipids	Penaresidin A	2013897	2229406	1938341	38.5	3.05	95.89
9.286	Sphingolipids	C16 Sphinganine	4341574	2595226	1327818	39.5	0.98	98.78
4.320	Sphingolipids	N-(hexadecanoyl)-deoxysphing-4-enine-1-sulfonate	43885	53141	55141	36.7	-0.48	84.30
0.538	Sphingolipids	LacCer(d18:1/20:0)	146241	178615	117352	32.9	0.45	64.91
1.352	Steroid and derivatives	Eplerenone	30349271	34477175	14683801	39.1	1.65	97.53
3.243	Steroid and derivatives	Dehydroepiandrosterone sulfate	572590	201752	134744	36.3	2.57	84.50
4.235	Steroid and derivatives	(6RS)-22-oxo-23,24,25,26,27-pentanorcholecalciferol 6,19-sulfur dioxide adduct	1672979	1201808	358931	38.2	-0.71	91.65
0.946	Steroid and derivatives	(25R)-26,26,26-trifluoro-1alpha,25-dihydroxyvitamin D3	867894	832898	389428	39.1	-2.45	98.41
5.925	Fatty acyl / fatty acids	Behenic acid	42259	35148	10297	37.1	-2.20	87.97
1.348	Benzene and substituted derivatives	Styrene	233731	243370	130195	38	2.56	92.84
1.881	sugar acids and derivatives	3-Deoxy-D-manno-octulosonate	200345	193577	134978	37.7	-0.31	88.97
0.918	sulfoxides (organosulfur)	Camelinin	2787182	1369484	701472	38.1	0.03	90.32
7.035	sulfoxides (organosulfur)	(Z)-[3-(Methylsulfinyl)-1-propenyl] 2-propenyl disulfide	174438	65731	19466	38	3.26	93.72
0.723	sulfoxides (organosulfur)	(Z)-[3-(Methylsulfinyl)-1-propenyl] 2-propenyl disulfide	68789	91326	94370	36.6	-0.13	82.98
2.382	Prenol lipids	(-)-trans-Carveol glucoside	195164	152723	97320	36.9	2.86	87.74
1.352	tetrahydroisoquinolines	1,2,3,4-Tetrahydroisoquinoline	280530	323881	109133	39	3.43	99.07
2.728	Tetrapyrroles and derivatives	Mono(glucosyluronic acid)bilirubin	804249	522404	239256	35.1	3.97	80.20
5.449	Prenol lipids	gamma-tocotrienol	794236	674731	513395	39.5	-1.34	99.20
1.840	Prenol lipids	15-Acetoxyscirpene-3,4-diol 4-O-a-D-glucopyranoside	1827330	6050962	514198	36.4	-2.91	85.45
6.689	Glycerolipids	TG(18:4(6Z,9Z,12Z,15Z)/18:4(6Z,9Z,12Z,15Z)/18:4(6Z,9Z,12Z,15Z))	263613	503851	406422	37.1	-2.13	88.09
0.681	Amino acids and derivatives	Glycylprolylhydroxyproline	42572219	4789122	322314	38.3	-2.90	95.15
1.008	Amino acids and derivatives	Glycylprolylhydroxyproline	66029495	7509071	1972658	38.9	-2.33	97.07
4.731	Prenol lipids	Lucidenic acid D1	172946	279888	164676	39.5	0.60	98.30
6.609	Prenol lipids	Lucidenic acid D1	99249	137250	115430	38.7	0.67	94.17
0.706	Indoles	Tryptamine	935311	393382	478562	37.4	3.32	90.95
3.758	Fatty acyl / fatty acids	Oleic acid	3153888	886103	45180	39.2	-1.19	97.48
3.438	Fatty acyl / fatty acids	9-heptadecylenic acid	327802	693099	5937	39.6	-1.03	99.31
4.709	Fatty acyl / fatty acids	7,12-octadecadiynoic acid	67015	155987	145600	39.2	2.67	98.93
4.994	Fatty acyl / fatty acids	7,11-octadecadiynoic acid	91879	101523	96148	38.8	2.04	96.39
5.312	Fatty acyl / fatty acids	17Z-octadecenoic acid	66077	54663	45133	37.7	3.81	93.20
3.397	Steroid and derivatives	(23S)-1alpha-hydroxy-25,27-didehydrovitamin D3 26,23-lactone	71483	62845	52411	36.5	1.56	84.43
7.094	Fatty acid / fatty esters	Behenyl linoleate	275319	383363	378176	36.5	-3.79	86.69

2.930	Steroid and derivatives	Physalolactone	1840569	1298784	487457	36	2.83	83.59
Day 158								
RT (min)	**Chemical class**	**Suggested compound**	**A1**	**A4**	**A8**	**Score**	**Mass Error (ppm)**	**Isotope Similarity**
1.473	Prenol lipids	Vomitoxin	510571	315624	184465	38.6	2.49	96.05
1.275	Prenol lipids	Vomitoxin	1014271	725797	474083	38.6	2.86	96.24
8.100	Polyketides / Phenylpropanoids	Hydrocinnamic acid	98515	69572	82813	38.8	3.53	98.27
1.637	(unclassified)	5'-(dimethylsulfonio)-5'-deoxyadenosine	115761	80465	31153	38.8	1.68	96.19
3.235	(unclassified)	Distichonic acid A	44912	39279	19620	36.3	0.26	81.93
3.403	(unclassified)	amiclenomycin	562741	318316	130658	39.3	1.76	98.62
1.493	(unclassified)	Choline bitartrate	363734	263868	176233	36.4	-2.52	85.24
6.609	Glycerophospholipids	PI(O-16:0/20:5(5Z,8Z,11Z,14Z,17Z))	204915	216339	248480	38.1	2.30	93.19
2.031	Amino acids and derivatives	N-benzylglycine	475798	129400	118236	37.2	3.25	90.04
12.00	Polyketides / phenylpropanoids	2'-Hydroxy-4',6'-dimethoxy-3'-methyldihydrochalcone	8636666	8700155	8742115	38.8	-3.58	98.26
3.214	Glycerolipids	MG(0:0/22:2(13Z,16Z)/0:0)	54904	52805	55222	39.2	0.93	97.19
2.043	Polyketides / phenylpropanoids	(S)-(E)-2'-(3,6-Dimethyl-2-heptenyl)-3',4',7-trihydroxyflavanone	808167	719174	512139	38.6	0.86	94.18
9.251	Indoles	Alkaloid AQC2	157478	128087	142769	37.5	2.93	90.76
0.710	Indoles	Indole-3-carbinol	996200	339458	426027	38.3	3.11	95.19
2.873	Polyketides / flavonoids	7-Chloro-3,4',5,6,8-pentamethoxyflavone	221085	137419	102713	37.9	1.41	91.01
0.798	Benzene and substituted derivatives	N-Acetylprocainamide	251851	199394	87129	38.5	2.32	95.28
0.799	Amino acids and derivatives	(S)-N-(4,5-Dihydro-1-methyl-4-oxo-1H-imidazol-2-yl)alanine	1006341	747404	660219	38.1	1.41	92.30
2.290	Alcohols and polyols	Pantothenic acid	170676	83635	80858	35.9	0.93	80.45
0.647	Alcohols and polyols	D-4-O-Methyl-myo-inositol	40868	79871	23804	37.5	-0.87	88.32
3.495	Alkaloids and derivatives	SN-38	253786	195230	192458	36.3	0.93	82.56
7.662	Glycerolipids	DG(P-14:0/18:1(9Z))	91128	83171	76786	37.4	1.51	88.58
1.330	Benzene and substituted derivatives	Hydroxykynurenine	404580	400493	243764	38.5	0.43	93.13
1.386	Benzene and substituted derivatives	N'-Formylkynurenine	235451	142109	70731	36.6	-2.97	86.30
1.806	Purine and derivatives	1-ethyladenine	725663	323157	18071	38.9	1.70	96.38
1.505	Benzene and substituted derivatives	N'-Formylkynurenine	346883	278032	150632	38.3	2.90	94.84
1.607	Benzene and substituted derivatives	fluorobenzoylpropionic acid	70126	38332	28947	38.8	1.13	95.22
3.025	Amino acids and derivatives	L-cis-Cyclo(aspartylphenylalanyl)	73489	35815	17861	36.7	-0.67	84.41
3.605	Amino acids and derivatives	L-cis-Cyclo(aspartylphenylalanyl)	119753	81529	39531	38.5	0.07	92.59
3.193	Amino acids and derivatives	L-cis-Cyclo(aspartylphenylalanyl)	97827	74732	50614	35.6	-3.32	81.70
3.084	Amino acids and derivatives	Levetiracetam	84257	45579	34810	39.5	1.74	99.39
0.952	Aldehyde	1-(3-Aminopropyl)-4-aminobutanal	22165	35096	1319	39.2	2.83	99.14
1.448	Amino acids and derivatives	Descarbonyl-lacosamide	208926	254904	155603	38.7	1.31	94.95
2.259	amines (alkyldiarylamines)	Isothipendyl	92463	151134	38511	38.1	0.89	91.62
4.661	Amino acids and derivatives	L,L-Cyclo(leucylprolyl)	192272	136092	50035	39.6	1.34	99.83
3.339	Amino acids and derivatives	L-Tryptophan	108763	94395	43687	39	1.95	97.19
2.500	Amino acids and derivatives	N-Acetylglutamine	120645	123598	52611	38.7	1.86	95.72

0.666	Amino acids and derivatives	N-Acetylhistidine	124700	187093	76150	39.4	0.81	98.06
0.856	Amino acids and derivatives	N-(1-Deoxy-1-fructosyl)valine	146145	117484	91114	38.5	0.83	93.39
2.188	Amino acids and derivatives	4-Aminobenzoyl-(beta)-alanine	72391	56006	37913	38.3	1.57	93.44
2.077	Amino acids and derivatives	Tyrosinamide	84972	69586	40169	35.9	2.00	82.14
0.834	Amino acids and derivatives	N-Carbamoyl-2-amino-2-(4-hydroxyphenyl)acetic acid	95514	98954	79303	39.6	0.27	98.28
1.003	Amino acids and derivatives	Coutaric acid	326658	120308	54677	37.8	1.28	90.38
0.811	Amino acids and derivatives	N-a-Acetyl-L-arginine	1968326	2330189	164501	38.7	0.33	93.87
1.238	Amino acids and derivatives	11-amino-undecanoic acid	4673206	3532131	5756222	39	2.49	98.14
3.254	Alcohols and polyols	Paromomycin	109093	111431	148121	35.5	2.31	80.15
1.001	Alcohols and polyols	Voglibose	195382	169905	149976	38.2	-3.78	95.32
1.037	Purine and derivatives	N1-methyladenine	431850	170093	32660	38.2	2.55	94.16
11.99	Benzene and substituted derivatives	Methamphetamine	95886	101833	99522	36.4	0.33	82.27
4.827	annonaceous acetogenins	Cohibin A	764960	88239	15217	38.6	1.72	95.26
7.132	annonaceous acetogenins	Cohibin A	120845	121594	47699	38.5	1.86	94.73
6.005	annonaceous acetogenins	Cohibin A	688095	143936	49570	38.9	2.15	97.05
1.729	Benzene and substituted derivatives	Sennidin C	64770	66816	30948	36.6	2.25	85.74
2.222	Aralkylamines / amines	Porphobilinogen	289199	112888	93261	38.1	2.91	93.72
2.031	Aralkylamines / amines	Porphobilinogen	75339	66477	35255	38.6	2.44	95.86
0.689	Benzene and substituted derivatives	S-2,5-Dimethyl-3-furanyl 3-methylbutanethioate	170399	147249	128377	38.3	-0.13	91.62
3.803	Pyrimidines and derivatives	Amobarbital	119235	228755	84762	39.3	0.27	96.68
1.863	Pyrimidines and derivatives	Aprobarbital	224093	154818	123857	38.3	2.36	94.18
1.985	Pyrimidines and derivatives	Metharbital	168206	117854	75229	37.1	2.50	88.44
10.01	Benzene and substituted derivatives	1,3,5-Triphenylcyclohexane	70555	53292	36268	37.3	-2.33	89.17
3.110	Benzene and substituted derivatives	4-phenylbutanic acid-O-sulphate	29737	33708	15312	38.4	-1.72	94.31
1.196	Benzene and substituted derivatives	N-Acetylarylamine	675176	89839	109488	38.1	3.33	94.23
3.006	Benzene and substituted derivatives	5-Phenyl-1,3-oxazinane-2,4-dione	986270	1035782	28469	39.1	1.73	97.63
3.065	Benzene and substituted derivatives	1-Nitronaphthalene-5,6-oxide	1035725	745051	537961	38	3.19	93.80
9.396	Benzene and substituted derivatives	Procarbazine	345069	472428	417089	38.7	0.86	94.57
0.710	Benzene and substituted derivatives	Acidissiminol epoxide	1936654	906707	42548	35.9	-1.00	80.78
2.937	Benzene and substituted derivatives	Udenafil	463140	1684456	193809	36.9	1.14	85.92
1.505	Benzene and substituted derivatives	Sildenafil	482421	1162831	179347	38.5	2.89	96.06
1.740	Benzene and substituted derivatives	N-Undecylbenzenesulfonic acid	1805610	879536	653342	38.8	-1.80	96.18
0.677	Benzene and substituted derivatives	Tiapride	43353	52713	28292	38.1	-0.25	90.76
2.591	Benzene and substituted derivatives	N1-(alpha-D-ribosyl)-5,6-dimethyl-benzimidazole	1639651	874587	981285	36.1	2.67	83.66
0.737	Benzene and substituted derivatives	Dimethylbenzimidazole	264803	300853	36441	39	2.73	98.03
2.758	Benzene and substituted derivatives	Desloratadine	913040	706127	687634	36.1	3.73	85.07
1.535	beta hydroxy acids and derivatives	Glutarylcarnitine	441497	159374	121154	38.1	1.97	93.08
2.732	beta hydroxy acids and derivatives	Pimelylcarnitine	84341	83847	58559	38.1	3.16	94.31
2.801	beta hydroxy acids and derivatives	2-Hexenoylcarnitine	127055	95878	164829	36.7	0.00	83.45
4.055	biotin and derivatives	Biotin	42955	31180	56243	38.6	1.05	94.33
2.976	Benzene and substituted derivatives	Telmisartan	253604	217353	153745	38.4	0.87	92.90

1.961	Benzene and substituted derivatives	Telmisartan	286759	334838	226441	36.3	-2.06	84.00
1.333	Benzene and substituted derivatives	Telmisartan	45618	73807	59130	35.8	-1.43	80.93
2.987	Benzene and substituted derivatives	Telmisartan	192985	171806	97417	38.4	0.84	93.11
1.523	Benzene and substituted derivatives	Olmesartan	70563	41679	12907	36.9	-2.61	87.71
3.517	Benzene and substituted derivatives	Biphenyl	72986	72347	65372	38	-2.51	92.88
3.335	Fatty acyl / fatty acids	13:0(12Me,12Me)	145656	17092	28697	38.6	-1.99	95.42
3.256	Fatty acyl / fatty acids	13:0(12Me,12Me)	103186	27078	32836	38.7	-1.90	95.74
5.152	Fatty acyl / fatty acids	19:0(11Me)	134862	55461	70651	38.7	-1.52	95.56
1.326	Prenol lipids	Lamioside	169646	224964	89964	36.5	-0.24	82.83
1.348	Prenol lipids	Flakinin A	259083	145307	162056	38.9	0.71	95.45
1.759	Prenol lipids	Flakinin A	139397	99627	65275	38.2	3.19	94.62
1.355	Prenol lipids	Parthenin	213928	85763	111638	35.9	3.55	83.46
3.412	Steroid and derivatives	Estradiol dipropionate	172857	175227	177883	37.7	3.68	92.63
4.909	Prenol lipids	(-)-Jolkinol A	145530	112601	147144	35.7	1.57	80.34
5.032	Prenol lipids	Helvolic acid	84280	80444	92110	38.1	0.86	91.77
3.267	Prenol lipids	7,8,7',8'-Tetradehydroastaxanthin	134652	91025	59183	37.4	-2.53	89.92
5.352	Benzene and substituted derivatives	Etomidate	26736	25326	16371	37.7	-2.51	91.25
1.036	Carboxylic acid esters	Ethyl 2-(methyldithio)propionate	1041087	283981	46919	37.1	-3.82	90.07
6.735	Prenol lipids / carotenoid	Ketospirilloxanthin	498411	292528	502931	38.9	3.41	98.72
4.676	Benzene and substituted derivatives	3,4-Dihydroxyphenylvaleric acid	102806	84240	43752	38.7	-3.59	97.51
5.940	Sphingolipids	Cer(t18:0/16:0)	822826	190609	127011	38.7	1.91	95.78
5.937	Sphingolipids	Cer(d14:1/20:0)	380066	62918	23917	37.1	-3.80	89.76
6.575	Sphingolipids	Cer(d18:0/18:0(2OH))	363596	76021	28189	39	1.74	97.27
6.365	Sphingolipids	Cer(d18:1/17:0)	280378	68332	26246	37.2	-0.81	86.75
6.853	Sphingolipids	N-Stearoylsphingosine	303397	149794	99572	38.4	2.03	94.39
1.557	Polyketides / flavonoids	Antiarone J	94834	52771	29475	37.8	2.18	91.66
2.347	Steroid and derivatives	(25S)-5alpha-cholestan-3beta,6alpha,7beta,8beta,15alpha,16beta,26-heptol	284696	211164	130571	36	0.97	81.41
1.473	Polyketides / phenylpropanoids	(Z)-3-Phenyl-2-propenal	297520	154464	75424	38.9	3.95	98.98
1.406	Carbohydrate and derivatives	D-arabinonate	197548	66384	73368	37.8	1.33	90.55
2.412	coumaric acid and derivatives	Caffeoylmalic acid	94313	82353	47372	36.4	-0.65	82.99
0.919	Amino acids and derivatives	Coutaric acid	386079	132795	71812	37.6	1.90	90.39
7.658	Glycerolipids	DG(16:0/18:3(9Z,12Z,15Z)/0:0)[iso2]	75355	67591	67283	36.2	-1.42	82.89
7.224	Glycerolipids	DG(18:4(6Z,9Z,12Z,15Z)/18:1(9Z)/0:0)[iso2]	74312	109720	8356	36.4	-3.15	85.92
8.189	Glycerolipids	DG(14:1(9Z)/22:2(13Z,16Z)/0:0)[iso2]	71365	41007	41201	36.2	-2.63	83.93
0.539	Glycerophospholipids	PA(22:6(4Z,7Z,10Z,13Z,16Z,19Z)/20:5(5Z,8Z,11Z,14Z,17Z))	85456	40191	20030	36.4	-3.01	85.37
4.826	Glycerophospholipids	PG(14:0/18:1(11Z))	983087	116581	8603	39.3	-0.81	97.59
4.617	Glycerophospholipids	PG(17:2(9Z,12Z)/16:0)	362698	89099	0	39.2	-0.80	96.89
5.442	Glycerophospholipids	PG(20:5(5Z,8Z,11Z,14Z,17Z)/18:0)	1047625	122379	1864	38.7	-2.72	96.56
4.903	Glycerophospholipids	PG(17:0/14:0)	109395	7474	0	35.4	3.63	81.43
0.919	Glycerophospholipids	PI(12:0/12:0)	254848	74484	14989	38.6	-2.88	96.60
5.538	Glycerophospholipids	PI(17:2(9Z,12Z)/0:0)	255722	138934	135280	36.8	0.93	85.29

1.003	Glycerophospholipids	PI(12:0/12:0)	298049	85601	31299	38.7	-2.84	96.62
3.057	dialkyldisulphides	1-(1-Propenylthio)propyl propyl disulfide	3989	59359	2307	36.6	1.32	84.48
3.553	dialkyldisulphides	1-(1-Propenylthio)propyl propyl disulfide	3307	61246	2320	36.6	1.46	84.55
7.028	dialkyldisulphides	1-(1-Propenylthio)propyl propyl disulfide	15564	141930	350	36.6	3.20	86.94
0.681	Amino acids and derivatives	6-diazo-5-oxo-L-norleucine	430304	393557	273567	39	2.63	98.01
5.995	Fatty acyl / fatty acids	Genipinic acid	954153	314858	45891	39.3	0.62	97.40
3.659	Fatty acyl / fatty acids	Tricosanedioic acid	229812	130889	115865	39.2	2.17	98.70
3.491	Amino acids and derivatives	Glycyl-Methionine	1161942	990116	1011364	38.4	-1.23	93.33
1.459	Amino acids and derivatives	Isoleucyl-Lysine	374383	37974	67224	39.4	1.01	98.23
1.326	Amino acids and derivatives	Alanyl-Glutamine	1018712	459343	405952	37.1	1.75	87.60
0.860	Amino acids and derivatives	Arginyl-Valine	372183	55582	57798	36.2	-0.31	81.60
1.547	Amino acids and derivatives	Asparaginyl-Proline	517655	337215	148293	38.1	3.32	94.53
2.424	Amino acids and derivatives	Glycyl-L-leucine	139201	24383	69819	39.4	1.99	99.52
2.812	Amino acids and derivatives	Glycyl-Phenylalanine	258016	112844	188794	36.6	2.18	85.41
1.615	Amino acids and derivatives	Glycyl-Tyrosine	64892	19113	22628	38.3	-3.62	95.83
2.435	Amino acids and derivatives	Isoleucyl-Threonine	466491	27861	41753	39.4	0.77	98.14
4.942	Amino acids and derivatives	Leucyl-phenylalanine	62405	16311	10602	37.8	-2.97	92.46
2.664	Amino acids and derivatives	L-gamma-glutamyl-L-valine	979163	464600	391958	35.6	-0.59	78.73
1.733	Amino acids and derivatives	Alanyl-Tyrosine	890121	409011	244634	35	-3.64	79.11
0.677	Amino acids and derivatives	Asparaginyl-Hydroxyproline	343533	250518	247666	38.9	0.38	94.73
2.070	Amino acids and derivatives	Asparaginyl-Isoleucine	1603100	1011346	764020	38.7	1.89	95.94
2.923	Amino acids and derivatives	Glutaminyl-Glutamate	586697	341522	176577	35.4	-2.94	80.37
2.321	Amino acids and derivatives	Trandolaprilat	106848	55491	41177	39	-0.22	95.04
1.216	Amino acids and derivatives	Asparaginyl-Proline	355804	384334	162750	37.8	2.96	92.39
1.497	Amino acids and derivatives	Asparaginyl-Proline	687938	464290	326923	38.5	3.58	96.76
3.330	Amino acids and derivatives	Aspartyl-Tryptophan	30333	19570	15124	36.7	-3.85	88.14
0.651	Amino acids and derivatives	Glycyl-L-leucine	68567	112503	42957	38.5	2.62	95.65
0.956	Amino acids and derivatives	Hydroxyprolyl-Glutamine	911855	1015673	559495	37.3	2.21	88.93
1.947	Amino acids and derivatives	Hydroxyprolyl-Isoleucine	552744	257562	209954	38.8	2.75	97.16
4.810	Amino acids and derivatives	L,L-Cyclo(leucylprolyl)	51348	62827	22299	39.5	1.25	98.87
1.326	Amino acids and derivatives	Prolyl-Alanine	152173	112447	130291	38.6	0.17	93.25
1.086	Amino acids and derivatives	Glutaminyl-Proline	263852	237147	219135	37	0.11	84.99
0.761	Amino acids and derivatives	Glycyl-L-leucine	221720	204681	152788	39.1	1.98	98.08
0.849	Amino acids and derivatives	Glycylproline	514594	534341	291915	38.2	1.42	92.89
2.827	Amino acids and derivatives	L-gamma-glutamyl-L-valine	570709	433993	299734	35.3	-3.02	80.30
2.976	Amino acids and derivatives	N5-Acetyl-N2-gamma-L-glutamyl-L-ornithine	164966	130485	102066	36.6	0.03	83.24
2.766	Amino acids and derivatives	N5-Acetyl-N2-gamma-L-glutamyl-L-ornithine	162172	140270	103722	36.1	1.71	82.69
3.224	Amino acids and derivatives	Isoleucyl-Valine	710078	43189	44623	39.4	1.53	98.88
2.207	Amino acids and derivatives	N5-Acetyl-N2-gamma-L-glutamyl-L-ornithine	110530	61734	54939	37.5	-2.09	89.75
5.438	Glycerolipid	1-(14-methyl-pentadecanoyl)-2-(8-[3]-ladderane-octanyl)-sn-glycerol	3449814	324748	12009	39.1	1.72	97.45
1.707	Prenol lipids	16,17-Dihydro-16a,17-dihydroxygibberellin A4 17-glucoside	894597	823560	572999	35.7	-3.35	82.55

4.823	Prenol lipids	Narasin	513783	22029	895	37.3	-3.97	91.27
0.767	Prenol lipids	Persicachrome	482240	156772	89350	35.8	2.59	82.07
4.356	Fatty acyl /Eicosanoids	LTE4	69746	166789	101495	37.1	3.95	90.05
5.948	Fatty acyl /Eicosanoids	Dichotellate A	68903	74836	64123	36.5	-0.97	83.88
3.404	Steroid and derivatives	Norselic acid C	76165	61939	56155	38.9	1.14	95.68
3.160	Fatty acyl / fatty acid	cis-9-palmitoleic acid	832648	67322	23680	39.2	-1.67	98.08
5.144	Fatty acyl / fatty acid	4Z,7Z,10Z,13Z,16Z,19Z,22Z,25Z-octacosaoctaenoic acid	2452858	2347445	1776875	39.5	-0.71	98.38
3.667	Fatty acyl / fatty acid	Palmitic acid	7675961	3737985	4905951	39.8	-0.36	99.48
3.037	Fatty acyl / fatty acid	3R,5S-Dimethyldodecanoic acid	278244	154590	190201	38.9	-2.10	97.00
4.017	Fatty acyl / fatty acid	Heptadecanoic acid	1185389	1191527	1058986	39.8	-0.55	99.48
1.839	Fatty acyl / fatty esters	2-Methylacetophenone	212789	109446	101210	36.5	-2.40	85.33
3.068	fatty acyl / eicosanoids	leukotriene F4	708936	366202	160043	34.5	2.23	75.05
2.420	Fatty acyl / fatty esters	(7Z,10Z,13Z,16Z)-docosatetraenoylcarnitine	206114	117716	97423	37.6	1.61	90.11
0.554	Fatty acyl / fatty esters	3-hydroxy-cis-5-octenoylcarnitine	812453	378489	303569	37.8	3.76	93.61
2.648	Fatty acyl / fatty esters	3-hydroxy-cis-5-octenoylcarnitine	2412025	1989707	3268702	39.4	0.41	97.53
4.518	Fatty acyl / fatty esters	Arachidyl carnitine	170990	181361	149798	39.4	1.54	98.71
5.255	Fatty acyl / fatty esters	O-behenoylcarnitine	116066	107590	89921	38.9	1.53	96.51
2.378	Fatty acyl / fatty esters	O-(17-carboxyheptadecanoyl)carnitine	171926	122890	91831	39.2	0.67	96.83
1.184	Fatty acyl / fatty esters	(9Z,12Z,15Z)-3-hydroxyoctadecatrienoylcarnitine	184938	154273	99204	39.5	0.73	98.36
4.244	Fatty acyl / fatty esters	Palmitoylcarnitine	1601210	1583378	1581924	38.7	2.01	96.07
0.855	Fatty acyl / fatty esters	(9Z)-3-hydroxydodecenoylcarnitine	24666	47411	48437	38.9	0.80	95.70
1.954	fatty acyl glycosides	Prenyl apiosyl-(1->6)-glucoside	223598	212378	92024	38.3	0.10	91.80
2.846	fatty acyl glycosides	3-Methyl-3-butenyl apiosyl-(1->6)-glucoside	871155	420010	460159	37.5	-0.31	87.65
2.945	fatty acyl glycosides	3-Methyl-3-butenyl apiosyl-(1->6)-glucoside	170849	94977	77441	38.3	-0.18	91.75
1.303	fatty acyl glycosides	1-(3-Methyl-2-butenoyl)-6-apiosylglucose	186080	132822	106776	37.9	-1.85	91.49
2.923	fatty acyl glycosides	3-Methyl-3-butenyl apiosyl-(1->6)-glucoside	170350	115966	100571	37.9	2.98	93.17
1.599	fatty acyl / fatty amides	N-(3-oxododecanoyl) homoserine lactone	434512	52271	23317	38	1.05	91.04
0.824	fatty acyl / fatty amides	N-(3-oxododecanoyl) homoserine lactone	153083	110495	52892	36.5	0.31	82.86
9.533	fatty acyl/fatty acid	methyl 8-[2-(2-formyl-vinyl)-3-hydroxy-5-oxo-cyclopentyl]-octanoate	132041	114408	110010	39.4	1.73	98.88
6.605	fatty acyl/fatty alcohol	phenolic phthiocerol	128541	44594	29784	38.1	1.76	92.70
9.571	fatty acyl/fatty ester	4,8-Dimethyl-4E,8E-decadien-10-olide	194276	189267	242145	39.4	1.64	99.07
3.006	fatty acyl/octadecanoids	(-)-11-hydroxy-9,10-dihydrojasmonic acid 11-beta-D-glucoside	23250	21142	17280	37.1	0.64	86.43
5.373	fatty acyl/fatty alcohol	phenolic phthiocerol	1922732	198933	4754	39.3	2.26	99.08
7.708	fatty acyl/fatty alcohol	phenolic phthiocerol	84036	87317	28854	38.2	1.40	92.72
2.412	Fatty acyl / fatty aldehyde	9Z,11E,13-Tetradecatrienal	281526	497828	317176	39.1	-2.92	98.88
5.156	fatty acyl / fatty amides	Docosanamide	152868	76765	66109	38.9	2.02	97.04
4.891	Fatty acyl / fatty esters	Mayolene-19	2503391	297488	6107	39.2	1.97	98.54
5.167	Fatty acyl / fatty esters	Mayolene-20	2701817	223899	7180	38.4	1.33	93.70
4.343	Fatty acyl / fatty esters	Mayolene-17	314602	31700	859	39.1	1.56	97.37
7.213	Fatty acyl / fatty esters	Mayolene-19	143089	118875	17581	37.9	1.44	91.15
6.076	Fatty acyl / fatty esters	Mayolene-19	424702	65519	10463	39.3	1.99	98.96

6.377	Fatty acyl / fatty esters	Mayolene-20	233848	82673	18871	38.5	-0.46	93.29
1.432	Fatty acyl / fatty esters	3-hydroxy-cis-5-octenoylcarnitine	748203	325416	235165	35.6	3.20	81.93
4.731	Polyketides / flavonoids	Laxiflorin	259200	163564	122542	39.5	0.81	98.69
6.609	Polyketides / flavonoids	Laxiflorin	171148	175548	253258	38.9	0.85	95.49
0.936	Polyketides / flavonoids	2',4',5,7-Tetramethoxy-8-methylflavanone	318637	273536	190249	38.4	3.68	96.32
8.979	Polyketides / flavonoids	Demethyltorosaflavone C	108966	87842	81548	38.1	-2.90	93.81
0.504	Polyketides / flavonoids	5,7-Dihydroxyflavone 7-benzoate	44154	32859	30843	38.2	2.79	94.12
5.816	Polyketides / flavonoids	Demethyltorosaflavone D	24329	7296	742652	38.7	0.72	94.41
2.030	Polyketides / flavonoids	Epilumaflavanone B	220296	136207	77042	39	1.66	97.04
0.795	Polyketides / flavonoids	Euchrenone a14	16976	16806	6871	37.4	-3.18	90.79
1.958	Polyketides / flavonoids	Euchrenone a14	82570	107243	55799	36	-2.16	82.71
1.226	Polyketides / flavonoids	Prebarbigerone	144225	64441	27849	38.7	0.70	94.52
0.635	Polyketides / flavonoids	Galangin 5,7-dimethyl ether	92663	94851	53728	36.4	-1.00	83.29
3.780	Polyketides / flavonoids	Lonchocarpenin	96394	79972	56903	38.4	1.32	93.71
1.215	Polyketides / flavonoids	Heteroflavanone B	457683	244875	134752	39	0.30	95.61
3.517	Polyketides / flavonoids	Artocommunol CA	257701	216345	154957	36.4	-0.63	82.89
1.470	Polyketides / flavonoids	Heteroflavanone B	71632	40198	24552	38.8	1.14	95.18
4.425	Polyketides / flavonoids	Isochamanetin	94516	93069	68658	36.6	-2.26	85.87
2.050	Polyketides / flavonoids	Quercetol B	68064	45078	34035	38.2	3.04	94.46
2.416	Benzene and substituted derivatives	Fluconazole	1283146	771364	813852	38.9	-2.86	97.92
1.355	furopyrans	Cyclocalopin F	403033	190260	207926	38.5	2.53	95.62
8.979	Amino acid and derivatives	Avenic acid A	1230135	1070909	952967	39.2	0.91	97.35
0.647	Amino acid and derivatives	4-Guanidinobutanoic acid	820691	756851	1027592	38.3	3.17	95.44
0.670	Amino acid and derivatives	(S)-4-Amino-5-oxopentanoate	142208	97816	68071	36	3.45	83.82
4.404	sugar acids and derivatives	Alginic acid	26632	20370	20976	36.9	-0.77	85.24
1.269	Amino acid and derivatives	gamma-Glutamyl-beta-aminopropiononitrile	670540	423050	327008	37.4	1.66	88.86
0.670	Amino acid and derivatives	gamma-glutamyl-ethylamide	161949	63662	34520	37.8	-1.42	90.76
2.564	Amino acid and derivatives	(2S,4S)-Pinnatanine	70150	61428	44748	36.7	1.95	85.67
6.609	glycerophospholipids	PI(O-20:0/20:5(5Z,8Z,11Z,14Z,17Z))	246223	190757	203089	36.9	2.40	87.51
5.224	glycerophospholipids	PC(12:0/13:0)	19076	0	0	37.3	1.04	87.58
6.072	glycerophospholipids	PE(16:1(9Z)/18:1(11Z))	37548	1963	8813	39.4	-0.26	97.08
1.744	glycerophospholipids	PI(22:6(4Z,7Z,10Z,13Z,16Z,19Z)/0:0)	21497	28297	11849	38	-1.00	90.97
1.599	glycerophospholipids	PI(13:0/12:0)	1904372	1416042	760936	38.8	-1.91	96.49
4.537	glycerophospholipids	PS(O-16:0/14:1(9Z))	25124	8667	0	36.7	0.09	83.56
4.826	glycerophospholipids	PS(P-16:0/16:1(9Z))	114610	5697	1061	39.2	0.31	96.61
4.268	Amino acid and derivatives	N-[(3a,5b,7b)-7-hydroxy-24-oxo-3-(sulfoxy)cholan-24-yl]-Glycine	82730	42279	54111	36.3	1.64	83.41
6.856	Glycerolipids	MGDG(18:2(9Z,12Z)/18:2(9Z,12Z))	1518538	486062	55360	39.1	-2.44	98.42
6.365	Glycerolipids	MGDG(18:2(9Z,12Z)/18:3(9Z,12Z,15Z))	8593243	2405099	73201	39.3	-2.46	99.27
0.623	Alkaloids and derivatives	Flazine methyl ether	191317	99063	55327	36.2	-1.77	83.02
0.651	Benzene and substituted derivatives	4-Aminohippuric acid	127209	102547	69455	38.1	-3.68	94.93
1.490	Benzene and substituted derivatives	4-Aminohippuric acid	57986	63426	33176	39.5	0.75	98.63

1.638	Benzene and substituted derivatives	4-Aminohippuric acid	143596	100292	54185	39.1	0.11	95.77
1.033	Amino acid and derivatives	N-Ribosylhistidine	1548064	1803690	703983	37.2	2.17	88.64
5.769	Prenol lipids / hopanoids	2-methylbacteriohopane-32,33,34,35-tetrol	142535	41737	3778	38.9	2.20	97.29
5.369	Prenol lipids / hopanoids	bacteriohopane-,32,33,34-triol-35-cyclitol	423253	72658	72721	39.2	1.88	98.29
4.366	Prenol lipids / hopanoids	adenosylhopane	179337	11716	306	37.1	2.21	88.35
0.862	Hydroxycoumarin	Mammea E/BB	1346575	1001307	823099	35.9	2.24	81.93
1.001	hypoxanthines	7-Methylguanine	177911	532153	62412	39	2.21	97.73
6.887	Indoles	Cyclobrassinone	136086	96660	101753	37.6	-2.72	91.32
1.950	Amino acid and derivatives	5-Hydroxy-L-tryptophan	52958	40692	21057	38.8	-3.32	97.93
4.932	Indoles	2-Indolecarboxylic acid	1399217	519271	121357	39	2.27	97.88
3.065	Indoles	2-Indolecarboxylic acid	344238	231080	168668	38.6	2.35	95.96
2.766	Indoles	Indoleacrylic acid	1653373	102236	148395	38.4	2.84	95.54
3.609	Indoles	1H-Indole-3-carboxaldehyde	336623	122775	100410	36.6	3.52	86.90
5.995	Indoles	3-Methylene-indolenine	1388747	291257	316751	38.7	4.14	98.40
5.995	Indoles	Indole-3-acetic acid	928655	203439	215159	39.1	2.40	98.16
3.323	Amino acid and derivatives	5-Methoxytryptophan	131283	79882	37558	37.5	2.00	90.04
2.207	isocoumarans (antidepressant)	Citalopram aldehyde	177151	110884	95407	37	2.27	87.48
3.837	Polyketides / flavonoids	Calopogoniumisoflavone A	60452	60996	43541	37.9	0.95	90.78
0.824	Amino acids and derivatives	N-Jasmonoylisoleucine	177558	93676	45156	37	1.24	86.58
4.362	Fatty acyl / octadecanoid	12-hydroxyjasmonic acid 12-O-beta-D-glucoside	691279	768030	1005101	36.7	1.08	84.74
1.473	Polyketides / phenylpropanoids	11-Hydroxy-12-methoxydihydrokawain	389806	177462	99029	38.5	2.60	95.73
1.306	Polyketides / phenylpropanoids	11-Hydroxy-12-methoxydihydrokawain	831420	456914	324840	37.2	3.57	90.34
3.190	Fatty acyl / eicosanoids	Lipoxin D4	96502	151894	123785	36.1	3.93	84.96
1.698	Polyketides	10-Deoxymethymycin	137727	96489	54911	39.5	0.76	98.63
2.793	Fatty acyl / fatty acid	Dethiobiotin	56554	31156	284056	39.2	1.63	97.79
5.133	Glycerophospholipids	PA(14:1(9Z)/18:0)	36101	2125	2127	37.5	-0.45	88.19
3.053	Glycerophospholipids	PA(12:0/0:0)	235571	142075	120754	37.1	-3.81	90.03
5.209	Glycerophospholipids	PA(16:0/18:2(9Z,12Z))	37305	3262	769	36.3	-0.81	82.34
2.107	Glycerophospholipids	PA(22:6(4Z,7Z,10Z,13Z,16Z,19Z)/0:0)	47590	50243	125724	37.5	2.05	90.10
0.855	Glycerophospholipids	PC(8:0/0:0)	24893	25546	26221	36.9	-2.93	88.03
6.906	Carbohydrate and derivatives	Sedoheptulose 1,7-bisphosphate	32853	38331	27094	38.4	2.89	95.33
2.679	Fatty acyl / Fatty amides	Pipericine	238991	72848	30691	37.9	1.80	91.61
2.416	Fatty acyl / Fatty amides	N-(4-benzenesulfonamide) arachidonoyl amine	1194413	813871	692623	36.7	3.53	87.74
5.133	Fatty acyl / Fatty amides	N-oleoyl glutamic acid	74926	21394	19417	37.5	3.88	92.08
2.793	Fatty acyl / Fatty amides	N-(5-hydroxy-pentyl) arachidonoyl amine	97558	79920	65536	38.9	1.34	96.18
0.864	Fatty acyl / Fatty amides	N,N-diethyl-3-hydroxybut-2-enamide	55400	52352	107057	36.2	2.01	83.56
3.503	Fatty acyl / Fatty amides	N-stearoyl serine	2045574	2021193	2099337	39.2	2.73	99.24
2.736	Fatty acyl / Fatty amides	Anandamide (20:2, n-6)	286066	84660	37541	38.7	2.17	96.25
4.252	N-acyl pyrrolidines	N-(14-Methylhexadecanoyl)pyrrolidine	257014	254383	245081	38.6	3.43	97.06
2.808	Amino acid and derivatives	L-N-(1H-Indol-3-ylacetyl)aspartic acid	146843	86527	94605	38	-2.64	93.12
3.625	Amino acid and derivatives	Tricosanoylglycine	125692	145763	116703	39	1.69	96.98

4.457	Amino acid and derivatives	Pentacosanoylglycine	4292978	4634019	3436790	39	2.89	98.57
3.205	Amino acid and derivatives	Suberylglycine	450667	499250	425990	37.8	-0.13	89.19
8.686	Amino acid and derivatives	N-Succinyl-L,L-2,6-diaminopimelate	85113	71765	56394	38.6	0.13	93.12
4.362	N-acyl-piperidines	Pipercitine	371558	317943	325814	39	2.99	98.31
3.766	N-acylpyrrolidines (pyrrolidines)	N-Hexadecanoylpyrrolidine	232149	169804	104191	36.5	3.73	86.79
6.369	Sphingolipids	Cer(d18:0/h17:0)	519623	129857	48190	38.6	2.03	95.37
4.709	Fatty acyl / octadecanoids	7-keto-stearic acid	78363	51334	54373	37.5	3.66	91.66
2.534	Fatty acyl / octadecanoids	12R-HOME(9E)	36295	11904	13858	37.1	-2.36	88.55
1.832	Carbohydrates and derivatives	Acaciabiuronic acid	73923	53212	13219	38.7	-0.64	94.51
1.539	Carbohydrates and derivatives	1,2,10-Trihydroxydihydro-trans-linalyl oxide 7-O-beta-D-glucopyranoside	116865	124958	51038	36.7	2.84	86.76
3.719	Carbohydrates and derivatives	1,2,10-Trihydroxydihydro-trans-linalyl oxide 7-O-beta-D-glucopyranoside	459687	450460	280238	38	-0.82	91.05
1.786	Carbohydrates and derivatives	1,2,10-Trihydroxydihydro-trans-linalyl oxide 7-O-beta-D-glucopyranoside	86486	45112	40235	36.6	-1.25	84.34
3.548	Carbohydrates and derivatives	2,4-Dihydroxy-7,8-dimethoxy-2H-1,4-benzoxazin-3(4H)-one 2-glucoside	544203	32067	14482	37.1	-0.05	85.57
1.573	Carbohydrates and derivatives	1,2,10-Trihydroxydihydro-trans-linalyl oxide 7-O-beta-D-glucopyranoside	101069	89560	67177	36.4	0.10	81.92
4.364	Carbohydrates and derivatives	2-[4-(3-Hydroxypropyl)-2-methoxyphenoxy]-1,3-propanediol 1-glucoside	205671	297132	192120	37.9	-3.02	93.31
5.275	Carbohydrates and derivatives	Phenethyl rutinoside	165678	127029	90673	35.8	-2.92	82.26
4.741	Carbohydrates and derivatives	Verbasoside	59152	57158	20111	38.7	0.49	94.19
2.923	Carbohydrates and derivatives	Benzyl beta-primeveroside	200892	149794	102181	37.4	-0.61	87.81
0.609	Benzene and substituted derivatives	4R,5R,6S-Trihydroxy-2-hydroxymethyl-2-cyclohexen-1-one 6-(2-hydroxy-6-methylbenzoate)	149416	61543	21556	35.6	2.50	81.19
9.396	Amino acid and derivatives	Thyrotropin releasing hormone	435052	561822	512411	39	-3.27	98.89
0.670	Amino acid and derivatives	Ophthalmic acid	820169	692937	880155	37.2	1.72	87.84
2.461	organosulfonic acids	Acrylic acid-2-acrylamido-2-methyl propane sulfonic acid copolymer	3428464	2771322	1356842	37.9	-3.82	93.94
6.205	other fatty acyls	N-(3-(hexadecanoyloxy)-heptadecanoyl)-L-ornithine	332225	48378	41678	38.9	0.97	95.74
1.793	Fatty acyl / fatty acids	12-oxo-5E,8E,10Z-heptadecatrienoic acid	48349	54114	56870	36.5	-1.88	84.91
5.793	Carbohydrates and derivatives	Imidazoleacetic acid ribotide	3310	2396	205510	38.4	-0.41	92.35
2.500	Carbohydrates and derivatives	Ptelatoside A	406034	427138	127743	38.8	-1.65	95.97
3.609	Carbohydrates and derivatives	2-Hydroxybenzaldehyde O-[xylosyl-(1->6)-glucoside]	104995	88476	33240	38.7	-1.51	95.51
3.795	Benzene and substituted derivatives	Ethopropazine	68825	24570	25892	36.2	3.82	85.58
1.515	Benzene and substituted derivatives	Thioridazine	87596	77003	53666	37.3	3.90	90.96
3.719	Benzene and substituted derivatives	3-Carbamoyl-2-phenylpropionaldehyde	304961	134282	66940	38.4	-3.95	96.44
1.355	Benzene and substituted derivatives	(4-Methylphenyl)acetaldehyde	121315	61220	82994	38.9	3.65	98.62
10.44	Benzene and substituted derivatives	Tropicamide	142210	45561	25194	37.1	-0.73	86.37
2.069	Benzene and substituted derivatives	Musanolone F	78949	79787	39588	38.7	-1.93	96.00
0.925	Benzene and substituted derivatives	Dopamine 4-sulfate	182962	156388	135966	35.2	-3.63	80.48
6.009	Glycerophospholipids	PC(12:0/17:1(9Z))	32835	499	819	38.9	0.34	94.69
5.335	Glycerophospholipids	PC(12:0/15:1(9Z))	12096	446	0	38	0.36	90.36
5.571	Glycerophospholipids	PC(14:1(9Z)/14:0)	12675	3117	0	39.1	-0.84	96.64
5.674	Glycerophospholipids	PC(14:1(9Z)/14:0)	20622	8403	1854	39.2	-0.31	96.19
5.765	Glycerophospholipids	PC(17:2(9Z,12Z)/13:0)	118762	29410	24	39	-0.42	95.41
6.005	Glycerophospholipids	PC(18:4(6Z,9Z,12Z,15Z)/13:0)	125927	19585	5092	38.7	-2.86	96.97
3.214	Glycerophospholipids	PC(11:0/11:0)	4294306	4316072	4392340	39	2.47	98.12

6.372	Glycerophospholipids	PC(17:2(9Z,12Z)/15:0)	33733	5006	0	38.2	-1.22	92.69
6.076	Glycerophospholipids	PC(20:5(5Z,8Z,11Z,14Z,17Z)/13:0)	91031	18559	2854	38.9	-1.56	96.50
6.495	Glycerophospholipids	PE(18:2(9Z,12Z)/21:0)	659019	77213	7577	37.1	-1.99	87.86
5.453	Glycerophospholipids	PE(18:4(6Z,9Z,12Z,15Z)/16:1(9Z))	148451	21539	1362	38.1	-3.03	93.89
6.597	Glycerophospholipids	PE(16:0/18:1(11Z))	61750	4107	359	37.5	-1.29	88.82
5.457	Glycerophospholipids	PE(16:1(9Z)/16:1(9Z))	245757	19164	0	39.6	-0.61	98.84
6.327	Glycerophospholipids	PE(16:1(9Z)/17:0)	67672	15657	12945	38.7	-0.98	94.93
6.005	Glycerophospholipids	PE(18:1(11Z)/14:0)	338046	47878	11341	39.8	-0.48	99.58
6.075	Glycerophospholipids	PE(18:1(11Z)/16:1(9Z))	294329	39348	687	39.7	-0.61	99.40
6.654	Glycerophospholipids	PE(18:1(11Z)/18:1(11Z))	77398	5747	573	37.9	-1.46	91.47
4.232	Glycerophospholipids	PG(14:0/16:1(9Z)	86786	4771	0	37	-1.53	87.08
0.897	Glycerophospholipids	PG(16:0/0:0)	152332	54586	21313	36.7	3.54	87.82
5.076	Glycerophospholipids	PG(16:0/16:0)	223610	17420	0	38.3	-1.05	92.71
5.072	Glycerophospholipids	PG(16:1(9Z)/17:0)	1807944	190425	6165	39.4	-0.86	97.81
5.163	Glycerophospholipids	PG(17:2(9Z,12Z)/18:0)	4316719	394561	0	39.5	-0.75	98.41
5.666	Glycerophospholipids	PG(18:1(11Z)/17:0)	1142749	60759	296	38.9	-1.12	95.84
5.369	Glycerophospholipids	PG(18:4(6Z,9Z,12Z,15Z)/18:0)	690073	87534	667	38.5	-3.24	96.50
1.618	Glycerophospholipids	PG(12:0/0:0)	155412	76836	75142	38.6	3.01	96.77
2.991	Glycerophospholipids	PG(22:2(13Z,16Z)/0:0)	277252	171654	141200	37	2.73	88.31
5.685	Glycerophospholipids	PG(12:0/17:0)	121657	66476	36285	36.1	3.98	84.95
4.339	Glycerophospholipids	PG(16:1(9Z)/16:1(9Z))	342012	28411	0	38.8	-0.90	95.21
4.891	Glycerophospholipids	PG(20:5(5Z,8Z,11Z,14Z,17Z)/16:0)	737960	163599	40760	37.2	-3.37	89.95
0.638	Glycerophospholipids	PG(O-18:0/0:0)	143517	72823	40249	37.7	-1.42	90.21
1.222	Glycerophospholipids	PG(22:1(11Z)/0:0)	435327	384106	274276	39.1	-1.93	97.58
5.369	Glycerophospholipids	PG(16:0/18:1(11Z))	4594015	500441	6528	39.8	-0.44	99.31
4.887	Glycerophospholipids	PG(18:1(11Z)/16:1(9Z))	3382843	580853	2493	39.6	-0.63	98.84
5.434	Glycerophospholipids	PG(18:1(11Z)/18:1(11Z))	6715710	639394	4187	39.7	-0.55	98.95
5.006	Glycerophospholipids	PG(17:0/20:5(5Z,8Z,11Z,14Z,17Z))	588772	609235	627249	39	0.55	95.49
4.709	Glycerophospholipids	PG(18:3(6Z,9Z,12Z)/14:0)	1292814	1347921	1398284	39	-2.44	98.01
4.529	Glycerophospholipids	PG(13:0/18:1(9Z))	237167	23673	0	38.7	-1.02	94.91
1.809	Glycerophospholipids	PG(22:1(11Z)/0:0)	1011086	769504	591087	38.9	-1.55	96.52
0.817	polyclic hydrocarbon	Santene	125067	74957	50427	38.7	3.60	97.67
2.671	polyethylene glycols	Heptaethylene glycol	235268	158209	114002	38.3	2.30	94.16
2.705	polyethylene glycols	Hexaethylene glycol	269386	194468	148012	36.2	2.72	84.05
2.900	polyethylene glycols	Heptaethylene glycol	128069	88626	63746	38.4	2.41	94.74
1.904	polyketides/flavonoids	Amorinin	31641	14061	4994	38.1	0.22	90.92
2.785	polyketides/flavonoids	Mammeisin	28484	18943	14024	36.9	1.27	85.96
1.535	polyketides/flavonoids	6,7,3',4'-Tetrahydroxyaurone 6-(4",6"-diacetylglucoside)	49080	28238	23553	35.9	3.19	83.45
2.496	polyketides/flavonoids	Catechin 7-O-alpha-L-rhamnopyranoside	75920	81722	58703	37.2	-3.70	90.21
9.643	polyketides/flavonoids	Pulcherrimin	32121	34680	29655	38	3.78	94.53
1.561	prenol lipids / isoprenoids	7'-hydroxyabscisic acid	115106	86134	45185	36.8	2.70	87.43

3.510	amino acids and derivatives	Ascorbalamic acid	161093	139475	149825	37.8	0.77	89.79
2.759	Fatty acyl / eicosanoids	2-glyceryl-PGD2	114937	54853	43939	36.3	-3.24	85.55
1.657	pteridines and derivatives	7-Hydroxy-6-methyl-8-ribityl lumazine	1647205	1089584	122735	37.3	-3.53	90.59
0.635	purine and derivatives	5'-n-propylthioadenosine	87555	76335	50147	35.6	-2.63	80.88
1.501	purines and derivatives	Guanine	8791773	271564	204198	35.3	-2.32	79.49
1.440	purines and derivatives	Guanine	3429851	154117	116279	39.1	1.83	97.57
0.757	purines and derivatives	Guanine	690768	228012	692556	39	2.21	97.73
1.421	purines and derivatives	Adenosine	414343	361683	147612	35.5	3.04	80.85
2.815	Benzene and substituted derivatives	Isomorellic acid	167371	111810	57545	36.9	-0.24	84.63
2.034	Benzene and substituted derivatives	Isomorellic acid	76919	56235	44308	37.1	1.36	87.18
2.347	Benzene and substituted derivatives	Morellinol	88755	63442	40691	36.4	-3.40	85.90
2.861	Benzene and substituted derivatives	Morellinol	119536	47234	52708	37.5	2.22	90.17
3.079	Benzene and substituted derivatives	Morellin	82929	47029	37547	37.8	2.88	92.17
2.359	Benzene and substituted derivatives	Morellinol	129122	59330	33868	39.5	1.00	98.69
1.493	pyridines and derivatives	4-Pyridoxolactone	142731	87884	45924	36.2	-0.36	81.51
0.898	pyridines and derivatives	4-Pyridoxic acid	386111	441192	235981	35.8	-3.53	83.00
2.070	pyridoxamine	Pyridoxamine	132238	382869	100188	38.8	2.34	97.02
1.433	pyrimidine ad derivatives	Zalcitabine (drug)	102150	77234	49535	39	-0.55	95.52
1.862	pyrimidine ad derivatives	3'-Azido-3'-deoxy-5'- O-beta-D-glucopyranuronosylthymidine	800898	578560	40747	37.6	-1.92	90.29
3.727	pyrimidine ad derivatives	Pentobarbital	194981	281106	154568	38.6	-2.27	95.73
2.008	pyrimidine ad derivatives	Aprobarbital	133662	351074	145993	37.1	2.89	88.94
3.171	pyrimidine ad derivatives	Aprobarbital	111009	100345	40594	37.8	1.62	90.74
1.330	pyrimidine ad derivatives	Thymidine	484310	596234	330009	36.6	2.18	85.48
1.001	pyrrolotriazines	3-Methylpyrrolo[1,2-a]pyrazine	202225	172300	240156	36.9	-1.12	86.01
8.979	Alcohols and polyols	Chlorogenoquinone	68088	63513	51911	37.9	3.77	94.01
3.171	quinoline and derivatives	Rufloxacin	276276	432307	73839	38.2	-0.25	91.29
2.896	quinoline and derivatives	8-hydroxyquinoline	830250	492110	419150	38.8	3.03	97.71
2.766	quinoline and derivatives	6-Methylquinoline	365608	148269	41585	38.2	1.53	92.94
2.450	quinoline and derivatives	8-hydroxyquinoline	263750	114210	83233	37.8	3.31	93.07
1.505	quinoline and derivatives	8-hydroxyquinoline	361151	264063	122219	38.5	2.83	95.77
1.360	quinoline and derivatives	8-hydroxyquinoline	245432	160244	81332	38.1	2.99	93.97
4.067	quinoline and derivatives	8-hydroxyquinoline	608616	215861	259718	38.4	3.06	95.59
3.614	Retenoid	Etretinate	88075	73458	56073	38.6	1.80	94.95
9.396	Polyketides / flavonoids	12a-Hydroxyisomillettone	172021	227994	204776	36.8	3.77	88.55
4.385	Fatty acyl / fatty acids	Stearic acid	10257394	4608210	6113407	39.9	0.10	99.37
1.866	Prenol lipids / sesquiterpenoids	Armillaricin	379773	222118	143683	39.5	0.61	98.17
5.144	Prenol lipids / Sesterpenoids	3-Hydroxy-10'-apo-b,y-carotenal	81179	61882	51096	37.6	-2.51	91.06
5.145	Prenol lipids / Sesterpenoids	3-Hydroxy-10'-apo-b,y-carotenal	126802	152316	158837	39.3	1.76	98.82
10.16	Sphingolipids	Sphinganine	133754	113612	107704	39.3	0.03	96.50
2.374	Sphingolipids	Penaresidin A	2112422	2111030	2159572	38.5	3.05	95.89
9.286	Sphingolipids	C16 Sphinganine	945121	783696	783210	39.5	0.98	98.78

4.320	Sphingolipids	N-(hexadecanoyl)-deoxysphing-4-enine-1-sulfonate	258619	5627	634	36.7	-0.48	84.30
1.352	Steroid and derivatives	Eplerenone	21152249	9502294	11791116	39.1	1.65	97.53
3.243	Steroid and derivatives	Dehydroepiandrosterone sulfate	34184	81506	47767	36.3	2.57	84.50
4.235	Steroid and derivatives	(6RS)-22-oxo-23,24,25,26,27-pentanorvitamin D3 6,19-sulfur dioxide adduct	372012	246167	297435	38.2	-0.71	91.65
0.946	Steroid and derivatives	(25R)-26,26,26-trifluoro-1alpha,25-dihydroxyvitamin D3	617276	431671	265704	39.1	-2.45	98.41
5.925	Fatty acyl / fatty acids	Behenic acid	35171	11460	4694	37.1	-2.20	87.97
1.348	Benzene and substituted derivatives	Styrene	167163	87041	78553	38	2.56	92.84
1.881	sugar acids and derivatives	3-Deoxy-D-manno-octulosonate	818587	234498	123835	37.7	-0.31	88.97
0.918	sulfoxides	Camelinin	549734	399049	228557	38.1	0.03	90.32
7.035	sulfoxides	(Z)-[3-(Methylsulfinyl)-1-propenyl] 2-propenyl disulfide	6384	128173	83	38	3.26	93.72
0.723	sulfoxides	(Z)-[3-(Methylsulfinyl)-1-propenyl] 2-propenyl disulfide	131889	187373	132413	36.6	-0.13	82.98
2.382	Prenol lipids	(-)-trans-Carveol glucoside	138800	109936	75183	36.9	2.86	87.74
1.352	tetrahydroisoquinolines	1,2,3,4-Tetrahydroisoquinoline	172104	71425	88931	39	3.43	99.07
2.728	tetrapyrrole and derivatives	Mono(glucosyluronic acid)bilirubin	83827	64595	25891	35.1	3.97	80.20
5.449	Prenol lipids	gamma-tocotrienol	468032	524895	387969	39.5	-1.34	99.20
1.840	Prenol lipids	15-Acetoxyscirpene-3,4-diol 4-O-a-D-glucopyranoside	127724	98849	101409	36.4	-2.91	85.45
6.689	Glycerolipids	TG(18:4(6Z,9Z,12Z,15Z)/18:4(6Z,9Z,12Z,15Z)/18:4(6Z,9Z,12Z,15Z))	551653	138320	91394	37.1	-2.13	88.09
0.681	Amino acids and derivatives	Glycylprolylhydroxyproline	146758	107778	94244	38.3	-2.90	95.15
1.008	Amino acids and derivatives	Glycylprolylhydroxyproline	1175172	945080	484876	38.9	-2.33	97.07
4.731	Prenol lipids	Lucidenic acid D1	258973	153784	117944	39.5	0.60	98.30
6.609	Prenol lipids	Lucidenic acid D1	125738	117240	140658	38.7	0.67	94.17
0.706	Amino acids and derivatives	Tryptamine	286196	154267	207496	37.4	3.32	90.95
4.709	Fatty acyl / fatty acids	7,12-octadecadiynoic acid	234012	155530	150917	39.2	2.67	98.93
3.438	Fatty acyl / fatty acids	9-heptadecylenic acid	908033	52230	1497	39.6	-1.03	99.31
3.758	Fatty acyl / fatty acids	Oleic acid	4185339	248451	43620	39.2	-1.19	97.48
4.994	Fatty acyl / fatty acids	7,11-octadecadiynoic acid	98856	103407	108627	38.8	2.04	96.39
5.312	Fatty acyl / fatty acids	17Z-octadecenoic acid	64540	55069	38874	37.7	3.81	93.20
3.397	Steroid and derivatives	(23S)-1alpha-hydroxy-25,27-didehydrovitamin D3 26,23-lactone	64364	54038	55053	36.5	1.56	84.43
7.094	Fatty acyl / fatty esters	Behenyl linoleate	282293	377570	400237	36.5	-3.79	86.69
2.930	Steroid and derivatives	Physalolactone	147432	418370	87892	36	2.83	83.59

Table A3 LC-Q-ToF analysis results of samples collected from SAMBR with changes in macronutrients. Glu: initial glucose feed; F: Glucose to fructose; N: organic to inorganic nitrogen source; F6 and N6 refers to samples collected 6 hours after the change in macronutrient; F24 and N24 refers to samples collected 24 hours after the change in macronutrient. (Chapter 5)

RT (min)	F6	F24	Glu	N6	N24	Chemical class	Suggested compound	Score	Mass Error (ppm)	Isotope Similarity
3.453	0	0	0	152822	149468	8-aminoquinoline	Tafenoquine	38.1	-4.79	96.17
4.030	0	0	0	51860	37056	Alkaloids	Chaetoglobosin Q	37.8	3.60	93.27
4.808	1226884	1736814	992672	722421	918060	Amino acids and analogues	Leucyl-phenylalanine	38.3	-3.67	96.04
1.934	451550	696254	1297736	1834088	1931639	Amino acids and analogues	D-Phenylalanine	39.1	-1.80	97.81
1.476	10962569	12394558	20044806	8803595	6274792	Amino acids and analogues	Guanine (isomer)	39.6	-0.05	98.08
1.187	903604	1175543	880281	2263749	2147180	Amino acids and analogues	L-Tyrosine	39.4	-1.33	98.76
8.142	393851	295671	567235	0	0	Amino acids and analogues	N-Undecanoylglycine	39.5	-0.23	97.79
4.584	33366	16073631	0	0	950397	Amino acids and analogues	Pentacosanoylglycine	39.3	0.78	97.31
3.300	0	0	0	415706	408921	Amino acids and analogues	Apetaline A	36.2	-3.16	84.93
1.541	757408	1305470	1710226	1944702	2430291	Amino acids and analogues	gamma-Glutamylisoleucine	37.9	-3.98	94.39
0.832	532792	774323	7369192	332543	233980	Amino acids and analogues	Guanine (isomer)	39.4	-0.95	98.36
1.305	262956	380668	1385113	1118789	1351174	Amino acids and analogues	Isoleucyl-Aspartate	36.7	-3.28	87.22
2.323	1193391	1512598	701481	710345	1086329	Amino acids and analogues	Isoleucyl-Threonine	38.6	-4.33	97.97
2.750	1092319	1604854	1288507	408250	579162	Amino acids and analogues	Isoleucyl-Valine	37.8	-5.46	95.12
2.609	766569	1440448	1467646	1672766	1876334	Amino acids and analogues	Isoleucylproline (isomer)	38.1	-4.81	96.26
2.879	457796	1139048	2090612	2103051	2263704	Amino acids and analogues	Isoleucylproline (isomer)	38	-5.18	95.88
0.829	328657	0	0	971	2086	Amino acids and analogues	Maculosin (Cyclo(L-pro-L-tyr))	39	1.96	97.43
1.930	436101	1253944	3285768	5734224	5706173	Aryl	Indoline	39.2	-1.42	97.95
3.001	0	0	0	168124	160327	Aryl	Pratosartan	37.6	6.40	95.36
2.564	0	0	0	119714	0	Aryl	4-(2,4,4-Trimethyl-2-pentanyl)phenol	38.9	3.55	98.57
1.191	589875	792931	1259000	1647431	1549524	Aryl	4-Acetyl-3-methylpyridine	39.4	-0.72	97.97
1.381	0	0	0	131902	166363	Aryl	Methyl violet 2B(1+)	35.7	9.24	88.89
0.923	0	0	0	81834	107486	Aryl	new fuchsin(1+)	36	9.80	90.52
2.109	0	0	0	11220	14882	Benzene and substituted derivatives	2-Dodecylbenzenesulfonic acid	39.7	-0.27	98.84
3.310	0	0	0	46255	29205	Benzene and substituted derivatives	Ananolignan L	35.4	-9.87	87.82
1.515	1686403	1441679	2004605	1116882	948330	Benzene and substituted derivatives	modafinil acid	37.8	1.83	91.17
2.312	0	63128	496226	0	0	Benzene and substituted derivatives	myrsinoic acid F	36.7	9.80	94.00
3.906	0	0	0	793250	723567	Benzene and substituted derivatives	Tanespimycin	36.1	1.36	82.22
0.756	43269	32303	27379	0	0	beta-lactam	cephalexin(1−)	37.6	0.67	89.03
0.785	263168	1330	0	100	331	Carbohydrates conjugates	Glycoprotein-phospho-D-mannose	38.7	4.53	98.92
0.737	0	3561432	0	0	0	Carboxylic acids	Butoctamide semisuccinate	39.4	-0.86	98.12
1.804	0	0	0	368349	404966	Carboxylic acids	Plantaricin BN	37.1	-5.14	91.62
2.056	0	0	0	234898	155484	Prenol lipids	ajugacumbin A chlorohydrin	35.9	4.80	85.15
2.096	0	0	0	42056	44542	Prenol lipids	12beta-acetoxyhuratoxin	36.3	2.77	84.63

2.890	0	0	0	51820	45110	Prenol lipids	fischeroside A	36.4	-6.97	89.73
2.300	0	0	0	65430	40461	Fatty acyls - Eicosanoids	12-Oxo-c-LTB3	37.3	0.98	87.51
3.578	0	0	0	94209	71609	Fatty acyls - Eicosanoids	20-Oxo-leukotriene E4	36.7	7.19	91.84
3.527	0	0	204961	0	0	Fatty acyls - fatty acids	9E-heptadecenoic acid	39	0.28	95.32
3.253	0	0	114279	0	0	Fatty acyls - fatty acids	trans-9-palmitoleic acid	39.1	1.02	96.86
0.682	0	1287555	0	0	0	Fatty acyls - fatty acids	11-Aminoundecanoic acid	39.3	0.21	96.58
0.824	518431	0	0	94141	464920	Fatty acyls - fatty acids	cis,cis-muconic acid	37.3	-9.70	97.04
5.546	0	41611	0	0	0	Fatty acyls - fatty acids	28:7(n-6) / 4Z,7Z,10Z,13Z,16Z,19Z,22Z-Octacosaheptaenoic Acid	38.9	-1.62	96.66
6.209	0	0	326661	2514211	892566	Fatty acyls - glycosides	1-(O-alpha-D-glucopyranosyl)-(1,3R,29S,31R)-dotriacontanetetrol	38.5	0.06	92.45
2.487	2584204	2320671	1068218	1919011	2735882	Fatty Acyls - fatty esters	3-hydroxy-cis-5-octenoylcarnitine	38.4	-2.42	94.92
4.141	1303702	1652763	749807	677678	867174	Fatty acyls - others	N-(6-aminohexanoyl)-6-aminohexanoic acid (isomer)	38	-4.16	95.09
3.847	1909472	2697301	1622826	983625	1512102	Fatty acyls - others	N-(6-aminohexanoyl)-6-aminohexanoic acid (isomer)	38.1	-4.57	95.58
5.310	0	0	537615	0	0	Glycerolipids	DG(13:0/20:3(8Z,11Z,14Z)/0:0)[iso2]	38.3	3.51	95.46
7.478	0	0	6164836	0	0	Glycerolipids	DG(20:1(11Z)/22:0/0:0)[iso2]	37.6	-4.99	93.79
5.710	4807	0	627622	0	0	Glycerolipids	DG(20:2(11Z,14Z)/22:6(4Z,7Z,10Z,13Z,16Z,19Z)/0:0)[iso2]	36.5	9.57	92.84
5.744	0	21374	1278291	3550194	2376871	Glycerolipids	DG(22:3(10Z,13Z,16Z)/22:6(4Z,7Z,10Z,13Z,16Z,19Z)/0:0)[iso2]	36.2	7.92	89.66
5.547	0	0	2324856	7210099	4631850	Glycerolipids	DG(22:6(4Z,7Z,10Z,13Z,16Z,19Z)/22:5(7Z,10Z,13Z,16Z,19Z)/0:0)	37.1	7.33	93.58
6.849	33796	358505	0	0	0	Glycerophospholipids	PG(16:0/16:0)	37.2	-6.65	93.54
4.000	0	0	0	80142	36531	Glycerophospholipids	LPIM2(18:1(9Z)/0:0)	38	-4.31	95.26
6.794	0	0	7306245	0	0	Glycerophospholipids	PA(24:1(15Z)/24:1(15Z))	37.6	5.73	94.49
4.923	0	0	2130985	0	0	Glycerophospholipids	PA(20:0/i-14:0)	35	-2.87	78.55
2.700	0	0	0	756149	840476	Glycerophospholipids	1-(18-mercaptooctadecanoyl)-sn-glycerol 3-phosphate	36.9	3.60	88.85
2.125	0	0	0	828686	798728	Glycerophospholipids	PC(6:2(3E,5E)/14:2(11E,13E))	35.8	8.44	88.32
3.404	0	27558	3634464	0	0	Glycerophospholipids	PC(O-8:0/O-8:0)	39.4	-1.39	98.53
4.753	0	0	1052001	7283928	6510278	Glycerophospholipids	PC(12:0/22:1(11Z))	34.6	7.07	80.95
4.956	0	0	879027	7902848	6746105	Glycerophospholipids	PC(13:0/22:1(11Z))	37.7	8.46	97.66
4.299	0	0	293681	2007139	1944492	Glycerophospholipids	PC(18:0/16:2(2E,4E))	36.1	7.34	88.61
1.789	0	0	0	206657	232121	Glycerophospholipids	LysoPE(0:0/22:5(4Z,7Z,10Z,13Z,16Z))	37.7	9.11	98.35
2.388	10	0	33327	163273	51839	Glycerophospholipids	PE(16:1(9Z)/0:0)	37.7	-1.29	90.02
4.852	0	0	379114	4136449	3672859	Glycerophospholipids	PE(21:0/18:2(9Z,12Z))	37.4	8.04	96.05
4.944	0	0	1042609	0	0	Glycerophospholipids	PG(12:0/19:0)	37.6	0.87	89.11
2.894	0	0	0	610824	549586	Glycerophospholipids	PG(20:5(5Z,8Z,11Z,14Z,17Z)/0:0)	36	-2.37	82.76
2.892	0	13608	139936	0	0	Glycerophospholipids	PG(O-18:0/0:0)	38.8	-2.05	96.39
4.717	0	0	0	176430	71279	Glycerophospholipids	PI(17:2(9Z,12Z)/0:0)	37.5	-7.78	96.26
4.040	0	0	0	187392	181743	Glycerophospholipids	1-stearoyl-sn-glycero-3-phosphoserine(1−)	37.7	-8.30	97.59
2.079	0	0	0	263733	267194	Glycerophospholipids	1,2-dioctanoyl-sn-glycero-3-phosphoserine(1−)	37.3	-6.58	93.96
3.788	0	0	0	146354	168130	Glycerophospholipids	1-heptadecanoyl-sn-glycero-3-phosphoserine(1−)	36.6	-9.46	93.50
5.513	0	0	230687	166813	111391	Glycosphingolipids	Oceanalin A	38.1	-0.47	91.31
1.149	119402	56532	69737	0	0	Hetrocyclic oxides	(2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO)	39.1	-1.11	96.79
2.628	400772	914298	2817041	3749123	3432223	Indoles	Indoleacrylic acid	39	-2.20	97.71
0.838	192345	537157	329784	3223631	7189797	Prenol lipids	(6E)-3,7,11-Trimethyl-6,10-dodecadien-1-yl trihydrogen diphosphate	36.1	7.67	88.95

4.825	0	0	0	20322	19032	Macrolide	(14E)-3-Ethyl-7-hydroxy-2,8,12,16-tetramethyl-5,13-dioxo-10-(2-oxoethyl)-4,17-dioxabicyclo[14.1.0]heptadec-14-en-9-yl 2-O-butyryl-3,4,6-trideoxy-3-(dimethylamino)hexopyranoside	37.5	-6.33	94.48
2.422	0	0	0	293810	298085	Macrolide	latrunculol A	37.4	7.76	95.67
1.526	3823138	4006616	7424345	4079195	3212448	Nucleosides and analogues	Deoxyinosine	38.7	3.79	98.00
1.397	1632905	1967938	1213088	1176816	816749	Nucleosides and analogues	Guanosine	38.7	-3.13	97.38
1.434	4460244	5324673	3821691	5299229	4882555	Nucleosides and analogues	Inosine	38.4	6.12	98.97
2.590	0	0	0	14992	11533	Polyketides	Rifamexil	39.2	-0.96	97.16
1.861	0	0	0	1064538	1098169	Polyketides	Euchrenone a14	35.9	6.20	86.36
0.752	159256	88986	0	0	0	Polyketides	Viscutin 1	36.6	5.28	89.07
8.686	5014249	1921194	2878555	0	0	Polyketides	Flavokawin A	36.7	9.82	94.29
5.672	0	0	253235	0	0	Polyketides	Mannosyl-1beta-phosphomycoketide C32	38	-0.27	90.36
7.632	0	0	6531486	0	0	Prenol lipids	3-demethylubiquinol-10	37.9	2.61	92.60
5.136	0	0	4566632	0	0	Prenol lipids	bacteriohopane-,32,33,34-triol-35-cyclitol	39.1	0.69	96.36
6.833	0	5920015	0	0	0	Prenol lipids	bacteriohopane-,32,33,34-triol-35-cyclitolguanine	38	-6.99	97.78
4.983	0	0	792075	0	0	Prenol lipids	bacteriohopane-31,32,33,34,35-pentol	38.2	4.01	95.88
4.599	0	0	1793932	0	0	Prenol lipids	bacteriohopane-32,33, 34-triol-35-carbamate	38.4	3.15	95.85
5.245	0	0	192611	265679	308060	Prenol lipids	N-tryptophanyl-35-aminobacteriohopane-32,33,34-triol	35.5	-6.98	85.40
5.344	0	0	2019191	1181134	482980	Prenol lipids	tg54	34.3	0.35	71.84
3.428	0	13955	534616	0	0	Prenol lipids	3-oxoglycyrrhetinic acid	37.4	4.94	92.91
1.766	0	0	0	435912	460017	Prenol lipids	15-Acetoxyscirpene-3,4-diol 4-O-a-D-glucopyranoside	36.2	-1.69	82.83
9.885	1321820	2081886	1300019	735426	1111808	Prenol lipids	4-O-Methylmelleolide	38.2	-0.29	91.46
2.907	0	0	0	416930	432134	Prenol lipids	Cinncassiol D2 glucoside	37.9	-5.49	95.63
2.997	0	0	0	407	2026	Prenol lipids	Hovenidulcioside A1	35.2	-9.88	86.61
5.684	0	0	9640072	0	0	Prenol lipids	Faradiol laurate	36.8	-7.79	92.96
1.968	0	0	0	736253	709885	Protein kinase	Sotrastaurin acetate	38.6	0.58	93.57
0.977	0	0	10207279	154525	124156	Purines and derivatives	Hypoxanthine (isomer)	39.6	-0.50	98.54
1.412	1911988	2360507	1296762	1408207	1268707	Purines and derivatives	Hypoxanthine (isomer)	39.5	0.79	98.22
1.492	3242235	3492289	5794274	2436445	1726591	Purines and derivatives	Hypoxanthine (isomer)	39.8	-0.15	99.19
2.509	0	6786	40474	0	0	Purines and derivatives	Seliciclib	37.5	3.15	91.40
1.059	0	0	8001985	325833	123022	Purines and derivatives	Xanthine	39.5	-0.61	98.07
2.620	0	0	0	241791	222501	Amino acids and analogues	N1,N8-bis(sinapoyl)-spermidine	36.9	-7.08	92.56
2.464	0	0	0	41474	26715	Prenol lipids	Melemeleone B	38.6	0.70	93.88
5.256	0	20613	812716	1001051	3299343	Sphingolipids	N-(2-hydroxyhexadecanoyl)-1-O-β-D-glucosyl-4-hydroxy-15-methylhexadecasphinganine	37.7	1.07	89.61
5.892	0	0	2292912	2631320	2075202	Sphingolipids	Cer(d18:0/14:0)	39	-0.52	95.73
4.857	0	16363	334473	2682835	2060730	Sphingolipids	CerP(d18:1/18:0)	37.2	-5.95	92.60
6.548	0	0	2515720	1841579	1413854	Sphingolipids	Cer(d18:0/16:0)	37.4	-5.34	93.02
4.961	0	0	273299	2457912	2493553	Sphingolipids	Cer(d18:0/18:0(2OH)) (isomer)	38.6	-1.81	95.09
6.521	0	0	6073848	8793014	7574014	Sphingolipids	Cer(d18:0/18:0(2OH)) (isomer)	39.3	-0.43	96.96
6.219	0	0	6511940	9200884	7471487	Sphingolipids	Cer(d18:0/h17:0)	39.2	-0.41	96.42
7.139	0	0	3147001	665271	0	Sphingolipids	Cer(d20:0/16:0)	38.5	-1.33	94.00

5.125	0	0	357465	1814780	712338	Sphingolipids	Cer(d15:2(4E,6E)/20:0)	37.9	-1.14	91.08
6.225	0	0	1457827	1317456	761917	Sphingolipids	Cer(d14:1/20:0) (isomer)	37.6	-0.94	89.17
4.343	9339	689322	505765	1357514	2757243	Sphingolipids	Cer(d14:1/20:0) (isomer)	36.8	-0.25	84.55
5.224	0	0	1577263	6654878	3933272	Sphingolipids	Cer(d14:1/20:0) (isomer)	39	0.64	95.74
6.811	0	0	1193024	1936335	1173328	Sphingolipids	Cer(d14:1/22:0) (isomer)	37.5	-1.38	89.33
4.934	0	38013	2394704	4717723	8699311	Sphingolipids	Cer(d14:1/22:0) (isomer)	37.5	-1.13	88.82
6.313	0	0	3299254	2932602	1975620	Sphingolipids	Cer(d14:1/22:1)	33.7	-0.43	68.94
5.738	0	0	316534	2935816	1633624	Sphingolipids	Cer(d15:2(4E,6E)/22:0)	37.8	-2.50	91.96
6.324	0	0	3103455	3432637	3118264	Sphingolipids	Cer(d18:0/15:0)	39.2	-0.07	96.06
6.948	0	0	2121677	2448174	1690794	Sphingolipids	Cer(d18:0/17:0)	37.1	-2.72	88.64
6.417	0	0	70527	3003298	1959210	Sphingolipids	Cer(d18:1/17:0) (isomer)	37.7	-0.68	89.48
4.671	0	0	103852	5006523	10112548	Sphingolipids	Cer(d18:1/17:0) (isomer)	38.9	-0.47	95.29
5.541	0	0	6262669	17267302	10432177	Sphingolipids	Cer(d18:1/17:0) (isomer)	35.4	-0.48	77.57
7.030	0	0	1123791	1432333	1026632	Sphingolipids	Cer(d18:1/19:0)	38.1	-3.29	94.48
4.699	0	0	7404126	0	0	Sphingolipids	Cer(m18:1(4E)/16:0)	39.4	-0.36	97.40
5.284	0	0	15665598	0	0	Sphingolipids	Cer(m18:1(4E)/18:0)	38.9	-1.48	96.21
5.505	35819	14639	846435	1595905	698215	Sphingolipids	PE-Cer(d14:1(4E)/22:0(2OH))	36.6	-2.75	86.07
5.289	0	0	276740	340736	113283	Sphingolipids	PE-Cer(d15:1(4E)/20:0(2OH))	37.3	-4.96	92.02
5.869	291	0	140661	188360	2946	Sphingolipids	PE-Cer(d15:1(4E)/22:0(2OH))	38.7	-3.50	97.50
6.328	301	0	49133	54492	43135	Sphingolipids	N-heptadecanoyl-4-hydroxy-15-methylhexadecasphinganine-1-phosphocholine	37.2	-4.18	90.73
5.916	8436	164096	4201705	9792268	9049098	Sphingolipids	N-hexadecanoyl-4-hydroxy-15-methylhexadecasphinganine-1-phosphocholine	38.7	-2.45	96.52
5.343	0	0	231867	185315	0	Sphingolipids	N-hexadecanoylphytosphingosine-1-phosphoethanolamine zwitterion	39	-3.14	98.47
5.525	0	0	1642394	1565466	8407816	Sphingolipids	N-(2-hydroxyheptadecanoyl)-1-O-β-D-glucosyl-4-hydroxy-15-methylhexadecasphinganine	37.7	1.01	89.62
6.411	0	0	1644293	2042866	1513865	Sphingolipids	N-(2-hydroxyicosanoyl)-15-methylhexadecasphing-4-enine	38.7	-0.76	94.40
5.946	0	0	927324	575198	1077781	Sphingolipids	N-(2-hydroxyoctadecanoyl)-1-O-β-D-glucosyl-4-hydroxy-15-methylhexadecasphinganine	35.3	-1.16	77.76
4.134	0	0	0	62666	39674	Steroids and derivatives	25-Acetyl-6,7-didehydrofevicordin F 3-glucoside	34.5	-8.96	82.32
4.419	3228	139647	0	0	15134	Steroids and derivatives	Bufotalin	36.4	7.02	89.97
3.963	0	0	0	316926	325021	Steroids and derivatives	DEXAMETHASONE PHENYLPROPIONATE	37.7	3.01	92.30
6.838	0	36556344	0	0	0	Steroids and derivatives	Goyaglycoside c	37.3	9.70	97.17
1.399	2315300	6862506	0	0	502146	Steroids and derivatives	Inspra	39.4	0.50	97.40
6.010	0	0	0	1175	0	Steroids and derivatives	Withalongolide H	37.5	4.19	92.42
4.014	0	0	0	432735	399828	Steroids and derivatives	2-deoxyecdysone 22-phosphate	37.4	8.33	96.26
0.715	0	0	0	0	359107	Steroids and derivatives	1-Hydroxyprevitamin D3 diacetate	36.6	-8.60	92.64
2.920	0	0	2441	316788	268376	Steroids and derivatives	11-acetoxy-3beta,6alpha-dihydroxy-9,11-seco-5alpha-cholest-7-en-9-one	37.5	5.58	93.80
4.501	0	0	352144	0	0	Steroids and derivatives	poriferast-5-en-3beta-yl beta-D-glucopyranoside (isomer)	37.8	5.25	94.87
4.769	0	0	1319706	0	0	Steroids and derivatives	poriferast-5-en-3beta-yl beta-D-glucopyranoside (isomer)	38.2	4.03	95.77
0.692	0	0	0	340069	2255	Sulphur oxoacid	tetrathionic acid	35.3	4.92	82.39
2.053	0	0	0	115401	93379	Prenol lipids	12alpha-Hydroxyamoorstatin	36.5	-9.62	93.13
8.416	6251408	4013193	8584421	174909	114561	Tetrapyrroles and derivatives	Biladiene-ab	37	5.69	91.44
2.365	0	0	0	234070	238627	Protein kinase	5,6-diphenyl-N-(2-piperazin-1-ylethyl)furo[2,3-d]pyrimidin-4-amine	34.7	8.49	83.13
1.136	0	1301229	0	0	0	unclassified	Melagatran	38.4	-2.67	95.30

0.721	175035	0	0	0	0	Alkaloids	17-O-deacetylvindolinium	37.5	-7.16	95.32
1.043	250769	799901	0	356617	548677	Amino acids and analogues	Arginyl-Isoleucine	38.3	-3.92	96.03
6.009	0	0	0	7363	1523	Amino acids and analogues	beta-Casomorphin (1-6)	37.5	-1.54	89.51
3.421	610906	1015751	992369	303317	479562	Amino acids and analogues	Isoleucyl-Isoleucine	37.6	-4.72	93.59
1.385	997929	939454	559085	818403	1157415	Amino acids and analogues	Isoleucyl-Lysine	38.3	-4.23	96.66
3.059	1053539	1359184	720826	635733	905929	Amino acids and analogues	Isoleucyl-Valine (isomer)	38	-4.47	95.39
2.487	764708	1261681	3558939	737532	1117600	Amino acids and analogues	Isoleucyl-Valine (isomer)	38.1	-4.41	95.70
2.582	0	0	0	21201	12629	Amino acids and analogues	Kinetensin 4-8	36	-5.69	86.73
0.748	1081263	0	0	0	0	Amino acids and analogues	L,L-Cyclo(leucylprolyl)	38.5	-1.44	93.99
4.465	708073	1110578	708499	374136	491338	Amino acids and analogues	Leucyl-phenylalanine	38.3	-4.35	96.64
2.601	0	0	0	145535	158418	Amino acids and analogues	Leukotriene C4 (ref Lipoxin C4)	38.1	-2.32	93.49
6.870	436832	450815	515242	0	0	Amino acids and analogues	N-Acetyl-leu-leu-tyr-amide	36	-8.73	89.73
2.126	0	0	24984	90569	66348	Amino acids and analogues	N-Acetylleucylleucyltyrosine	35.9	3.25	83.50
4.730	0	0	0	31226	37054	Amino acids and analogues	Perindopril arginine	37.4	-3.85	91.57
3.543	451028	728408	937626	869007	928910	Amino acids and analogues	Phenylalanylproline	38.6	-1.71	94.86
2.209	0	0	0	92990	101099	Amino acids and analogues	S-(PGA1)-glutathione	39	-0.81	95.80
2.455	0	40486	0	0	0	unclassified	Antibiotic G418	37.8	-4.85	94.51
1.000	0	334797	0	0	0	Aryl	buphenine	35.8	7.15	86.96
1.831	0	0	0	109319	118470	Aryl	Pentoxyverine Citrate	34.3	-9.60	82.02
0.756	28354	21498	53002	0	0	Benzene and substituted derivatives	4-Phenyl-1H,3H-naphtho[1,8-cd]pyran-1,3-dione	38.3	4.51	96.67
3.520	0	0	0	170943	137505	Benzene and substituted derivatives	Morellinol	36.7	-7.72	92.17
2.121	0	0	0	125458	119047	beta-lactam/antibiotic	Tobicillin	35.3	4.85	81.96
1.229	0	0	0	53056	40419	Carbohydrates conjugates	4-O-acetyl-2,3-di-O-methyl-α-L-fucopyranose	38	2.20	92.72
1.754	0	0	66452	10743	19530	Carbohydrates conjugates	Dibekacin	39.2	1.83	98.16
2.104	0	0	0	5373	5213	Carbohydrates conjugates	N,N'-diacetylchitobiose	38.6	-2.58	96.09
0.776	345020	231809	0	0	0	Carbohydrates conjugates	α-D-Galp-(1→3)-α-D-Glcp-(1→3)-α-L-Rhap-(1→4)-D-ribitol-5-phosphate	38.4	0.14	92.21
1.728	0	0	0	427091	541744	Fatty Acyls - fatty esters	O-suberoylcarnitine(1−)	37.9	-6.89	97.48
1.069	0	0	0	51095	38211	Carboxylic acids	Candoxatrilat	37	-8.87	94.88
9.361	606561	860831	485127	0	0	Carboxylic acids	9,17-dioxo-1,2,3,4,10,19-hexanorandrostan-5-oate	39.6	0.10	98.27
3.948	0	0	53923	49351	75498	Fatty acyls - fatty acids	Ionomycin	36.4	0.09	82.33
3.662	0	0	0	238231	228873	Fatty acyls - Eicosanoids	14,15-HxA3-D(11S)	37.8	6.25	96.22
2.319	0	0	0	94652	62175	Fatty acyls - Eicosanoids	Lipoxin C4 (ref Leukotriene C4)	35.9	3.96	84.28
2.006	0	0	19138	0	0	Fatty acyls - Eicosanoids	(9alpha,11alpha,13E,15S)-11,15-Dihydroxy-6,9-epoxyprosta-5,13-dien-1-oic acid	36.3	7.78	90.33
2.317	0	0	64522	0	0	Fatty acyls - Eicosanoids	11-deoxy-PGF1a	38	-1.56	91.90
4.978	0	0	1155033	0	0	Fatty acyls - fatty acids	FAHFA(16:1(9Z)/9-O-18:0)	35.6	6.13	84.86
6.963	0	0	86682	0	0	Fatty acyls - fatty acids	27:2(5Z,9Z)(25Me)	37.9	-1.61	91.47
4.818	23107	0	0	0	0	Fatty acyls - fatty acids	Nonadecylic acid	38	-0.59	90.85
8.934	467755	392728	642034	0	0	Fatty acyls - fatty acids	7-tridecynoic acid	39.4	0.19	97.41
3.806	0	0	16786	0	0	Fatty acyls - fatty acids	9E-heptadecenoic acid	38.3	0.46	92.17
5.768	0	0	266137	854141	289729	Fatty acyls - glycosides	1-(O-alpha-D-glucopyranosyl)-29-keto-(1,3R,31R)-dotriacontanetriol	35.5	0.45	78.23
1.743	0	0	0	65914	46107	Fatty acyls - glycosides	Glucosylgalactosyl hydroxylysine	38.4	2.44	94.87

2.010	0	0	0	33287	22131	Fatty acyls - fatty amides	EI-1511-5	34.7	8.56	82.89
4.007	0	0	0	37840	19447	Fatty acyls - fatty amides	Manumycin	37.7	4.32	93.35
10.215	501838	360874	656212	0	0	Fatty acyls - fatty amides	S-Acetyldihydrolipoamide	37.6	2.23	90.50
1.206	1987817	1702088	1512122	689539	0	Furans	Nitrafudam hydrochloride	35.7	1.45	80.49
4.605	0	62	21230	64894	46083	Glycerolipids	1-palmitoyl-2-lauroyl-sn-glycero-3-phospho-1D-myo-inositol(1−)	37.2	0.77	86.85
4.036	0	0	53995	74604	67572	Glycerolipids	DG(17:2(9Z,12Z)/22:6(4Z,7Z,10Z,13Z,16Z,19Z)/0:0)[iso2]	37.4	7.36	95.45
5.125	0	0	2058952	1366886	689917	Glycerolipids	DG(22:6(4Z,7Z,10Z,13Z,16Z,19Z)/22:6(4Z,7Z,10Z,13Z,16Z,19Z)/0:0)	36.1	8.26	89.52
5.529	0	0	61630	0	0	Glycerolipids	DG(12:0/22:3(10Z,13Z,16Z)/0:0)[iso2]	36.5	2.09	85.07
4.736	0	0	63159	0	0	Glycerolipids	DG(13:0/18:3(9Z,12Z,15Z)/0:0)[iso2]	36.6	3.58	87.00
4.944	0	0	93219	0	0	Glycerolipids	DG(13:0/20:4(5Z,8Z,11Z,14Z)/0:0)[iso2]	36.1	3.14	84.07
5.491	56	0	74941	80937	45375	Glycerolipids	DG(22:4(7Z,10Z,13Z,16Z)/22:6(4Z,7Z,10Z,13Z,16Z,19Z)/0:0)[iso2]	34.5	8.20	81.41
5.437	0	0	260077	1079157	511788	Glycerolipids	1-O-beta-D-Glucopyranosyl-2,3-di-O-(8-hexadecenoyl)glycerol	35.1	5.49	81.63
2.651	14519	7272	0	0	4090	Glycerolipids	Butyrin (Glycerol tributanoate/1,2,3-Propanetriyl tributanoate)	38.9	1.20	96.15
10.679	0	0	1315209	0	0	Glycerolipids	TG(21:0/22:0/22:1(11Z))[iso6]	37.5	-2.17	89.86
10.740	0	0	1390390	0	0	Glycerolipids	TG(22:0/22:0/22:1(11Z))[iso3]	37.7	-1.89	90.60
5.141	0	0	141234	0	0	Glycerophospholipids	PA(18:0/14:1(9Z))	36.5	-1.93	84.90
5.201	0	0	86155	0	0	Glycerophospholipids	PA(16:0/18:2(9Z,12Z))	36.9	-2.69	87.72
5.738	0	0	921051	1573314	811406	Glycerophospholipids	PA(19:0/20:3(8Z,11Z,14Z))	36.3	9.94	92.30
1.393	46690	144896	0	0	0	Glycerophospholipids	PA(21:4(6Z,9Z,12Z,15Z)/0:0)	38.3	-3.13	95.36
2.974	0	0	102270	17227	3323	Glycerophospholipids	PA(O-18:0/0:0)	37.4	-0.52	87.74
6.466	83	5947	1235559	0	0	Glycerophospholipids	PC(O-16:0/13:0)	38.8	-1.64	95.76
4.451	27	25	28698	56276	56141	Glycerophospholipids	PC(13:0/20:1(11Z))	33.5	6.77	75.17
4.638	0	8657	201256	1265068	1231677	Glycerophospholipids	PC(15:0/20:2(11Z,14Z))	36.8	3.82	88.44
4.353	0	0	29136	71336	73260	Glycerophospholipids	PC(16:0/18:2(10E,12Z))	38.2	6.86	98.63
4.890	0	0	46464	112587	107562	Glycerophospholipids	PC(18:0/18:2(6Z,9Z))	37.8	7.00	96.95
5.289	0	2403	295545	853534	480834	Glycerophospholipids	PC(18:0/20:4(8Z,10Z,12Z,14Z))	36.7	5.90	90.39
2.102	0	0	0	10694	14515	Glycerophospholipids	PC(6:2(3E,5E)/14:2(11E,13E))	36.8	7.36	92.12
3.083	0	0	97780	5909	0	Glycerophospholipids	PC(O-16:1(11Z)/0:0)	38.7	-1.23	95.10
5.957	0	0	213002	811392	566090	Glycerophospholipids	PE(14:0/18:1(11Z))	36.2	-1.78	83.27
4.627	0	0	1256631	0	0	Glycerophospholipids	PE(17:0/16:0)	36.1	-2.32	83.28
4.989	0	0	1163172	0	0	Glycerophospholipids	PE(17:0/17:0)	35.8	-2.90	82.54
4.802	0	0	125953	0	0	Glycerophospholipids	PE(18:1(11Z)/17:0)	33.8	-5.26	75.30
5.185	0	0	1386843	0	0	Glycerophospholipids	PE(19:0/16:0) (isomer)	36.2	-8.51	90.55
6.121	0	183237	226443	670244	290323	Glycerophospholipids	PE(19:0/16:0) (isomer)	35.9	-2.09	81.99
4.633	0	0	841898	0	0	Glycerophospholipids	PE(20:3(8Z,11Z,14Z)/15:0)	33.8	-8.65	78.76
4.846	0	0	201233	904948	969023	Glycerophospholipids	PE(21:0/20:5(5Z,8Z,11Z,14Z,17Z))	37.3	6.77	94.18
2.236	0	0	148422	1169988	666479	Glycerophospholipids	PE(16:1(9Z)/0:0)	38.5	0.49	93.11
4.495	0	0	123707	97669	121477	Glycerophospholipids	PG(O-20:0/14:1(9Z))	33.4	9.70	77.81
6.076	506	1299	31156	116970	98855	Glycerophospholipids	PG(16:0/19:0)	36.9	-2.70	87.77
5.623	101	0	41901	53813	41330	Glycerophospholipids	PG(16:1(9Z)/19:0)	36.9	-1.76	86.58
1.995	9958	0	144464	0	0	Glycerophospholipids	PG(15:0/0:0)	37.5	-0.64	88.31

2.443	2908	305	47373	19127	32819	Glycerophospholipids	PG(17:0/0:0)	38.2	0.18	91.42
5.409	0	0	109473	33365	14390	Glycerophospholipids	PG(18:1(11Z)/16:0)	35.5	-1.89	79.61
4.375	0	0	44938	0	0	Glycerophospholipids	PG(a-13:0/i-16:0)	37.5	-3.78	91.74
3.998	0	0	55988	0	0	Glycerophospholipids	PI(15:0/13:0)	35.5	-3.27	81.37
7.499	87	0	44988	155540	130862	Glycerophospholipids	PS(24:0/24:0)	36.3	-3.71	85.82
7.374	0	0	152514	978952	861573	Glycerophospholipids	PS(24:1(15Z)/24:1(15Z))	37.7	-3.57	92.80
1.848	0	325619	0	0	0	Glycerophospholipids	PI(13:0/12:0)	38.1	-4.03	95.41
7.032	0	0	0	149	0	Glycerophospholipids	2-O-glutaroyl-1-O-palmitoyl-sn-glycero-3-phosphocholine(1−)	37	-6.79	92.72
3.625	0	0	96359	0	0	Indoles	Auricularine	36.4	2.50	84.74
3.483	0	0	0	34556	23473	Hydroxyquinones	Trierixin	36	-4.93	85.57
3.308	0	0	0	11393	17450	Macrolide	(1R,3S,9R,10S,13R,15E,17E,19E,21E,23R,25S,26R,27S)-23-[(3-Amino-3,6-dideoxy-beta-D-manno pyranosyl) oxy]-10-ethyl-1,3,9,27-tetrahydroxy-13-methyl-7,11-dioxo-12,29-dioxabicyclo [23.3.1]nonacosa-15,17,19,21-tetraene-26-carboxylic acid	37	8.32	94.30
2.593	225117	279510	4952	1427411	1359367	Macrolide	Novamethymycin	36.5	-8.29	91.54
4.271	0	0	48721	0	0	Glycerolipids	MG(0:0/20:2(11Z,14Z)/0:0)	38.8	-0.59	94.69
1.747	2162391	784084	579445	468491	525860	N-aryl piperazine	Brexpiprazole	37.3	-2.57	89.58
1.366	0	0	0	582159	551002	Nucleosides and analogues	Adenosine	39	-3.18	98.73
1.423	2674711	3025464	2459391	2947380	2268532	Nucleosides and analogues	Guanosine	38.8	0.41	94.48
1.187	420436	560759	1757364	1134000	1053294	Polyketides	4-Hydroxycinnamic acid	39.7	-0.56	99.00
1.701	0	0	0	5886	2663	Polyketides	N1,N5,N10-Tris-trans-p-coumaroylspermine	38.4	-0.51	92.67
1.444	0	0	0	409006	432361	Piperazine	Rhodotorulic acid	36.5	-7.89	91.24
1.339	0	0	0	398	0	Alkaloids	(-)-Anaferine	38.9	-1.40	96.19
4.419	0	23825	0	0	5285	Polyketides	Brosimacutin H	36.7	8.82	93.48
5.042	0	0	0	2718	1504	Prenol lipids	Hovenidulcioside A2	37.1	8.52	94.83
6.182	0	0	0	26186	17217	Prenol lipids	15-epi-lupulin B	36.9	-6.90	92.34
2.590	0	0	0	2766	1739	Prenol lipids	Cephalomannine	36.7	-9.25	93.57
3.044	0	0	0	12137	14277	Prenol lipids	Rediocide A	35.4	3.62	81.43
4.503	0	0	0	103946	61352	Prenol lipids	14-Deacetylnudicauline	36	-8.40	89.51
3.923	0	0	0	30275	6978	Prenol lipids	RPR112698	36.9	3.20	88.09
1.823	0	0	0	177203	194121	Prenol lipids	Cinncassiol C1 19-glucoside	37	-1.86	87.19
1.873	0	0	0	1646	626	Prenol lipids	Dulcoside A	36.7	-8.75	93.20
5.016	0	0	1043364	0	0	Prenol lipids	Erythrodiol 3-decanoate	37	-7.62	93.63
4.170	0	0	0	430155	657466	Pteridines and derivatives	5,6,7,8-tetrahydrobiopterin radical cation	38.5	5.09	98.38
1.518	1840882	1989244	3138214	1808829	1486734	Purines and derivatives	Hypoxanthine	39.1	2.98	99.12
2.350	63003	0	0	6748	10092	Purines and derivatives	methylxanthine	39.6	-0.23	98.16
1.461	646185	797909	1526952	469497	330779	Purines and derivatives	Xanthine	38.5	2.65	95.88
0.958	244255	455398	1332760	357258	380452	Pyridines and derivatives	Nicotinic acid	39.2	-1.73	98.12
7.008	0	669882	0	178534	69746	Pyridines and derivatives	Ilorasertib	34.9	-8.44	83.99
1.644	1012648	1017514	2128473	1220613	867871	Pyrimidines and derivatives	3'-Hydroxyhexobarbital	38.3	-2.90	94.96
0.920	1248017	1281843	540604	1355732	957220	Pyrimidines and derivatives	Cytosine	39	-2.89	98.25
1.412	51545	61543	1212705	94275	35589	Pyrimidines and derivatives	Thymine (isomer)	38	-1.58	92.13
1.888	420719	412666	1116134	164523	141346	Pyrimidines and derivatives	Thymine (isomer)	39.4	-1.94	99.27

0.901	12995	18481	1328640	15127	7976	Pyrimidines and derivatives	Uracil	39.1	-2.32	98.15
1.754	0	0	0	573121	584184	Pyrroles	Atorvastatin(1−)	35.6	-3.89	82.33
7.588	0	2048	93724	834272	680482	Sphingolipids	1-O-myristoyl-Cer(d18:1/18:0)	37.9	-2.70	92.89
4.731	0	0	51082	0	0	Sphingolipids	N-octadecanoylsphingosine 1-phosphate(2−)	37	-3.71	89.15
6.017	0	0	32362	51196	30497	Sphingolipids	Cer(d18:0/14:0)	37	-2.37	87.92
6.709	0	0	653211	923312	602076	Sphingolipids	Cer(d18:0/16:0)	36.1	-2.45	83.51
6.657	0	0	29692	79230	45307	Sphingolipids	Cer(d18:0/18:0(2OH))	36.8	-3.24	87.96
6.410	0	0	37051	82032	48754	Sphingolipids	Cer(d18:0/h17:0) (isomer)	36.3	-3.13	85.01
4.671	0	0	2260066	1133367	1231503	Sphingolipids	Cer(d18:0/h17:0) (isomer)	38.4	-0.96	93.18
6.110	0	1211	704602	908978	574969	Sphingolipids	Cer(d14:1(4E)/22:0(2OH))	34.3	-1.33	73.16
5.903	0	0	379148	699523	366672	Sphingolipids	Cer(d14:1/20:0)	37.1	-1.86	87.93
5.651	0	0	1214523	32110	0	Sphingolipids	Cer(d14:1/22:1)	37.9	0.66	90.28
4.310	0	0	178251	722932	1109180	Sphingolipids	Cer(d15:2(4E,6E)/20:0)	37.7	-0.02	88.33
4.857	0	0	692327	1223416	1728782	Sphingolipids	Cer(d15:2(4E,6E)/22:0)	38.5	-1.25	94.20
6.454	0	0	36587	49793	29651	Sphingolipids	Cer(d18:0/15:0)	37.5	-2.18	89.96
5.202	0	0	398158	634694	535218	Sphingolipids	Cer(d18:1/19:0)	36.2	-3.60	85.24
6.417	0	0	3136198	880083	350226	Sphingolipids	Cer(m18:1(4E)/18:0)	35.2	-3.98	80.79
6.624	0	0	4448	45402	36715	Sphingolipids	N-octadecanoyl-4-hydroxy-15-methylhexadecasphinganine-1-phosphocholine	36.8	-5.71	90.59
5.569	0	1662	280133	1414154	437745	Sphingolipids	SM(d18:0/12:0)	36.6	-1.61	84.93
5.996	0	697	100264	893500	260246	Sphingolipids	SM(d18:0/13:0)	38	-5.03	95.59
6.542	0	0	13961	27705	0	Sphingolipids	SM(d18:0/15:0)	36.4	-5.23	88.06
5.032	0	0	56226	86497	73950	Sphingolipids	PE-Cer(d14:1(4E)/20:0(2OH))	37.3	-3.30	90.25
5.481	0	1262	236031	993960	424487	Sphingolipids	PE-Cer(d14:1(4E)/20:0)	37.3	-2.71	89.48
5.645	0	0	901683	172965	100383	Sphingolipids	PE-Cer(d14:1(4E)/22:0(2OH))	37.5	-2.08	89.78
5.163	0	0	86627	71557	57229	Sphingolipids	PE-Cer(d14:2(4E,6E)/22:0(2OH))	33.4	-3.44	71.09
6.432	0	205	4353	90310	45142	Sphingolipids	SM(d18:0/16:1(9Z))	36.5	-4.16	87.18
5.662	0	0	748140	1338297	843682	Sphingolipids	N-hexadecanoyl-15-methylhexadecaphytosphingosine	38.4	-1.51	94.04
6.295	0	0	68441	79824	168075	Sphingolipids	N-(2-hydroxynonadecanoyl)-1-O-β-D-glucosyl-4-hydroxy-15-methylhexadecasphinganin	38.6	2.72	96.09
6.953	0	0	434475	964935	688542	Sphingolipids	N-icosanoyl-4-hydroxy-15-methylhexadecasphinganine	38.3	-1.77	93.64
2.109	0	0	0	31877	29766	Steroids and derivatives	3,3-Difluoro-17-methyl-5α-androstan-17β-ol	37	4.67	90.60
1.952	1003	0	645978	565826	409488	Steroids and derivatives	Cyclopamine	39.2	-0.28	96.36
3.034	0	0	0	522	0	Steroids and derivatives	Corchorusoside E	36.4	-0.44	82.50
3.031	0	0	0	347534	353194	Steroids and derivatives	Ptilosteroid B	35.1	7.53	83.84
4.577	0	0	102373	0	0	Steroids and derivatives	Campesteryl glucoside	37.1	3.61	89.80
1.092	0	431769	0	0	0	Tetralins	(1R,9S)-10-(Cyclopropylmethyl)-1-ethyl-4-hydroxy-13-methyl-10-azatricyclo[7.3.1.0~2,7~]trideca-2,4,6-trien-8-one	35.8	7.31	87.09
2.989	0	0	0	413856	409374	Tetrapyrroles and derivatives	Deuteroporphyrin IX	34.7	-5.58	80.04
1.854	0	0	0	39722	28497	Tetrapyrroles and derivatives	Epoxypheophorbide a(1−) (isomer)	36.4	0.71	83.06
2.662	0	0	0	198988	205365	Tetrapyrroles and derivatives	Epoxypheophorbide a(1−) (isomer)	34.6	6.94	80.89
6.838	0	406587	0	0	0	Carboxylic acids	Amoxicilloyl-butylamine	37.6	5.39	94.35

3.948	0	0	0	335117	310006	unclassified	(1alpha,3alpha,6alpha,14alpha,15alpha,16beta)-8-Acetoxy-3,6,10,13,15-penta-hydroxy-1,16-dimethoxy-4-(methoxymethyl)-20-methylaconitan-14-yl benzoate	35.3	-3.69	80.66

Table A4 LC-Q-ToF analysis of membrane foulants (Chapter 6).

m/z	RT (min)	Chemical class	Suggested compound	Score	Mass Error (ppm)	Isotope Similarity
625.32755	11.10	Alkaloids	Neferine	37.5	0.55	88.31
416.22898	0.520	Alkaloids	17-O-deacetylvindolinium	38.3	-3.83	95.83
146.09295	0.957	Amino acids and analogues	4-Guanidinobutanoic acid	39	3.77	99.17
118.08696	0.698	Amino acids and analogues	5-Aminopentanoic acid	38.1	6.04	97.25
175.11939	0.629	Amino acids and analogues	L-Arginine	39.2	2.50	98.89
440.41065	3.652	Amino acids and analogues	Pentacosanoylglycine	39.2	1.89	98.37
325.18463	1.448	Benzene and substituted derivatives	2-Dodecylbenzenesulfonic acid	38.3	1.05	92.53
192.13796	11.18	Benzene and substituted derivatives	N,N-Diethylbenzeneacetamide	38.3	-1.71	93.46
279.09272	11.12	Benzene and substituted derivatives	Sulfamethazine	37.6	6.11	95.10
317.05484	0.663	Benzene and substituted derivatives	Melanin	36.4	-6.11	89.02
455.18848	1.045	Benzene and substituted derivatives	alpha-CEHC glucuronide	37.5	-5.92	94.31
343.12967	3.931	Benzene and substituted derivatives	Dictyoquinazol C	38.1	2.40	93.15
257.04841	3.881	Benzene and substituted derivatives	[4-(3-oxopentyl)phenyl]oxidanesulfonic acid	38.3	-1.97	93.84
257.04843	3.664	Benzene and substituted derivatives	[4-(3-oxopentyl)phenyl]oxidanesulfonic acid	38.5	-1.88	94.73
271.06388	4.537	Benzene and substituted derivatives	{[(1E)-1-(4-methoxyphenyl)pent-1-en-3-yl]oxy}sulfonic acid	37.7	-2.53	91.36
285.07967	5.430	Benzene and substituted derivatives	{[1-(4-methoxyphenyl)-4-methylpent-1-en-3-yl]oxy}sulfonic acid	38	-1.93	92.50
299.09520	6.261	Benzene and substituted derivatives	{3-[(1Z)-3-hydroxy-2-pentylprop-1-en-1-yl]phenyl}oxidanesulfonic acid	37.2	-2.22	88.58
267.07191	0.736	Carbohydrates and derivatives	2(alpha-D-Mannosyl)-D-glycerate	39.3	-0.92	97.48
277.08954	0.751	Carbohydrates and derivatives	3,4,5-trihydroxy-6-[(3-methylbut-2-enoyl)oxy]oxane-2-carboxylic acid	37.2	-8.15	95.33
390.08707	6.771	Carbohydrates and derivatives	3-Methylbutyl glucosinolate	38.2	-4.20	96.07
431.11598	6.771	Carbohydrates and derivatives	6-[1-(6,7-dimethoxy-2H-1,3-benzodioxol-5-yl)-3-oxopropoxy]-3,4,5-trihydroxyoxane-2-carboxylic acid	37.5	-5.64	93.98
341.10885	0.781	Carbohydrates and derivatives	Alpha-Lactose	39.6	-0.24	98.07
341.10873	0.721	Carbohydrates and derivatives	Alpha-Lactose	39.2	-0.59	96.75
707.56919	6.077	Carbohydrates and derivatives	N-hexadecanoyl-4-hydroxy-15-methylhexadecasphinganine-1-phosphocholine	38.9	-0.81	95.70
503.16126	0.797	Carbohydrates and derivatives	Raffinose	38.8	-0.98	95.08
309.10072	7.763	Carbohydrates and derivatives	1-Pentadecanecarboxylic acid	36.5	8.86	92.52
399.09535	0.675	Carbohydrates and derivatives	5-(3',4',5'-Trihydroxyphenyl)-gamma-valerolactone-3'-O-glucuronide	37.8	5.17	94.77
271.06383	4.842	Carbohydrates and derivatives	phenyl-1-thio-beta-D-galactopyranoside	37.8	-2.72	92.38
421.22685	1.557	Fatty acyls - Fatty acid esters	2-Methylacetophenone	39.4	0.71	97.87
275.20003	0.680	Fatty Acyls - Fatty Acids	(10Z,14E,16E)-10,14,16-Octadecatrien-12-ynoic acid	38.2	-1.92	93.08
202.18035	1.335	Fatty Acyls - Fatty Acids	11-amino-undecanoic acid	39.5	0.94	98.43
202.18050	0.504	Fatty Acyls - Fatty Acids	11-amino-undecanoic acid	39.4	1.71	99.10
253.21735	12.49	Fatty Acyls - Fatty Acids	2,4-dimethyl-2E-tetradecenoic acid	38.5	0.17	92.57

253.21768	2.418	Fatty Acyls - Fatty Acids	2,4-dimethyl-2E-tetradecenoic acid	38.8	1.49	95.58
227.12865	6.809	Fatty Acyls - Fatty Acids	2Z-Dodecenedioic acid	39.4	-1.00	98.35
407.29565	4.646	Fatty Acyls - Fatty Acids	4Z,7Z,10Z,13Z,16Z,19Z,22Z,25Z-octacosaoctaenoic acid	39.6	0.24	98.40
279.23326	2.593	Fatty Acyls - Fatty Acids	5E,12Z-octadecadienoic acid	39.1	1.09	96.63
277.21764	2.239	Fatty Acyls - Fatty Acids	6,10,14-octadecatrienoic acid	39.1	1.19	97.15
188.12820	0.804	Fatty Acyls - Fatty Acids	8-Amino-7-oxononanoate	36.1	0.40	81.00
255.23350	2.874	Fatty Acyls - Fatty Acids	Isopalmitic acid	39.2	2.15	98.42
367.35755	12.44	Fatty Acyls - Fatty Acids	Mycosanoic acid (C24)	38.2	-1.63	92.75
227.20193	2.268	Fatty Acyls - Fatty Acids	Myristic acid	38	1.21	91.23
283.26472	3.590	Fatty Acyls - Fatty Acids	Stearic acid	39.4	1.63	98.78
281.24897	3.029	Fatty Acyls - Fatty Acids	trans-2-oleic acid	39.1	1.28	96.88
323.11621	8.720	Fatty Acyls - glycosides	3,4,5-trihydroxy-6-{[(2E)-2-methyl-3-phenylprop-2-en-1-yl]oxy}oxane-2-carboxylic acid	36	7.96	89.12
323.11632	8.312	Fatty Acyls - glycosides	3,4,5-trihydroxy-6-{[(2E)-2-methyl-3-phenylprop-2-en-1-yl]oxy}oxane-2-carboxylic acid	36.5	8.31	91.75
277.18090	12.48	Fatty acyls - Fatty Alcohol	Panaxytriol	38.4	-0.05	91.82
302.19622	2.200	Fatty acyls - Fatty Esters	3-hydroxy-cis-5-octenoylcarnitine	39.6	0.08	98.14
302.19625	2.513	Fatty acyls - Fatty Esters	3-hydroxy-cis-5-octenoylcarnitine	39.6	0.15	98.11
209.15445	8.960	Fatty acyls - Fatty Esters	(E)-2-Octenyl 2-methyl-(E)-2-butenoate	39.2	-1.19	97.27
529.49856	8.483	Fatty acyls - Fatty Esters	Linolenyl stearate	38.6	-0.84	94.16
291.19680	1.232	Fatty Acyls - Octadecanoids	12,13S-EOT	39	0.79	95.96
297.24321	1.655	Fatty Acyls - Octadecanoids	2R-hydroxy-oleic acid	38.8	-1.05	95.47
329.23252	8.014	Fatty Acyls - Octadecanoids	5,8,12-TriHOME(9)	37.4	-2.51	89.91
327.21685	7.668	Fatty Acyls - Octadecanoids	9,12,13,TriHODE	37.1	-2.59	88.82
295.22815	1.683	Fatty Acyls - Octadecanoids	alpha-artemisic acid	39.1	0.95	96.42
295.22789	1.432	Fatty Acyls - Octadecanoids	alpha-artemisic acid	39.6	0.09	97.96
293.21193	1.452	Fatty Acyls - Octadecanoids	alpha-kamlolenic acid	39	-0.98	96.32
293.21265	1.201	Fatty Acyls - Octadecanoids	beta-kamlolenic acid	38.9	1.45	96.37
261.13123	2.764	Glycerolipids	Glycerol tripropanoate	37.4	-7.81	95.90
575.47099	5.447	Glycerolipids	DG(13:0/20:3(8Z,11Z,14Z)/0:0)[iso2]	38	5.02	95.93
653.51009	5.028	Glycerolipids	DG(17:2(9Z,12Z)/22:4(7Z,10Z,13Z,16Z)/0:0)[iso2]	35.9	-7.57	88.08
699.59497	8.991	Glycerolipids	DG(20:4(5Z,8Z,11Z,14Z)/22:1(13Z)/0:0)	37.7	3.96	93.00
715.53571	5.744	Glycerolipids	DG(22:6(4Z,7Z,10Z,13Z,16Z,19Z)/22:5(7Z,10Z,13Z,16Z,19Z)/0:0)	36.9	8.55	93.81
691.59302	6.321	Glycerolipids	TG(12:0/14:1(9Z)/14:1(9Z))[iso3]	35.7	8.55	87.74
758.57726	4.834	Glycerophospholipids	PC(12:0/22:1(11Z))	37.2	8.87	95.71
772.59309	5.085	Glycerophospholipids	PC(13:0/22:1(11Z))	37.7	8.93	98.30
774.60594	5.077	Glycerophospholipids	PC(13:0/22:1(11Z))	38	6.74	97.81
786.60004	6.694	Glycerophospholipids	PC(18:0/18:2(9Z,12Z))	38.9	-0.88	95.56
704.52215	4.734	Glycerophospholipids	PE(16:0/17:0)	38.1	-2.02	93.13
732.55344	5.310	Glycerophospholipids	PE(16:0/19:0)	38.5	-1.96	94.78
718.53771	5.085	Glycerophospholipids	PE(17:0/17:0)	37	-2.11	87.31
721.50588	7.724	Glycerophospholipids	PG(12:0/20:1(11Z))	37.8	6.20	95.81
531.27531	0.942	Glycerophospholipids	PG(20:5(5Z,8Z,11Z,14Z,17Z)/0:0)	37.5	6.71	95.15

967.63312	6.675	Glycerophospholipids	PI(22:0/22:6(4Z,7Z,10Z,13Z,16Z,19Z))	37.7	6.32	95.81
473.26560	0.942	Glycerophospholipids	PA(21:4(6Z,9Z,12Z,15Z)/0:0)	39.5	-1.41	99.00
869.70346	7.515	Glycerophospholipids	PA(24:1(15Z)/24:1(15Z))	38.3	4.69	97.04
1325.90261	7.743	Glycopeptidolipid	GPL P-II	36.7	7.06	91.66
188.07069	2.684	Indoles and derivatives	Indoleacrylic acid	39.6	0.45	98.36
174.08766	0.903	Keto acids and derivatives	2-Oxoarginine	39.4	1.97	99.48
174.08769	0.831	Keto acids and derivatives	2-Oxoarginine	39.3	2.14	99.29
249.14942	11.11	Others	Piperdial	38.8	-0.80	95.12
265.11094	7.767	Others	Nevirapine	36.9	5.47	90.99
430.24445	0.767	Others	Melagatran	39.1	-1.00	96.60
112.98566	0.599	Others	Trifluoroacetic acid	39.7	0.63	99.26
316.21212	0.531	Others	Butoctamide hydrogen succinate	39.4	0.86	98.25
195.05100	0.682	Others	Galactonic acid	39.9	-0.12	99.49
80.96481	6.806	Others	Hydrogen sulfite	37.9	-4.66	94.68
577.19820	0.721	Others	8-Acetoxypinoresinol 4-glucoside	35.5	9.58	88.25
335.14518	0.778	Others	Lipoyllysine	37.8	-1.74	91.24
184.17007	12.43	Others	Tecostanine	39.3	2.60	99.82
297.15236	11.08	Polyketides	Glepidotin C	35.8	9.18	89.03
311.04386	2.517	Polyketides	Caftaric acid	36.6	9.62	93.71
243.03292	2.951	Polyketides	{[(3E)-2-hydroxy-4-phenylbut-3-en-1-yl]oxy}sulfonic acid	38.7	-1.41	95.02
399.07035	6.813	Polyketides	3,5,7,4'-Tetrahydroxy-8-C-(3-methylsuccinoyl)flavone	37.1	-4.52	90.83
355.07968	6.771	Polyketides	5-Hydroxy-6-methoxy-3',4'-methylenedioxyfurano[2",3":7,8]flavanone	37.2	-4.38	91.00
645.18222	6.768	Polyketides	6-({3,7-dihydroxy-2-[3-hydroxy-10-(3-methoxyphenyl)-2-oxo-4-oxatricyclo[4.3.1.0Â³,â□·]decan-8-yl]-4-oxo-3,4-dihydro-2H-1-benzopyran-5-yl}oxy)-3,4,5-trihydroxyoxane-2-carboxylic acid	37.2	1.27	87.70
447.08825	6.771	Polyketides	6-[(7,8-dihydroxy-4-oxo-2-phenyl-4H-chromen-5-yl)oxy]-3,4,5-trihydroxyoxane-2-carboxylic acid	35.2	-8.83	85.91
453.16730	10.62	Polyketides	Chamuvaritin	36.9	-5.21	90.66
313.11076	7.030	Polyketides	Naringenin trimethyl ether	36.3	8.32	90.52
439.14249	0.728	Polyketides	Villinol	36	8.56	89.67
437.19314	10.62	Polyketides	5,7-dihydroxy-3-[3-hydroxy-4-methoxy-5-(3-methylbut-2-en-1-yl)phenyl]-8-(3-methylbut-2-en-1-yl)-4H-chromen-4-one	37.8	-6.25	96.25
437.19443	0.935	Polyketides	5,7-dihydroxy-3-[3-hydroxy-4-methoxy-5-(3-methylbut-2-en-1-yl)phenyl]-8-(3-methylbut-2-en-1-yl)-4H-chromen-4-one	38.4	-3.28	95.80
527.15858	0.801	Polyketides	6-(2-{8,8-dimethyl-2-oxo-2H,8H-pyrano[2,3-f]chromen-3-yl}-5-methoxyphenoxy)-3,4,5-trihydroxyoxane-2-carboxylic acid	35.8	7.21	86.96
300.19781	0.752	Polyketides	1-(dimethylamino)-2-methyl-3,4-diphenylbutane-1,3-diol	36.5	6.70	90.20
546.48894	4.287	Prenol lipids	35-aminobacteriohopane-32,33,34-triol	39.2	1.58	98.10
660.48718	4.005	Prenol lipids	adenosylhopane	38.5	2.07	95.08
750.55734	7.717	Prenol lipids	bacteriohopane-,32,33,34-triol-35-cyclitolguanine	37.8	-7.14	97.24
561.45544	5.060	Prenol lipids	bacteriohopane-31,32,33,34,35-pentol	38	5.32	96.33
588.46431	4.698	Prenol lipids	bacteriohopane-32,33, 34-triol-35-carbamate	38.9	1.63	96.27
708.53763	4.030	Prenol lipids	bacteriohopanetetrol cyclitol	37.9	-4.62	95.02
353.21387	11.08	Prenol lipids	Etretinate	37.5	4.67	93.11
212.20081	12.47	Prenol lipids	Ethyl menthane carboxamide	39.8	-0.39	99.43
339.19897	11.08	Prenol lipids	Piperochromenoic acid	37.1	7.07	93.41

415.21108	10.62	Prenol lipids	4-O-Methylmelleolide	39.2	-1.05	97.45
451.19974	9.947	Prenol lipids	8-Butanoylneosolaniol	35.9	5.27	85.45
423.16856	9.174	Prenol lipids	Taraxinic acid glucosyl ester	36	5.90	86.87
137.04643	1.708	Purine and derivatives	Hypoxanthine	38.1	4.71	95.93
137.04643	1.190	Purine and derivatives	Hypoxanthine	38.4	4.75	97.34
151.02628	1.297	Purine and derivatives	Xanthine	39.3	0.86	97.36
153.04124	1.304	Purine and derivatives	Xanthine	39	3.51	99.02
266.08921	1.666	Purine Nucleosides and analogues	Adenosine (Adenine with D-ribose)	39.6	-1.00	99.16
268.10384	1.491	Purine Nucleosides and analogues	Adenosine (Adenine with D-ribose)	39.7	-0.70	99.48
251.07837	1.697	Purine Nucleosides and analogues	Deoxyinosine	39.3	-0.81	97.46
152.05732	1.674	Purine Nucleosides and analogues	Guanine	38.9	4.23	99.23
152.05719	1.514	Purine Nucleosides and analogues	Guanine	39.1	3.33	99.33
152.05719	1.746	Purine Nucleosides and analogues	Guanine	39	3.32	99.06
355.15764	9.212	Purine Nucleosides and analogues	S-adenosyl-methioninamine (dcSAM)	36.2	5.22	86.80
125.03561	2.223	Pyrimidine and derivatives	Thymine	39.8	-0.34	99.24
112.05121	1.045	Pyrimidine Nucleosides and analogues	Cytosine	38.3	6.05	98.47
1293.88024	6.740	Sphingolipids	Ganglioside GM3 (d18:0/26:1(17Z))	38.1	2.56	93.48
1291.86521	6.473	Sphingolipids	Ganglioside GM3 (d18:1/26:1(17Z)))	38.4	3.04	95.81
600.46604	4.462	Sphingolipids	N-(hexadecanoyl)-deoxysphing-4-enine-1-sulfonate	39.3	-1.13	97.83
679.53775	5.401	Sphingolipids	N-hexadecanoylphytosphingosine-1-phosphoethanolamine zwitterion	39.2	-1.06	97.04
742.54634	4.490	Sphingolipids	Termitomycesphin A	36.5	-1.52	84.25
1265.84847	6.389	Sphingolipids	NeuAcalpha2-3Galbeta1-4Glcbeta-Cer(d18:1/24:0)	38.4	2.24	94.75
1291.86490	6.401	Sphingolipids	NeuAcalpha2-3Galbeta1-4Glcbeta-Cer(d18:1/26:1(17Z))	38.1	2.80	93.85
703.53822	5.619	Sphingolipids	PE-Cer(d14:1(4E)/22:0(2OH))	37.3	-1.90	88.98
703.53820	5.866	Sphingolipids	PE-Cer(d14:1(4E)/22:0(2OH))	37.4	-1.94	89.46
705.55355	5.881	Sphingolipids	PE-Cer(d14:1(4E)/22:0(2OH))	38.1	-0.80	91.37
729.55148	6.077	Sphingolipids	PE-Cer(d14:2(4E,6E)/24:1(15Z)(2OH))	37.2	-3.61	90.00
691.53706	5.294	Sphingolipids	PE-Cer(d15:1(4E)/20:0(2OH))	37.7	-2.04	90.73
717.55390	5.944	Sphingolipids	PE-Cer(d15:1(4E)/22:0(2OH))	38.7	-1.82	95.81
719.56828	5.949	Sphingolipids	PE-Cer(d15:1(4E)/22:0(2OH))	38.2	-2.07	93.69
566.55046	6.077	Sphingolipids	Cer(d14:1/22:0)	38.7	-0.37	93.98
584.56082	6.664	Sphingolipids	Cer(d18:0/18:0(2OH))	39.5	-0.71	98.25
570.54536	6.347	Sphingolipids	Cer(d18:0/h17:0)	39.5	-0.39	97.84
552.53487	5.744	Sphingolipids	Cer(d18:1/17:0)	38.8	-0.27	94.24
572.52471	5.942	Sphingolipids	Cer(t18:0/16:0(2OH))	39.4	-0.25	97.55
538.51901	5.405	Sphingolipids	N-Palmitoylsphingosine	38.5	-0.66	93.36
663.53819	7.743	Sphingolipids	SM(d18:0/13:0)	36.3	-8.09	90.53
465.30463	2.535	Steroids and derivatives	cholesterol sulfate	38	0.49	90.45
369.17320	10.02	Steroids and derivatives	5alpha-androstane-3alpha-ol-17-one sulfate	35.9	-2.48	82.57
663.45198	11.12	Steroids and derivatives	Goyaglycoside c	37	8.03	93.89
663.45305	7.747	Steroids and derivatives	Goyaglycoside c	37.4	9.65	97.61

415.27786	0.946	Steroids and derivatives	Sodium deoxycholate	36	-9.71	90.82
595.54117	6.765	Steroids and derivatives	CE(14:0)	35	-8.02	84.14
533.35093	2.294	Steroids and derivatives	1alpha,25-dihydroxy-22-oxavitamin D3 3-hemiglutarate/ 1alpha,25-dihydroxy-22-oxacholecalciferol 3-hemiglutarate	38	6.86	97.77
409.31128	4.786	Steroids and derivatives	calicoferol D	39.8	0.19	99.06
485.35851	0.573	Steroids and derivatives	1-Hydroxyprevitamin D3 diacetate	37.6	-8.32	97.18
415.21226	0.939	Steroids and derivatives	Eplerenone	39.3	1.79	98.48
561.41931	4.638	Steroids and derivatives	Campesteryl glucoside	37.9	5.78	95.97
575.43477	4.610	Steroids and derivatives	poriferast-5-en-3beta-yl beta-D-glucopyranoside	37.9	5.30	95.85
575.43505	4.907	Steroids and derivatives	poriferast-5-en-3beta-yl beta-D-glucopyranoside	37.7	5.78	95.14
393.14465	3.428	Alkaloids	SN-38	38.6	0.38	93.65
672.52527	2.413	Amino acids and analogues	2,3-dipalmitoyl-S-glycerylcysteine	37.1	3.18	89.14
198.07649	0.797	Amino acids and analogues	DL-Dopa	38.8	2.04	96.58
219.13370	0.644	Amino acids and analogues	Isoleucyl-Serine	39.5	-1.05	98.97
321.13059	5.216	Amino acids and analogues	Isomugineic acid	38.8	4.21	99.14
321.13057	5.270	Amino acids and analogues	Isomugineic acid	38.7	4.15	98.52
383.20379	12.04	Amino acids and analogues	Leu-Asn-His	38.9	0.11	94.58
182.08135	1.369	Amino acids and analogues	L-Tyrosine	39.4	0.97	98.18
290.08579	1.674	Amino acids and analogues	N-Succinyl-2-amino-6-ketopimelate	38	-4.35	95.15
148.06102	0.675	Amino acids and analogues	O-Acetylserine	39	3.95	99.50
131.08263	0.618	Amino acids and analogues	Ornithine	39.7	0.21	98.89
128.03528	1.232	Amino acids and analogues	Pyrrolidonecarboxylic acid	39.7	-0.32	98.90
217.15440	1.312	Amino acids and analogues	Valyl-Valine	39	-1.27	96.35
244.19025	2.113	Amino acids and analogues	N-Undecanoylglycine	39	-1.94	97.46
179.14243	11.14	Benzene and substituted derivatives	4-Methyl-1-phenyl-2-pentanol	37.9	-3.41	93.39
275.07474	1.704	Benzene and substituted derivatives	modafinil acid	37.2	4.01	90.55
166.08647	2.024	Benzene and substituted derivatives	N-benzylglycine	39.5	1.28	98.99
135.04515	2.151	Benzene and substituted derivatives	Phenylacetic acid	38.9	-0.03	94.45
473.21860	0.927	Benzene and substituted derivatives	Austalide B	39.4	1.06	98.38
280.09713	2.223	Benzene and substituted derivatives	Graveolinine	39.4	1.11	98.27
519.20255	1.557	Benzene and substituted derivatives	Divanillyltetrahydrofuran ferulate	37.7	0.22	88.94
316.17545	3.580	Benzene and substituted derivatives	Rotigotine	36.4	7.89	90.93
285.07954	5.784	Benzene and substituted derivatives	{[1-(4-methoxyphenyl)-4-methylpent-1-en-3-yl]oxy}sulfonic acid	37.2	-2.37	88.88
443.24760	4.325	Benzene and substituted derivatives	Antibiotic GR 95647X	36.1	8.30	89.81
349.18318	3.523	Carbohydrates and derivatives	(1S,2S,4S)-1,8-Epoxy-p-menthane-2,7-diol 2-O-b-D-glucoside	37.6	-7.21	96.03
267.07206	1.754	Carbohydrates and derivatives	3-oxo-3-[(3,4,5,6-tetrahydroxyoxan-2-yl)methoxy]propanoic acid	37.6	3.75	92.15
266.12233	0.717	Carbohydrates and derivatives	D-1-[(3-Carboxypropyl)amino]-1-deoxyfructose	38.2	-4.15	95.88
179.05606	0.781	Carbohydrates and derivatives	D-Fructose	39.7	-0.29	98.77
424.07301	6.771	Carbohydrates and derivatives	Gluconasturtiin	39.2	-0.08	96.24
1151.37138	0.804	Carbohydrates and derivatives	maltoheptaose	36.1	-1.45	82.24
989.31988	0.759	Carbohydrates and derivatives	Maltohexaose	37	-0.35	85.39
220.08242	1.502	Carbohydrates and derivatives	N-Acetylmannosamine	39.5	-1.08	98.74

397.07438	6.809	Carbohydrates and derivatives	3,4,5-trihydroxy-6-{[4-methoxy-6-(3-oxoprop-1-en-1-yl)-2H-1,3-benzodioxol-5-yl]oxy}oxane-2-carboxylic acid	36	-8.18	88.88
321.23819	11.01	Fatty Acyls - Eicosanoids	15-deoxy-delta-12,14-PGJ2-d4	37.7	6.14	95.56
337.23571	2.870	Fatty Acyls - Eicosanoids	8R,9S-cis-epoxy-10S-hydroxy-eicosa-11Z,14Z-dienoic acid.	37.5	-8.06	96.74
295.26429	3.436	Fatty Acyls - Fatty Acids	13-Cyclohexyltridecanoic acid	38.7	0.12	93.42
196.97605	0.694	Fatty Acyls - Fatty Acids	(Â±)-Sulfobutanedioic acid	39.4	-0.51	97.48
277.21560	1.424	Fatty Acyls - Fatty Acids	2E,4E,6E,11Z-octadecatetraenoic acid	36.7	-2.18	86.07
267.23316	2.774	Fatty Acyls - Fatty Acids	2-heptadecylenic acid	38.6	0.75	93.79
249.18637	1.743	Fatty Acyls - Fatty Acids	4,7,10-hexadecatrienoic acid	39.2	1.45	97.69
311.29559	4.394	Fatty Acyls - Fatty Acids	Arachidic acid	38.7	0.13	93.63
279.23035	1.439	Fatty Acyls - Fatty Acids	Columbinic acid	38.5	-5.43	98.54
381.37343	6.469	Fatty Acyls - Fatty Acids	Mycosanoic acid (C25)	38.2	-0.99	92.26
381.37307	12.44	Fatty Acyls - Fatty Acids	Mycosanoic acid (C25)	37.3	-1.93	88.58
395.38870	12.44	Fatty Acyls - Fatty Acids	Mycosanoic acid (C26)	37.6	-1.91	90.17
367.35795	6.061	Fatty Acyls - Fatty Acids	Mycosanoic acid (C24)	38.9	-0.56	95.00
241.21735	11.61	Fatty Acyls - Fatty Acids	Pentadecanoic acid	39.4	0.19	97.39
241.21766	2.503	Fatty Acyls - Fatty Acids	Pentadecanoic acid	39.1	1.48	97.49
160.13354	0.949	Fatty Acyls - Fatty Acids	DL-2-amino-octanoic acid	39.2	2.13	98.46
425.11165	5.346	Fatty Acyls - glycosides	6-{[3,4-dihydroxy-4-(1-oxo-1H-isochromen-3-yl)butan-2-yl]oxy}-3,4,5-trihydroxyoxane-2-carboxylic acid	36.3	6.37	88.84
125.09712	5.407	Fatty acyls - Fatty Alcohol	1,5E-Octadien-3-ol	39	-0.57	95.53
302.19652	0.481	Fatty acyls - Fatty Esters	3-hydroxy-cis-5-octenoylcarnitine	39.5	1.07	98.73
593.38554	12.00	Fatty Acyls - Lineolic acids	Hericenone E	37.7	1.30	90.22
311.22256	1.020	Fatty Acyls - Octadecanoids	8R,11S-DiHODE	38.9	-0.71	95.33
309.20785	0.919	Fatty Acyls - Octadecanoids	9-HpOTrE	38.9	2.31	97.26
297.24355	1.818	Fatty Acyls - Octadecanoids	Isoricinoleic Acid	38.7	0.12	93.53
253.09256	0.747	Glycerolipids	Galactosylglycerol	38.8	-1.30	95.59
655.52427	5.014	Glycerolipids	DG(17:2(9Z,12Z)/22:4(7Z,10Z,13Z,16Z)/0:0)[iso2]	37.1	-8.14	94.68
707.64973	8.119	Glycerolipids	DG(20:1(11Z)/22:0/0:0)[iso2]	37.7	-7.18	96.41
551.50101	7.663	Glycerolipids	DG(P-14:0/18:1(9Z))	36.1	-4.32	85.48
735.65648	7.096	Glycerolipids	TG(12:0/14:1(9Z)/17:0)[iso6]	37.3	9.20	96.50
733.64113	6.603	Glycerolipids	TG(14:1(9Z)/14:1(9Z)/15:0)[iso3]	36.3	9.64	91.92
760.59121	4.820	Glycerophospholipids	PC(12:0/22:1(11Z))	37.7	8.07	97.36
786.60847	5.459	Glycerophospholipids	PC(14:0/22:1(11Z))	37.8	8.44	98.32
784.59313	4.968	Glycerophospholipids	PC(16:0/20:2(11Z,14Z))	36.7	8.85	93.29
758.56987	6.850	Glycerophospholipids	PC(18:0/16:2(2E,4E))	38.6	0.58	93.87
744.55232	5.424	Glycerophospholipids	PE(18:1(11Z)/18:1(11Z))	34.8	-1.97	76.55
734.56840	5.306	Glycerophospholipids	PE(19:0/16:0)	36.6	-1.41	84.85
722.50485	1.687	Glycerophospholipids	1,2-dipalmitoyl-sn-glycero-3-phospho-(1'-sn-glycerol)(1−)	37	-6.08	91.94
721.50642	4.450	Glycerophospholipids	PG(12:0/20:1(11Z))	37.8	6.95	96.88
747.52276	5.533	Glycerophospholipids	PG(12:0/22:1(11Z))	36	6.15	87.01
773.53340	5.632	Glycerophospholipids	PG(18:1(11Z)/18:1(11Z))	39.1	-0.53	96.14
705.51190	7.538	Glycerophospholipids	PG(P-16:0/16:1(9Z))	37.3	7.66	95.20

751.48602	5.032	Glycerophospholipids	PG(P-16:0/20:5(5Z,8Z,11Z,14Z,17Z))	35.7	-7.88	87.51
803.62337	6.389	Glycerophospholipids	PG(P-20:0/19:1(9Z))	36.4	9.12	92.29
333.05889	0.637	Glycerophospholipids	1-(sn-Glycero-3-phospho)-1D-myo-inositol	39.5	-1.01	98.96
713.42200	1.131	Glycerophospholipids	PI(13:0/12:0)	39.2	-2.18	98.45
958.74782	8.204	Glycerophospholipids	PS(24:0/24:0)	38.1	-0.35	90.94
711.49431	4.908	Glycerophospholipids	PA(18:4(6Z,9Z,12Z,15Z)/19:0)	37.4	-2.28	89.67
739.52501	5.656	Glycerophospholipids	PA(18:4(6Z,9Z,12Z,15Z)/21:0)	38.5	-3.00	96.03
607.47319	7.747	Glycerophospholipids	PA(O-16:0/14:0)	34.5	5.73	79.18
1235.83678	6.576	Glycopeptidolipid	GPL C-II	36.6	9.40	93.48
172.07269	0.903	Keto acids and derivatives	2-Oxoarginine	39.3	-0.46	97.25
439.20349	7.743	Others	Amoxicilloyl-butylamine	37.6	5.75	94.37
129.01931	0.682	Others	Glutaconic acid	39.9	-0.14	99.66
200.09225	0.736	Others	3-Methyl-3H-imidazo[4,5-f]quinoxalin-2-amine	35.7	-4.10	83.08
407.16479	1.674	Polyketides	3-(3-hydroxyphenyl)-2-phenyl-4-[(E)-2-phenylethenyl]-2,3-dihydro-1-benzofuran-6-ol	36.7	1.53	85.48
317.17285	0.660	Polyketides	[8]-Dehydrogingerdione	35.6	-9.37	88.23
369.08463	0.675	Polyketides	5-Hydroxy-6-methoxycoumarin 7-glucoside	37.5	5.16	93.58
339.07486	3.797	Polyketides	Aesculin	36.5	7.95	91.14
307.06141	5.430	Polyketides	3',4'-Methylenedioxy-[2",3":7,8]furanoflavanone	37.6	0.70	88.68
409.02520	6.806	Polyketides	6-Hydroxyluteolin 6,3'-dimethyl ether 7-sulfate	37.2	4.18	90.82
341.14207	8.461	Polyketides	Brosimacutin C	35.8	7.65	87.55
331.08258	6.809	Polyketides	Dihydrotricetin 7,3'-dimethyl ether	37.2	0.76	86.97
571.03933	12.47	Polyketides	Isorhamnetin 3-glucuronide-7-sulfate	35.8	-1.05	80.43
355.19400	10.36	Polyketides	Nitenin	35.2	7.06	84.01
423.10581	3.428	Polyketides	Thonningine A	37.8	-3.88	93.43
571.14882	0.797	Polyketides	2",4",6"-Triacetylglycitin	36.2	5.43	87.38
657.09781	0.667	Polyketides	3,4,5-trihydroxy-6-({7,8,11,12,13,21,22,23-octahydroxy-3,16-dioxo-2,17,20-trioxatetracyclotricosa-4,6,8,10,12,14-hexaen-6-yl}oxy)oxane-2-carboxylic acid	36.3	5.08	87.36
327.12635	7.721	Polyketides	2',3',4',6'-Tetramethoxychalcone	35.3	7.79	85.41
363.25149	3.025	Prenol lipids	6-O-Acetylaustroinulin	36.7	-7.12	91.28
562.48317	3.782	Prenol lipids	35-aminobacteriohopane-31,32,33,34-tetrol	37.9	0.33	89.80
571.40349	5.018	Prenol lipids	Hericenone C	38	7.32	98.05
851.69198	8.343	Prenol lipids	3-demethylubiquinol-10	37.9	0.93	90.64
481.26169	4.381	Prenol lipids	Citronellyl beta-sophoroside	37.4	-5.52	93.26
557.38761	4.797	Prenol lipids	3beta,15alpha-Diacetoxylanosta-8,24-dien-26-oic acid	37.8	7.09	97.19
625.55044	5.888	Prenol lipids	Faradiol laurate	37.9	-7.98	98.33
531.40771	5.271	Prenol lipids	alpha-Tocopherol succinate	37	6.24	92.05
135.03136	1.506	Purine and derivatives	Hypoxanthine	39.2	0.92	97.33
137.04648	1.521	Purine and derivatives	Hypoxanthine	38.3	5.13	97.55
135.03156	1.700	Purine and derivatives	Hypoxanthine	39	2.43	97.77
136.06242	0.953	Purine Nucleosides and analogues	Adenine	38.8	4.77	99.72
252.10893	1.540	Purine Nucleosides and analogues	Deoxyadenosine	37.3	-0.75	87.55

253.09279	1.464	Purine Nucleosides and analogues	Deoxyinosine	39.1	-1.34	97.01
152.05715	0.858	Purine Nucleosides and analogues	Guanine	39.2	3.10	99.70
152.05726	0.961	Purine Nucleosides and analogues	Guanine	38.5	3.77	97.03
150.04214	1.502	Purine Nucleosides and analogues	Guanine	39.9	0.02	99.42
150.04212	1.666	Purine Nucleosides and analogues	Guanine	39.8	-0.09	99.08
282.08396	1.502	Purine Nucleosides and analogues	Guanosine	39.2	-1.54	97.63
284.09842	1.514	Purine Nucleosides and analogues	Guanosine	39.3	-1.84	98.76
127.05073	2.052	Pyrimidine and derivatives	Thymine	38.3	4.15	96.18
127.05070	2.223	Pyrimidine and derivatives	Thymine	39	3.97	99.70
267.07445	1.510	Pyrimidine and derivatives	formycin B	38.7	3.57	97.92
112.05114	1.186	Pyrimidine nucleosides and analogues	Cytosine	38.2	5.43	97.14
241.08295	2.037	Pyrimidine Nucleosides and analogues	Thymidine	32.2	-0.17	60.99
565.04502	12.38	Pyrimidine Nucleosides and analogues	UDPglucose	33.8	-4.81	74.64
243.06203	1.342	Pyrimidine Nucleosides and analogues	Uridine	39.3	-0.95	97.84
1255.79365	6.473	Sphingolipids	GalNAcbeta1-3Galalpha1-4Galbeta1-4Glcbeta-Cer(d18:1/18:0)	38	4.09	94.93
1279.86532	6.740	Sphingolipids	Ganglioside GM3 (d18:1/25:0)	37.7	3.16	92.11
1279.86494	6.629	Sphingolipids	Ganglioside GM3 (d18:1/25:0)	37.8	2.86	92.29
600.46876	1.893	Sphingolipids	N-(3E-hexadecenoyl)-deoxysphing-4-enine-1-sulfonate	36.6	5.23	89.19
721.58386	6.446	Sphingolipids	N-heptadecanoyl-4-hydroxy-15-methylhexadecasphinganine-1-phosphocholine	38.7	-2.15	96.24
705.55266	5.652	Sphingolipids	PE-Cer(d14:1(4E)/22:0(2OH))	37.4	-2.07	89.72
689.52258	5.289	Sphingolipids	PE-Cer(d15:1(4E)/20:0(2OH))	38.1	-1.93	92.56
689.52279	5.384	Sphingolipids	PE-Cer(d15:1(4E)/20:0(2OH))	37.4	-1.62	89.02
556.52950	6.003	Sphingolipids	Armillaramide	39.4	-0.79	97.91
564.53256	6.477	Sphingolipids	Cer(d14:1/22:1)	35.3	-4.36	81.60
512.50342	5.987	Sphingolipids	Cer(d18:0/14:0)	39.6	-0.59	98.50
526.51895	6.408	Sphingolipids	Cer(d18:0/15:0)	39.2	-0.80	96.94
642.47973	4.382	Sphingolipids	N-oleoylsphingosine 1-phosphate(2−)	35.6	-9.32	88.48
474.28628	2.601	Steroids and derivatives	Hydrocortamate	37.2	0.35	86.28
437.23555	4.126	Steroids and derivatives	Flurandrenolide	38.4	4.95	97.89
393.20956	3.843	Steroids and derivatives	Paramethasone	37	6.08	92.02
479.30415	11.90	Steroids and derivatives	22-deoxy-20,21-dihydroxyecdysone	34.6	5.68	79.25
471.30802	0.759	Steroids and derivatives	(25R)-26,26,26-trifluoro-1alpha,25-dihydroxyvitamin D3 / (25R)-26,26,26-trifluoro-1alpha,25-dihydroxycholecalciferol	39.4	-0.08	96.97
497.28039	2.294	Alkaloids	prochaetoglobosin II	38.4	1.05	93.31
452.27812	1.565	Alkaloids	Cytochalasin Opho	37.1	-3.13	89.32
338.19325	3.074	Alkaloids	3,6-Ditigloyloxytropan-7-ol	36.2	-8.75	90.47
216.12242	3.074	Amino acids and analogues	1-hydroxyoct-3-enoylglycine	38.7	-2.87	96.67
246.15576	0.633	Amino acids and analogues	Alanyl-Arginine	36.2	-1.23	82.36
187.10772	1.220	Amino acids and analogues	Alanyl-Proline	38.9	-0.02	94.38
304.16220	0.644	Amino acids and analogues	Arginyl-Glutamic acid	38.7	2.16	96.26
274.18703	0.781	Amino acids and analogues	Arginyl-Valine	39.3	-1.23	97.92
321.13108	8.956	Amino acids and analogues	Avenic acid A	37.5	2.29	90.15

350.20608	0.660	Amino acids and analogues	Coutaric acid	35.5	-3.87	82.27
209.05991	0.728	Amino acids and analogues	Cysteinyl-Serine	38	4.10	94.64
130.08687	0.595	Amino acids and analogues	D-Pipecolic acid	38.8	4.74	99.51
130.08694	0.968	Amino acids and analogues	D-Pipecolic acid	38.6	5.28	99.07
261.14410	1.563	Amino acids and analogues	gamma-Glutamylisoleucine	39.3	-1.55	98.24
219.09727	0.861	Amino acids and analogues	Glutamylalanine	39.3	-1.28	98.25
189.12351	0.968	Amino acids and analogues	Glycylleucine	36.2	0.77	82.15
245.18541	3.241	Amino acids and analogues	Isoleucyl-Isoleucine	38	-2.27	92.93
245.18542	3.531	Amino acids and analogues	Isoleucyl-Isoleucine	39.2	-2.23	98.73
258.18177	0.919	Amino acids and analogues	Isoleucyl-Lysine	37.9	-2.10	91.84
233.14914	1.426	Amino acids and analogues	Isoleucyl-Threonine	39.1	-1.90	97.54
233.14903	2.311	Amino acids and analogues	Isoleucyl-Threonine	39.2	-2.40	98.71
231.16970	2.669	Amino acids and analogues	Isoleucyl-Valine	39	-2.69	98.18
231.16978	2.482	Amino acids and analogues	Isoleucyl-Valine	38.9	-2.33	97.17
229.15529	2.665	Amino acids and analogues	Isoleucyl-Valine	38.3	-2.06	93.96
229.15534	2.913	Amino acids and analogues	Isoleucyl-Valine	38.3	-1.87	93.67
231.16982	2.917	Amino acids and analogues	Isoleucyl-Valine	39	-2.19	97.78
173.10440	0.618	Amino acids and analogues	L-Arginine	39.6	-0.01	98.24
132.03027	0.637	Amino acids and analogues	L-Aspartic acid	39.6	0.31	98.34
357.21418	1.127	Amino acids and analogues	Leu-Gln-Pro	38.2	2.63	94.30
156.07705	0.621	Amino acids and analogues	L-Histidine	39.5	1.89	99.71
154.06213	0.614	Amino acids and analogues	L-Histidine	39.4	-0.45	97.73
198.12365	0.641	Amino acids and analogues	L-Histidine trimethylbetaine	39.6	-0.26	98.36
132.10244	1.495	Amino acids and analogues	L-Leucine	38.9	4.12	99.25
147.11324	0.595	Amino acids and analogues	L-Lysine	38.9	2.95	98.15
145.09816	0.587	Amino acids and analogues	L-Lysine	38.8	-0.64	94.94
116.07132	0.743	Amino acids and analogues	L-Proline	38.4	6.25	99.07
180.06650	1.358	Amino acids and analogues	L-Tyrosine	39.2	-0.62	96.80
345.13060	1.499	Amino acids and analogues	Mytilin B	39.1	0.74	96.44
187.10790	1.411	Amino acids and analogues	N6-Acetyl-L-lysine	37.9	-4.89	95.15
187.10802	0.960	Amino acids and analogues	N6-Acetyl-L-lysine	38.4	-4.23	96.76
203.13885	0.892	Amino acids and analogues	N-alpha-acetyl lysine methyl ester	39.6	-0.82	98.89
242.17567	7.751	Amino acids and analogues	N-Undecanoylglycine	38.9	-2.06	97.08
263.13837	3.424	Amino acids and analogues	Phenylalanylproline	38.9	-2.48	97.45
187.10775	0.869	Amino acids and analogues	Prolyl-Alanine	38.6	0.14	93.26
130.05030	1.236	Amino acids and analogues	Pyrrolidonecarboxylic acid	39.2	3.32	99.79
130.05044	0.675	Amino acids and analogues	Pyrrolidonecarboxylic acid	38.8	4.46	99.09
277.14029	8.941	Amino acids and analogues	Saccharopine	38.5	3.18	96.35
217.15421	1.914	Amino acids and analogues	Valyl-Valine	38.9	-2.12	97.15
263.16474	11.12	Benzene and substituted derivatives	3,5-Bis(1,1-dimethylethyl)-4-hydroxy-benzoic acid ethyl ester	38.4	-2.01	94.35
150.00168	12.47	Benzene and substituted derivatives	4-Thiocyanatophenol	35	-1.49	76.77

368.16839	2.505	Benzene and substituted derivatives	Amisulpride	35.2	9.33	86.19
180.06566	0.797	Benzene and substituted derivatives	Hippuric acid	39.2	0.79	96.81
212.12784	1.537	Benzene and substituted derivatives	Isoproterenol	37.5	-1.31	88.91
307.19179	0.919	Benzene and substituted derivatives	Methylgingerol	38.1	0.99	91.79
307.19147	0.672	Benzene and substituted derivatives	Methylgingerol	38.4	-0.06	92.18
275.07442	1.510	Benzene and substituted derivatives	modafinil acid	35.3	2.84	80.08
136.07591	1.369	Benzene and substituted derivatives	N-Acetylarylamine	39.4	1.63	99.05
281.05279	1.499	Benzene and substituted derivatives	Niflumic Acid	37.9	-5.49	95.74
183.01197	11.08	Benzene and substituted derivatives	Polystyrene sulfonate	37.9	-0.94	90.86
220.14716	12.48	Benzene and substituted derivatives	Procarbazine	36.6	7.33	91.28
447.24588	11.03	Benzene and substituted derivatives	SR 49498	36.5	-9.90	93.10
302.24960	2.520	Benzene and substituted derivatives	Trihexyphenidyl	36.8	5.85	90.51
327.07778	7.743	Benzene and substituted derivatives	triphenyl phosphate	39.4	-0.89	97.97
491.23211	1.295	Benzene and substituted derivatives	Glimepiride	35.9	-0.33	79.80
370.08255	0.781	Benzene and substituted derivatives	Lansoprazole	37	-1.65	86.79
289.05405	1.754	Benzene and substituted derivatives	N-Desalkyl flurazepam	34.6	0.70	73.94
382.23912	2.199	Benzene and substituted derivatives	(E,E,E)-Sylvatine	38.1	0.91	91.52
521.31560	11.82	Benzene and substituted derivatives	Metabolite M6	38	4.34	95.13
373.07138	6.806	Benzene and substituted derivatives	Neodiospyrin	37.8	-1.01	90.01
280.09776	0.728	Benzene and substituted derivatives	Graveoline	37.9	3.38	93.38
121.02990	12.47	Benzene and substituted derivatives	methyl-1,4-benzoquinone	38.6	3.23	96.72
255.03280	3.382	Benzene and substituted derivatives	[(3-methyl-2-oxo-4-phenylbut-3-en-1-yl)oxy]sulfonic acid	37.2	-1.84	88.31
271.06372	4.351	Benzene and substituted derivatives	[4-(4-methyl-3-oxopentyl)phenyl]oxidanesulfonic acid	37	-3.13	88.87
387.11396	0.721	Benzene and substituted derivatives	Sulfinpyrazone sulfide	34.2	-8.53	80.68
465.08672	1.944	Benzene and substituted derivatives	BL IV	35.3	8.57	86.22
316.17553	2.981	Benzene and substituted derivatives	Alizapride	38	-4.04	94.63
273.05174	3.439	Benzene and substituted derivatives	cis,trans-5'-Hydroxythalidomide	39	0.18	95.08
407.00141	2.223	Benzene and substituted derivatives	6-Hydroxy-5-[(4-sulfophenyl)azo]-2-naphthalenesulfonic acid	36.2	0.23	81.24
547.40351	1.767	Benzene and substituted derivatives	endo-1,4-beta-Xylanase	35.1	5.23	81.65
457.14043	3.436	Carbohydrates and derivatives	12-Hydroxynevirapine glucuronide	36.2	8.60	90.60
895.69531	7.785	Carbohydrates and derivatives	1-archaetidyl-D-myo-inositol	36.2	-4.99	86.68
431.11522	7.721	Carbohydrates and derivatives	6-[1-(6,7-dimethoxy-2H-1,3-benzodioxol-5-yl)-3-oxopropoxy]-3,4,5-trihydroxyoxane-2-carboxylic acid	35.8	-7.40	87.39
165.04033	0.682	Carbohydrates and derivatives	Arabinonic acid	39.4	-0.80	97.80
241.09160	0.614	Carbohydrates and derivatives	D-erythro-D-galacto-octitol	38.3	-5.35	97.83
105.01921	0.759	Carbohydrates and derivatives	Glyceric acid	39.3	-1.16	97.90
341.16366	0.778	Carbohydrates and derivatives	Jasmolone glucoside	35	9.02	84.99
827.26574	0.759	Carbohydrates and derivatives	Maltopentaose	36.9	-2.01	86.91
665.21364	0.896	Carbohydrates and derivatives	Maltotetraose	36.9	-1.41	86.16
372.06936	1.209	Carbohydrates and derivatives	MurNAc-6-P	38.4	-2.03	94.63
423.16111	1.452	Carbohydrates and derivatives	N,N'-diacetylchitobiose	38.5	-2.19	95.35
476.30589	4.381	Carbohydrates and derivatives	Netilmicin	37.5	-4.17	92.14

770.28227	2.037	Carbohydrates and derivatives	Phyllanthusol B	36.2	-7.02	88.99
325.04236	3.428	Carbohydrates and derivatives	Pseudouridine 5'-phosphate	28	-2.43	43.12
864.64239	7.263	Carbohydrates and derivatives	β-D-galactosyl-(1→4)-β-D-glucosyl-(1↔1')-N-hexadecanoylsphinganine	36.7	1.99	85.87
383.10151	8.960	Carbohydrates and derivatives	5-(3',4'-Dihydroxyphenyl)-gamma-valerolactone-4'-O-glucuronide	35.3	8.16	85.53
399.25120	11.05	Fatty acyls - Docosanoids	4,5-epoxy-17R-HDHA	36.5	-4.50	87.48
361.23582	2.588	Fatty acyls - Docosanoids	7,8-DiHDPE	37.1	-7.21	93.56
263.16554	0.931	Fatty Acyls - Eicosanoids	12-Oxo-2,3-dinor-10,15-phytodienoic acid	38.3	1.03	92.88
445.22399	1.554	Fatty Acyls - Eicosanoids	17,18-dehydro-clavulone I	37.6	4.30	93.00
333.20308	10.92	Fatty Acyls - Eicosanoids	5S,6-Ep-18S-HEPE	36.6	-8.91	92.77
323.18463	0.603	Fatty Acyls - Eicosanoids	Dinor-PGD2	37.1	-5.44	91.79
391.22960	5.010	Fatty Acyls - Eicosanoids	Lubiprostone	38.1	1.39	92.10
299.18582	6.215	Fatty Acyls - Eicosanoids	Tetranor-PGF1alpha	38.1	-1.93	92.63
311.25903	2.102	Fatty Acyls - Fatty Acids	10-oxo-nonadecanoic acid	38.6	-0.44	93.66
429.31741	1.988	Fatty Acyls - Fatty Acids	(2E,17R)-17-[(3,6-dideoxy-α-L-arabino-hexopyranosyl)oxy]octadec-2-enoic acid	35.7	-8.54	87.95
457.34999	2.557	Fatty Acyls - Fatty Acids	(2E,19R)-19-[(3,6-dideoxy-α-L-arabino-hexopyranosyl)oxy]eicos-2-enoic acid	36.8	-5.21	89.95
313.23762	9.791	Fatty Acyls - Fatty Acids	(9Z)-(7S,8S)-Dihydroxyoctadecenoic acid	37.4	-2.60	90.19
267.23278	12.48	Fatty Acyls - Fatty Acids	16:1(6Z)(15Me)	37.7	-0.64	89.29
279.23267	12.49	Fatty Acyls - Fatty Acids	16:2(2E,4E)(4Me,6Me[S])	37.4	-1.01	87.98
269.21184	12.50	Fatty Acyls - Fatty Acids	16-hydroxy-9E-hexadecenoic acid	39.2	-1.39	97.69
309.28006	3.701	Fatty Acyls - Fatty Acids	17Z-octadecenoic acid	37.8	0.51	89.64
187.09741	5.407	Fatty Acyls - Fatty Acids	2,4-Dimethylpimelic acid	38.5	-0.94	93.52
239.20189	2.215	Fatty Acyls - Fatty Acids	2,5-dimethyl-2E-tridecenoic acid	38.2	0.98	92.10
363.32632	4.839	Fatty Acyls - Fatty Acids	24:2(5Z,9Z)	38.1	-1.46	92.26
419.38899	6.461	Fatty Acyls - Fatty Acids	27:2(5Z,9Z)(25Me)	37	-1.10	86.27
257.21165	11.14	Fatty Acyls - Fatty Acids	2-hydroxy-pentadecanoic acid	37.6	-2.20	90.49
225.11283	5.517	Fatty Acyls - Fatty Acids	3,7-Dimethyl-2E,6E-decadien-1,10-dioic acid	38.2	-1.78	92.90
275.20169	1.182	Fatty Acyls - Fatty Acids	3,8-octadecadiynoic acid	38.7	0.12	93.85
279.23020	11.10	Fatty Acyls - Fatty Acids	5,8,11-octadecatrienoic acid	37.2	-5.95	92.78
301.21684	12.49	Fatty Acyls - Fatty Acids	5Z,8Z,14Z-Eicosatrien-11-ynoic acid	37.2	-1.55	87.82
277.21738	1.440	Fatty Acyls - Fatty Acids	6,10,14-octadecatrienoic acid	38.8	0.28	94.20
359.22014	2.239	Fatty Acyls - Fatty Acids	7,9,13,17-tetramethyl-7S,14S-dihydroxy-2E,4E,8E,10E,12E,16-octadecahexaenoic acid	36.4	-7.35	90.27
299.20010	12.43	Fatty Acyls - Fatty Acids	8,11,14,18-Eicosatetraynoic acid	37.7	-5.17	94.44
243.19607	11.08	Fatty Acyls - Fatty Acids	alpha-hydroxy myristic acid	38.5	-2.06	94.90
243.19609	11.02	Fatty Acyls - Fatty Acids	alpha-hydroxy myristic acid	38.3	-1.94	93.92
316.33070	3.074	Fatty Acyls - Fatty Acids	Arachidic acid(d3)	37.8	5.59	95.36
397.33247	12.49	Fatty Acyls - Fatty Acids	Axillarenic acid	37.6	0.34	88.40
215.13851	1.967	Fatty Acyls - Fatty Acids	Dethiobiotin	39	-2.39	97.86
371.31628	3.519	Fatty Acyls - Fatty Acids	Docosanedioic acid	38.4	1.87	94.41
369.30095	12.43	Fatty Acyls - Fatty Acids	Docosanedioic acid	37.6	-0.21	88.26
339.28640	2.679	Fatty Acyls - Fatty Acids	Glycidyl oleate	34.9	-8.77	84.00
341.23187	0.781	Fatty Acyls - Fatty Acids	methyl 9,12-dihydroxy-13-oxo-10-octadecenoate	36.7	-4.33	88.40

501.30517	11.10	Fatty Acyls - Fatty Acids	Mupirocin	25.2	-1.27	27.67
423.41964	12.45	Fatty Acyls - Fatty Acids	Mycocerosic acid (C28)	37.9	-2.64	92.39
395.38907	6.860	Fatty Acyls - Fatty Acids	Mycosanoic acid (C26)	38.2	-0.96	92.01
397.33224	4.109	Fatty Acyls - Fatty Acids	Tetracosanedioic acid	38.1	-0.25	90.64
383.31849	12.49	Fatty Acyls - Fatty Acids	Tricosanedioic acid	36.4	4.71	87.37
146.11794	0.755	Fatty Acyls - Fatty Acids	2R-aminoheptanoic acid	39.2	2.64	99.23
174.14901	2.273	Fatty Acyls - Fatty Acids	3R-aminononanoic acid	38.9	0.88	95.51
189.15972	0.621	Fatty Acyls - Fatty Acids	7,8-Diaminononanoate	39.5	-0.19	97.70
187.09809	12.49	Fatty Acyls - Fatty Acids	Azelaic acid	38.7	2.70	96.67
296.09731	0.682	Fatty Acyls - glycosides	(S)-malyl alpha-D-glucosaminide	36.8	-1.01	85.37
675.54085	5.923	Fatty Acyls - glycosides	1-(O-alpha-D-glucopyranosyl)-29-keto-(1,3R,31R)-dotriacontanetriol	37.4	0.42	87.40
601.46870	4.630	Fatty Acyls - glycosides	1-(O-alpha-D-glucopyranosyl)-3-keto-(1,27R)-octacosanediol	38.7	0.35	94.15
333.18787	4.156	Fatty Acyls - glycosides	2,6-Dimethyl-6-O-beta-D-quinovopyranosyl-7-octadecenoic acid	37.2	-8.76	95.50
383.13702	0.911	Fatty Acyls - glycosides	3,4,5-trihydroxy-6-{[5-(4-methoxyphenyl)-3-oxopentan-2-yl]oxy}oxane-2-carboxylic acid	37.3	5.89	93.06
503.32029	2.798	Fatty Acyls - glycosides	3-O-alpha-L-rhamnopyranosyl-3-hydroxydecanoyl-3-hydroxydecanoic acid	37.4	-4.49	92.44
197.19064	11.08	Fatty acyls - Fatty Alcohol	10E-Tridecen-2S-ol	38.2	-2.24	93.53
277.18024	11.20	Fatty acyls - Fatty Alcohol	Panaxytriol	37.2	-2.44	89.14
218.10307	2.265	Fatty Acyls - Fatty alcohol	Pantothenic acid	38.3	-1.47	93.13
220.11778	2.265	Fatty Acyls - Fatty alcohol	Pantothenic acid	39.5	-0.79	98.42
529.46220	7.534	Fatty acyls - Fatty Alcohol	Sabadelin	38.8	-0.79	94.80
205.15951	11.11	Fatty Acyls - Fatty aldehyde	9Z,11E,13-Tetradecatrienal	38.7	-1.37	95.09
388.25370	3.843	Fatty Acyls - Fatty amides	N-linoleoyl taurine	36.5	5.40	88.52
204.12294	0.766	Fatty acyls - Fatty Esters	L-Acetylcarnitine	39	-0.48	95.63
286.20086	2.882	Fatty acyls - Fatty Esters	(2E)-octenoylcarnitine	39.4	-1.49	98.72
458.34814	1.809	Fatty acyls - Fatty Esters	O-(17-carboxyheptadecanoyl)carnitine	37.4	1.14	88.36
365.34213	5.603	Fatty acyls - Fatty Esters	11-Docosenyl acetate	38.3	-1.03	92.68
183.13869	6.813	Fatty acyls - Fatty Esters	6E-Nonenyl acetate	37.7	-1.97	90.87
339.32613	12.44	Fatty acyls - Fatty Esters	Eicosyl acetate	36.7	-2.14	85.92
339.32659	5.234	Fatty acyls - Fatty Esters	Eicosyl acetate	38.1	-0.78	91.59
473.43658	2.296	Fatty acyls - Fatty Esters	Linolenyl myristate	37.8	0.38	89.32
531.44462	6.489	Fatty acyls - Fatty Esters	Mayolene-16	36.5	5.13	88.57
353.34159	12.42	Fatty acyls - Fatty Esters	tridecyl decanoate	36.8	-2.57	87.04
353.34218	5.648	Fatty acyls - Fatty Esters	tridecyl decanoate	37.6	-0.93	89.12
593.38616	10.35	Fatty Acyls - Lineolic acids	Hericenone E	38.6	2.35	95.76
225.14925	6.352	Fatty Acyls - Lineolic acids	Methyl dihydrojasmonate	38.2	-1.64	93.05
313.23843	1.675	Fatty Acyls - Octadecanoids	10S-HpOME	38.7	-0.02	93.74
297.24322	12.50	Fatty Acyls - Octadecanoids	2R-hydroxy-oleic acid	38.6	-1.01	94.35
329.23318	0.657	Fatty Acyls - Octadecanoids	5,8,12-TriHOME(9)	38.5	-0.52	93.03
289.17746	0.561	Fatty Acyls - Octadecanoids	8-hydroxy-13,17-octadecadiene-9,11-diynoic acid	33.6	-8.18	77.29
311.22263	1.452	Fatty Acyls - Octadecanoids	8R,11S-DiHODE	38.4	-0.50	92.84
327.21647	0.607	Fatty Acyls - Octadecanoids	9,12,13,TriHODE	38.4	-3.73	96.42

309.20802	1.031	Fatty Acyls - Octadecanoids	9-HpOTrE	38.5	2.87	95.97
295.22594	1.417	Fatty Acyls - Octadecanoids	alpha-kamlolenic acid	38.7	-2.84	96.72
407.42967	4.650	Fatty acyls - others	11-Methylheptacosan-2-one	36.9	9.39	95.00
751.53169	6.077	Glycerolipids	(2S)-1-O-(7Z,10Z)-hexadecadienoyl-2-O-linoleoyl-3-O-β-D-galactopyranosyl-sn-glycerol	36.6	-5.04	88.73
793.51412	5.226	Glycerolipids	1,2-Di-O-palmitoyl-3-O-(6-sulfoquinovopyranosyl)glycerol	37.8	0.00	89.16
301.16622	2.065	Glycerolipids	Glycerol tributanoate	38.3	1.85	93.78
411.34927	12.49	Glycerolipids	MG(0:0/22:1(13Z)/0:0)	36.5	3.11	86.25
781.58185	7.039	Glycerolipids	MGDG(18:1(9Z)/18:1(9Z))	38	-2.14	92.69
589.48560	5.715	Glycerolipids	DG(12:0/22:3(10Z,13Z,16Z)/0:0)[iso2]	37.1	3.14	89.01
547.43942	4.798	Glycerolipids	DG(13:0/18:3(9Z,12Z,15Z)/0:0)[iso2]	36.9	4.78	89.89
573.45282	5.044	Glycerolipids	DG(13:0/20:4(5Z,8Z,11Z,14Z)/0:0)[iso2]	36.9	0.65	85.14
651.49413	4.594	Glycerolipids	DG(17:2(9Z,12Z)/22:5(7Z,10Z,13Z,16Z,19Z)/0:0)[iso2]	34.3	-8.07	80.36
639.49418	4.674	Glycerolipids	DG(18:4(6Z,9Z,12Z,15Z)/20:2(11Z,14Z)/0:0)[iso2]	34.8	-8.14	83.00
665.50964	4.895	Glycerolipids	DG(18:4(6Z,9Z,12Z,15Z)/22:3(10Z,13Z,16Z)/0:0)[iso2]	35.2	-8.12	85.25
691.62894	5.744	Glycerolipids	DG(19:0/22:1(13Z)/0:0)[iso2]	35.6	6.26	85.01
699.59387	12.46	Glycerolipids	DG(20:0/22:5(7Z,10Z,13Z,16Z,19Z)/0:0)[iso2]	36.9	2.38	87.46
723.58585	5.104	Glycerolipids	DG(22:1(13Z)/22:6(4Z,7Z,10Z,13Z,16Z,19Z)/0:0)	35.3	-8.79	86.21
775.71599	11.03	Glycerolipids	TG(15:0/o-18:0/14:1(9Z))	36.5	-3.24	86.18
857.66760	7.088	Glycerolipids	TG(13:0/20:5(5Z,8Z,11Z,14Z,17Z)/20:5(5Z,8Z,11Z,14Z,17Z))[iso3]	38.4	2.60	95.24
893.76236	11.01	Glycerolipids	TG(13:0/20:5(5Z,8Z,11Z,14Z,17Z)/22:1(11Z))[iso6]	30	3.46	53.87
839.70922	10.51	Glycerolipids	TG(14:0/15:0/22:5(7Z,10Z,13Z,16Z,19Z))	35.2	-3.69	80.32
851.71431	10.43	Glycerolipids	TG(14:1(9Z)/20:4(5Z,8Z,11Z,14Z)/18:1(11Z))	34.5	2.34	75.26
853.72538	10.65	Glycerolipids	TG(15:0/15:0/22:5(7Z,10Z,13Z,16Z,19Z))[iso3]	37.1	-3.04	89.16
881.75631	10.88	Glycerolipids	TG(16:0/16:0/22:5(4Z,7Z,10Z,13Z,16Z))	37.3	-3.35	90.43
857.66433	6.759	Glycerolipids	TG(17:2(9Z,12Z)/18:4(6Z,9Z,12Z,15Z)/18:4(6Z,9Z,12Z,15Z))[iso3]	36.2	-1.21	82.21
977.85310	11.32	Glycerolipids	TG(18:3(6Z,9Z,12Z)/21:0/22:2(13Z,16Z))[iso6]	39	-1.19	96.24
1033.91815	11.76	Glycerolipids	TG(21:0/22:2(13Z,16Z)/22:3(10Z,13Z,16Z))[iso6]	38.2	1.24	92.42
973.86350	11.41	Glycerolipids	TG(22:6(4Z,7Z,10Z,13Z,16Z,19Z)/22:1(13Z)/o-18:0)	37.2	4.26	90.77
695.61741	7.587	Glycerolipids	TG(i-20:0/i-12:0/8:0)	37.2	-1.45	87.93
717.56813	7.014	Glycerophospholipids	1-O-[(Z)-tetradec-1-enyl]-2-O-[(Z)-octadec-9-enoyl]-sn-glycero-3-phosphocholine	37	2.01	87.30
666.44724	6.557	Glycerophospholipids	1-palmitoyl-2-lauroyl-sn-glycero-3-phospho-(1'-sn-glycerol)(1−)	37.9	0.91	90.72
760.57734	2.363	Glycerophospholipids	1-O-palmitoyl-2-O-[1-14C]-linoleoyl-sn-glycero-3-phosphocholine	37.7	-4.31	93.52
761.37221	2.559	Glycerophospholipids	2'-O-(α-D-Manp)-(1-octadecanoyl-sn-glycero-3-phospho-1'-myo-inositol) (18:0/0:0)	35.7	-1.06	79.87
1307.89526	6.995	Glycerophospholipids	CL(8:0/i-12:0/18:2(9Z,11Z)/23:0)	36.7	-4.58	88.81
690.50748	6.123	Glycerophospholipids	PC(12:0/17:1(9Z))	36	0.94	81.06
688.49498	6.121	Glycerophospholipids	PC(12:0/17:1(9Z))	34.9	3.92	79.03
718.54482	6.736	Glycerophospholipids	PC(12:0/19:1(9Z))	33.5	9.32	77.80
728.53035	4.168	Glycerophospholipids	PC(12:0/20:2(11Z,14Z))	36.1	9.28	90.92
728.53066	4.085	Glycerophospholipids	PC(12:0/20:2(11Z,14Z))	35.3	9.71	87.17
756.56124	4.734	Glycerophospholipids	PC(14:0/20:2(11Z,14Z))	34.3	8.40	80.68
788.62068	5.462	Glycerophospholipids	PC(14:0/22:1(11Z))	36.7	5.45	89.68

770.57650	5.121	Glycerophospholipids	PC(15:0/20:2(11Z,14Z))	34.5	7.73	81.01
770.57677	4.658	Glycerophospholipids	PC(15:0/20:2(11Z,14Z))	34.8	8.09	83.15
766.54680	4.017	Glycerophospholipids	PC(15:0/20:4(5Z,8Z,11Z,14Z))	35.5	9.87	88.32
786.60736	4.968	Glycerophospholipids	PC(16:0/20:2(11Z,14Z))	36.9	8.43	94.11
800.61643	7.084	Glycerophospholipids	PC(17:0/20:2(11Z,14Z))	39.5	0.06	97.40
756.55324	6.848	Glycerophospholipids	PC(17:2(9Z,12Z)/17:0)	37.6	-2.16	90.51
766.53050	1.672	Glycerophospholipids	PC(20:5(5Z,8Z,11Z,14Z,17Z)/15:0)	36.1	-9.96	91.24
828.55869	5.990	Glycerophospholipids	PC(22:6(4Z,7Z,10Z,13Z,16Z,19Z)/18:2(9Z,12Z))	36	4.59	85.44
854.57485	6.125	Glycerophospholipids	PC(22:6(4Z,7Z,10Z,13Z,16Z,19Z)/20:3(8Z,11Z,14Z))	35.1	5.06	81.46
860.75243	10.56	Glycerophospholipids	PC(O-20:0/22:0)	34.8	6.70	81.62
690.50620	4.486	Glycerophospholipids	PE(16:0/16:0)	37.4	-2.50	90.03
734.56297	7.534	Glycerophospholipids	PE(16:0/19:0)	35.2	-8.81	85.90
450.26244	1.561	Glycerophospholipids	PE(16:1(9Z)/0:0)	38.4	-0.37	92.54
678.50047	6.237	Glycerophospholipids	PE(17:0/14:0)	36.2	-9.39	91.48
718.53729	5.426	Glycerophospholipids	PE(17:0/17:0)	36.6	-2.69	86.30
782.57499	4.820	Glycerophospholipids	PE(17:0/22:4(7Z,10Z,13Z,16Z))	37.2	7.11	94.09
766.54246	4.485	Glycerophospholipids	PE(18:0/20:5(5Z,8Z,11Z,14Z,17Z))	34.8	5.66	80.64
716.52057	4.638	Glycerophospholipids	PE(18:1(11Z)/16:0)	34.6	-4.20	78.09
730.53651	4.988	Glycerophospholipids	PE(18:1(11Z)/17:0)	38.1	-3.71	94.69
796.59010	5.077	Glycerophospholipids	PE(18:4(6Z,9Z,12Z,15Z)/22:0)	37.3	6.30	93.46
850.62728	6.942	Glycerophospholipids	PE(22:0/22:5(4Z,7Z,10Z,13Z,16Z))	36.7	-5.60	89.72
798.60712	5.397	Glycerophospholipids	PE(22:2(13Z,16Z)/18:0)	36.7	6.62	91.09
842.57582	6.273	Glycerophospholipids	PE(22:6(4Z,7Z,10Z,13Z,16Z,19Z)/22:2(13Z,16Z))	36.1	6.27	87.72
735.52035	5.715	Glycerophospholipids	PG(12:0/21:0)	37.2	2.98	89.67
693.47051	5.732	Glycerophospholipids	PG(13:0/17:1(9Z))	35.9	0.57	80.14
745.49983	5.052	Glycerophospholipids	PG(16:1(9Z)/18:1(11Z))	38.8	-3.59	98.11
749.53218	5.907	Glycerophospholipids	PG(17:0/17:0)	36	-2.17	82.38
787.55115	6.040	Glycerophospholipids	PG(17:0/20:2(11Z,14Z))	35.6	2.14	80.65
787.54813	5.961	Glycerophospholipids	PG(17:2(9Z,12Z)/20:0)	36	-1.69	82.22
761.53241	5.765	Glycerophospholipids	PG(18:1(11Z)/17:0)	36.9	-1.83	86.58
567.36456	1.226	Glycerophospholipids	PG(22:1(11Z)/0:0)	36.8	-1.92	86.16
845.54130	5.430	Glycerophospholipids	PG(22:6(4Z,7Z,10Z,13Z,16Z,19Z)/20:2(11Z,14Z))	36	8.85	89.83
499.33469	4.713	Glycerophospholipids	PG(O-18:0/0:0)	36.8	-9.52	94.46
499.33458	4.797	Glycerophospholipids	PG(O-18:0/0:0)	36.4	-9.74	92.87
837.54825	5.803	Glycerophospholipids	1-hexadecanoyl-2-octadecanoyl-sn-glycero-3-phospho-D-myo-inositol	38.1	-1.91	92.71
699.40639	0.767	Glycerophospholipids	PI(12:0/12:0)	39.2	-2.16	98.51
699.40620	0.687	Glycerophospholipids	PI(12:0/12:0)	39	-2.45	97.75
723.41593	2.551	Glycerophospholipids	PI(12:0/14:1(9Z))	34.4	9.57	82.38
851.56431	6.112	Glycerophospholipids	PI(13:0/22:0)	38.3	-1.39	93.30
887.56831	7.225	Glycerophospholipids	PI(20:4(8Z,11Z,14Z,17Z)/18:0)	37.6	4.40	93.11
585.33952	1.268	Glycerophospholipids	PI(P-18:0/0:0)	39.6	-0.52	98.76

762.52729	4.374	Glycerophospholipids	PS(20:0/14:0)	38.3	-2.32	94.44
694.49523	6.557	Glycerophospholipids	PS(O-16:0/14:0)	36.5	-9.40	92.61
790.58832	2.074	Glycerophospholipids	PS(P-16:0/21:0)	36.6	-9.28	93.22
818.52631	5.426	Glycerophospholipids	PS(P-18:0/22:6(4Z,7Z,10Z,13Z,16Z,19Z))	35.2	-9.55	86.38
647.45885	7.538	Glycerophospholipids	PA(14:1(9Z)/18:0)	36.9	-8.94	94.47
741.54983	5.953	Glycerophospholipids	PA(19:0/20:3(8Z,11Z,14Z))	37.2	9.38	96.22
799.62509	6.641	Glycerophospholipids	PA(21:0/22:2(13Z,16Z))	36.7	4.95	89.11
205.09701	2.684	Indoles and derivatives	L-Tryptophan	39.4	-0.71	97.85
159.02804	1.190	Keto acids and derivatives	2-Maleylacetate	38.6	-4.80	98.51
172.07280	0.827	Keto acids and derivatives	2-Oxoarginine	39.8	0.19	99.02
276.10715	1.514	Others	1,6-anhydro-N-acetylmuramic acid	37.7	-2.30	91.10
402.21358	0.474	Others	11-O-demethyl-17-O-deacetylvindolinium(1+)	37.5	-3.36	91.63
389.05093	2.837	Others	1-Phosphatidyl-D-myo-inositol	37.4	4.81	92.44
146.04588	0.667	Others	N-hydroxy-N-isopropyloxamate	39.2	-0.03	96.02
477.01273	6.802	Others	P1-uridyl-P2-phenyl diphosphate	35.9	4.52	84.87
193.07163	0.846	Others	D-4-O-Methyl-myo-inositol	39.4	-0.67	98.00
265.11079	6.809	Others	Nevirapine	36.5	4.90	88.16
430.24444	0.683	Others	Melagatran	39.3	-1.04	97.72
297.13313	0.889	Others	Trimethylolpropane triacrylate	39.1	-0.47	96.30
191.01958	1.110	Others	Citric acid	39.3	-0.79	97.67
291.07045	1.521	Others	Isoprothiolane	36.9	-5.10	90.13
597.51812	5.168	Others	Hydrabamine	36.2	6.53	88.25
111.00873	1.102	Others	3-Furoic acid	39.4	-0.30	97.55
80.96478	7.767	Others	Sulfite	37.7	-4.93	94.38
113.02444	0.736	Others	cis-Acetylacrylate	39.6	0.18	98.06
497.19749	1.514	Others	(7R*,8R*)-3-Methoxy-3',4,7,9,9'-pentahydroxy-8,4'-oxyneolignan 4-xyloside	36.2	-8.57	90.36
495.18254	1.502	Others	(7R*,8R*)-3-Methoxy-3',4,7,9,9'-pentahydroxy-8,4'-oxyneolignan 4-xyloside	35.8	-9.36	89.37
204.05255	0.976	Others	Lipoamide	37.6	1.58	90.09
204.05259	1.735	Others	Lipoamide	37.4	1.76	89.36
487.36014	2.245	Others	5-O-[8-(cis-2,6-dimethylmorpholino)octylcarbamoyl]eseroline	35	-8.48	84.48
152.98863	0.682	Others	1,1'-Thiobisethanethiol	35.7	9.36	88.85
161.04551	0.781	Others	Levoglucosan	39.4	-0.21	97.28
412.32181	1.596	Others	Cyclopamine	36.2	1.95	83.57
571.32394	0.798	Others	Avermectin B1b aglycone	37.4	-4.57	92.41
871.57242	7.374	Others	Pheophytin a	38.5	-0.89	93.73
569.31416	4.831	Others	Protoporphyrinogen IX	35.5	3.39	81.44
175.04307	0.553	Others	Methylthio 2-(propanoyloxy)propanoate	37.3	-2.07	89.21
305.02988	0.553	Polyketides	2-(3,4-Dihydroxybenzoyloxy)-4,6-dihydroxybenzoate	37	-1.35	86.62
377.08530	0.778	Polyketides	3-(4-hydroxy-3,5-dimethoxyphenyl)-1-(2,4,6-trihydroxy-3-methoxyphenyl)propane-1,2-dione	35.7	-6.62	85.79
165.05494	1.369	Polyketides	cis-p-Coumaric acid	38.5	1.97	95.10
641.32937	11.02	Polyketides	N1,N5,N10-Tris-trans-p-coumaroylspermine	35.9	-6.24	86.58

309.15508	11.08	Polyketides	Sinapine	36	-9.98	90.99
233.15568	12.50	Polyketides	3-[(1Z)-2-hexyl-3-hydroxyprop-1-en-1-yl]phenol	38.1	4.16	95.26
357.07899	2.185	Polyketides	{[(6E)-3-oxo-1,7-diphenylhepta-4,6-dien-1-yl]oxy}sulfonic acid	36.2	-3.44	85.10
449.05253	6.809	Polyketides	[2,2-dimethyl-6-(3,5,7-trihydroxy-4-oxo-4H-chromen-2-yl)-3,4-dihydro-2H-1-benzopyran-3-yl]oxidanesulfonic acid	37.2	-5.03	91.55
453.18774	8.324	Polyketides	3',4'-Dihydroxy-7-methoxy-8-(3-methylbut-2-enyl)-2'"-(1-hydroxy-1-methylethyl)-furano-(4",5":6,5)favanone	35.6	-6.71	85.42
333.02545	2.517	Polyketides	3,5,6,7,2',3',4'-Heptahydroxyflavone	37.4	0.72	87.71
399.07000	7.767	Polyketides	3,5,7,4'-Tetrahydroxy-8-C-(3-methylsuccinoyl)flavone	35	-5.39	81.19
443.17019	8.438	Polyketides	6-[(3,3-dimethyloxiran-2-yl)methyl]-5-hydroxy-7-methoxy-2-(3,4,5-trimethoxyphenyl)-3,4-dihydro-2H-1-benzopyran-4-one	36.2	-2.15	83.53
323.03359	3.439	Polyketides	6-Chlorocatechin	36.3	2.47	84.19
453.18778	8.171	Polyketides	Derrichalcone	35.5	-6.64	85.24
453.18770	8.476	Polyketides	Derrichalcone	35.4	-6.81	84.88
453.18700	10.42	Polyketides	Derrichalcone	35.5	-8.36	86.57
453.18753	7.927	Polyketides	Derriflavanone	35.2	-7.19	84.21
477.17187	2.109	Polyketides	Dichotosinin	35	-9.93	85.62
467.20574	1.554	Polyketides	Eriotriochin	38	-1.47	91.97
335.09279	7.023	Polyketides	Glabrone	37.3	0.87	87.76
529.15153	2.052	Polyketides	Mahuannin D	36.2	4.21	85.91
707.18191	0.781	Polyketides	Patuletin 3,7-bis(3-acetylrhamnoside)	37.3	-1.39	88.13
371.07547	6.806	Polyketides	Stemonal	36.6	-4.76	88.64
655.21882	1.392	Polyketides	Triphyllin A	35.5	-8.44	87.06
303.03430	1.495	Polyketides	{3-[(2E)-3-phenylprop-2-enoyl]phenyl}oxidanesulfonic acid	37.7	3.40	92.50
365.03378	6.809	Polyketides	{6-hydroxy-3-[3-(3-hydroxyphenyl)-3-oxoprop-1-en-1-yl]-2-methoxyphenyl}oxidanesulfonic acid	36.7	0.32	84.02
557.13306	0.740	Polyketides	Piceatannol 4'-galloylglucoside	36.4	5.37	88.42
327.12627	7.824	Polyketides	2',3',4',6'-Tetramethoxychalcone	35.6	7.53	86.68
431.00777	6.809	Polyketides	3-hydroxy-2-[3-methoxy-4-(sulfooxy)phenyl]-5-sulfino-3,4-dihydro-2H-1-benzopyran-7-olate	35.9	-7.96	88.45
437.19272	10.08	Polyketides	Artocarpin	36.2	-7.20	89.20
449.12569	6.775	Polyketides	Artonin P	35.7	5.80	85.09
305.17583	0.691	Prenol lipids	5'-Carboxy-gamma-chromanol	38.4	-0.01	92.19
397.20139	0.935	Prenol lipids	Fukanemarin A	39.5	1.11	99.01
431.19189	10.99	Prenol lipids	S-Furanopetasitin	35.8	4.91	84.81
383.14047	7.743	Prenol lipids	Nerolidyl diphosphate	37.5	5.67	94.02
662.50047	4.485	Prenol lipids	adenosylhopane	39	0.15	95.00
748.54796	4.798	Prenol lipids	bacteriohopane-,32,33,34-triol-35-cyclitolguanine	38.7	-0.24	93.87
561.45489	5.285	Prenol lipids	bacteriohopane-31,32,33,34,35-pentol	36.8	4.33	88.98
724.53338	3.515	Prenol lipids	bacteriohopane-31,32,33,34-tetrol-35-cyclitol	38	-3.36	93.80
724.53201	10.94	Prenol lipids	bacteriohopane-31,32,33,34-tetrol-35-cyclitol	36.6	-5.25	89.27
297.27954	12.43	Prenol lipids	Pristanic acid	38.3	-1.24	92.87
205.16036	1.826	Prenol lipids	(+)-Mayurone	38.7	2.79	96.86
437.25738	11.91	Prenol lipids	(-)-Fusicoplagin A	36.7	6.61	91.22
469.32864	0.565	Prenol lipids	3,21-dioxoolean-18-en-28-oic acid	37.3	-5.53	92.83
441.31241	4.165	Prenol lipids	dolichyl-4 phosphate	36.3	-0.93	82.82

562.40207	2.294	Prenol lipids	3-hexaprenyl-4,5-dihydroxybenzoate	39.4	0.72	97.77
391.26411	4.646	Prenol lipids	3-Hydroxy-10'-apo-b,y-carotenal	39.1	-0.37	96.11
407.26184	11.89	Prenol lipids	Apo-10'-violaxanthal	36.2	6.54	88.40
611.36369	12.00	Prenol lipids	(24E)-3beta,15alpha,22S-Triacetoxylanosta-7,9(11),24-trien-26-oic acid	35.6	7.75	86.57
443.33306	2.275	Prenol lipids	(all-E)-6'-Apo-y-caroten-6'-al	37.9	5.01	95.37
695.59104	6.187	Prenol lipids	3-Hexadecanoyloleanolic acid	36	-8.99	90.04
533.30687	5.399	Prenol lipids	Ganoderic acid I	36.1	-7.57	89.09
575.39805	5.237	Prenol lipids	Pouogenin C	37.8	6.65	96.68
531.37014	4.405	Prenol lipids	Protoxylocarpin B	37.3	4.01	91.36
301.14063	11.58	Purine and derivatives	Abacavir 5'-carboxylic acid	39.3	-0.38	97.00
135.03127	1.190	Purine and derivatives	Hypoxanthine	39.7	0.27	98.70
153.04093	1.217	Purine and derivatives	Xanthine	39.2	1.48	97.94
151.02613	1.217	Purine and derivatives	Xanthine	39.9	-0.14	99.44
265.10510	5.521	Purine Nucleosides and analogues	5'-amino-5'-deoxyadenosine	38.5	-1.36	94.22
136.06241	1.540	Purine Nucleosides and analogues	Adenine	38.6	4.70	98.26
136.06231	1.491	Purine Nucleosides and analogues	Adenine	38.5	3.98	97.23
134.04721	1.476	Purine Nucleosides and analogues	Adenine	39.4	-0.07	96.96
134.04720	0.949	Purine Nucleosides and analogues	Adenine	39.8	-0.11	98.95
266.08891	1.457	Purine Nucleosides and analogues	Adenosine (Adenine with D-ribose)	38.7	-2.13	96.28
252.10892	1.590	Purine Nucleosides and analogues	Deoxyadenosine	38.4	-0.79	92.86
150.04209	0.850	Purine Nucleosides and analogues	Guanine	39.2	-0.28	96.56
150.04211	1.422	Purine Nucleosides and analogues	Guanine	39.7	-0.17	98.88
152.05727	1.441	Purine Nucleosides and analogues	Guanine	39	3.87	99.51
150.04210	1.575	Purine Nucleosides and analogues	Guanine	39.8	-0.22	99.15
284.09870	1.563	Purine Nucleosides and analogues	Guanosine	39.7	-0.88	99.45
124.04008	0.976	Pyridines and derivatives	Nicotinic acid	37.7	6.27	95.61
253.11592	1.864	Pyrimidine and derivatives	3'-Hydroxyhexobarbital	37	-9.38	95.37
268.10363	1.674	Pyrimidine and derivatives	formycin A	38	-1.52	91.97
271.05556	3.439	Pyrimidine Nucleosides and analogues	5-Carboxy-2'-deoxyuridine	36.3	-5.94	88.35
112.05126	0.938	Pyrimidine Nucleosides and analogues	Cytosine	34.7	6.47	80.94
227.06710	1.495	Pyrimidine Nucleosides and analogues	Deoxyuridine	39.3	-1.08	97.99
113.03515	1.396	Pyrimidine Nucleosides and analogues	Uracil	38.5	5.34	98.69
111.01985	1.380	Pyrimidine Nucleosides and analogues	Uracil	39.5	-1.32	99.16
522.52393	4.789	Sphingolipids	Cer(m18:1(4E)/16:0)	37.8	-1.01	90.35
800.62395	5.774	Sphingolipids	Culinariside	37.7	-2.21	91.36
1283.82456	7.096	Sphingolipids	Galbeta1-3GalNAcbeta1-4Galbeta1-4Glcbeta-Cer(d18:1/20:0)	38	3.70	94.14
1283.82596	6.835	Sphingolipids	Galbeta1-3GalNAcbeta1-4Galbeta1-4Glcbeta-Cer(d18:1/20:0)	35.9	4.79	85.11
1007.63365	11.19	Sphingolipids	Ganglioside GA2 (d18:1/12:0)	37.3	6.36	93.85
1293.8799	7.096	Sphingolipids	Ganglioside GM3 (d18:0/26:1(17Z))	38.3	2.27	93.99
1251.8335	5.911	Sphingolipids	Ganglioside GM3 (d18:1/23:0)	38.3	2.84	94.97
1279.8637	6.328	Sphingolipids	Ganglioside GM3 (d18:1/25:0)	37.9	1.86	91.51

596.56102	6.534	Sphingolipids	N-(2-hydroxyicosanoyl)-15-methylhexadecasphing-4-enine	39.6	-0.37	98.32
614.57269	5.980	Sphingolipids	N-(2-hydroxyicosanoyl)-4-hydroxy-15-methylhexadecasphinganine	38.9	1.45	96.49
568.53049	6.233	Sphingolipids	N-(2-hydroxyoctadecanoyl)-15-methylhexadecasphing-4-enine	38.1	0.98	91.50
572.43525	4.309	Sphingolipids	N-(tetradecanoyl)-deoxysphing-4-enine-1-sulfonate	37.8	-0.30	89.38
572.43481	4.101	Sphingolipids	N-(tetradecanoyl)-deoxysphing-4-enine-1-sulfonate	37.5	-1.07	89.04
744.56139	4.488	Sphingolipids	Termitomycesphin A	37.8	-0.85	90.27
742.54612	4.277	Sphingolipids	Termitomycesphin A	36.2	-1.81	83.03
1047.7210	6.744	Sphingolipids	NeuAcalpha2-3Galbeta-Cer(d18:1/20:0)	34.7	-8.77	83.05
663.54129	6.010	Sphingolipids	N-hexadecanoylsphinganine-1-phosphoethanolamine zwitterion	36.1	-3.41	84.34
649.48933	4.778	Sphingolipids	PE-Cer(d14:1(4E)/18:0(2OH))	33.4	-3.38	71.11
675.50653	4.956	Sphingolipids	PE-Cer(d14:1(4E)/20:0(2OH))	37.3	-2.57	89.69
731.56871	6.315	Sphingolipids	PE-Cer(d14:1(4E)/24:0(2OH))	36.7	-2.93	87.06
689.52230	5.715	Sphingolipids	PE-Cer(d15:1(4E)/20:0(2OH))	36.9	-2.34	87.31
691.53783	5.713	Sphingolipids	PE-Cer(d15:1(4E)/20:0(2OH))	37.8	-0.93	90.24
556.52876	6.378	Sphingolipids	Armillaramide	38.4	-2.12	94.43
566.54931	6.923	Sphingolipids	Cer(d14:1/22:0)	38.4	-2.41	94.67
564.53445	5.885	Sphingolipids	Cer(d14:1/22:1)	34.6	-1.01	74.25
578.54854	5.953	Sphingolipids	Cer(d15:2(4E,6E)/22:0)	37.9	-3.70	94.04
524.50173	5.873	Sphingolipids	Cer(d16:1/17:0)	33.5	-3.81	71.93
512.50284	6.507	Sphingolipids	Cer(d18:0/14:0)	37.3	-1.72	88.71
540.53425	7.324	Sphingolipids	Cer(d18:0/16:0)	38.5	-1.43	94.32
540.53456	6.686	Sphingolipids	Cer(d18:0/16:0)	39.2	-0.85	97.23
554.54917	7.060	Sphingolipids	Cer(d18:0/17:0)	38.1	-2.72	93.67
582.54422	6.658	Sphingolipids	Cer(d18:0/18:0(2OH))	36.4	-4.22	87.10
568.52974	6.340	Sphingolipids	Cer(d18:0/h17:0)	36.5	-2.27	85.36
552.53384	6.534	Sphingolipids	Cer(d18:1/17:0)	38.1	-2.15	92.96
568.56540	7.313	Sphingolipids	Cer(d20:0/16:0)	39.1	-1.62	97.63
680.69620	8.048	Sphingolipids	Cer(d20:0/24:0)	36.6	6.88	90.65
570.50952	5.978	Sphingolipids	Cer(t18:0/16:0(2OH))	37.5	-1.36	89.07
626.57169	7.308	Sphingolipids	Cer(t18:0/20:0(2OH))	37.1	-1.92	87.79
646.51162	4.881	Sphingolipids	CerP(d18:1/18:0)	36.3	-8.34	90.82
925.66977	9.758	Sphingolipids	Ins-1-P-Cer(t18:0/2-OH-24:0)(1−)	34.1	9.08	80.71
586.52086	7.018	Sphingolipids	N-arachidonoylsphingosine	34.3	2.54	74.54
687.54293	6.269	Sphingolipids	SM(d16:1/17:0)	35.1	-2.49	78.29
689.55544	6.271	Sphingolipids	SM(d16:1/17:0)	36.1	-5.47	86.59
661.52743	6.074	Sphingolipids	SM(d18:0/13:0)	37.8	-2.37	91.70
675.54657	6.399	Sphingolipids	SM(d18:0/14:0)	37.8	2.84	92.45
689.55796	6.666	Sphingolipids	SM(d18:0/15:0)	37.6	-3.38	92.06
701.55847	6.547	Sphingolipids	SM(d18:0/16:1(9Z))	34.5	-2.60	75.45
781.62617	7.048	Sphingolipids	SM(d18:0/22:3(10Z,13Z,16Z))	37.6	5.60	94.33
661.52586	5.641	Sphingolipids	N-tridecanoylsphingosine-1-phosphocholine	36.2	-3.09	84.80

705.64845	6.057	Steroids and derivatives	cholest-5-en-3b-yl (13Z-docosenoate)	33.4	-9.98	78.14
469.29821	11.03	Steroids and derivatives	(17alpha,23S)-17,23-Epoxy-29-hydroxy-27-norlanosta-1,8-diene-3,15,24-trione	36.2	7.18	89.27
661.43847	4.462	Steroids and derivatives	Goyaglycoside c	36.4	9.61	92.69
367.23054	1.973	Steroids and derivatives	3-Oxochola-1,4,6-trien-24-oic Acid	35.7	7.25	86.59
475.34566	2.734	Steroids and derivatives	11-acetoxy-3beta,6alpha-dihydroxy-9,11-seco-5alpha-cholest-7-en-9-one.	36	5.79	86.73
479.30391	10.37	Steroids and derivatives	22-deoxy-20,21-dihydroxyecdysone	34.9	5.16	80.61
419.31573	4.168	Steroids and derivatives	24-northornasterol A	37.4	0.33	87.20
463.30547	1.809	Steroids and derivatives	3-dehydroecdysone	35.3	0.12	76.76
533.30650	5.117	Steroids and derivatives	Cucurbitacin J	35.9	-8.25	88.52
475.32523	3.203	Steroids and derivatives	1alpha-hydroxy-23-[3-(1-hydroxy-1-methylethyl)phenyl]-22,22,23,23-tetradehydro-24,25,26,27-tetranorvitamin D3	35.8	9.61	89.38
475.32498	4.652	Steroids and derivatives	1alpha-hydroxy-23-[3-(1-hydroxy-1-methylethyl)phenyl]-22,22,23,23-tetradehydro-24,25,26,27-tetranorcholecalciferol	35.3	9.08	86.43
479.31747	2.682	Steroids and derivatives	EB 1213	36.9	1.65	86.55
573.38269	3.991	Steroids and derivatives	Vitamin D2 3-glucuronide	37.7	7.18	96.75
945.47221	6.070	Steroids and derivatives	1alpha,3beta,22R-Trihydroxyergosta-5,24E-dien-26-oic acid 3-O-b-D-glucoside 26-O-[b-D-glucosyl-(1->2)-b-D-glucosyl] ester	35.5	2.27	80.30
703.55131	7.014	Steroids and derivatives	ecdysone palmitate	37.4	0.82	87.83
651.60322	8.047	Steroids and derivatives	16:0 Sitosteryl ester	35.2	-8.18	85.01
651.60224	12.48	Steroids and derivatives	16:0 Sitosteryl ester	35.3	-9.68	87.08
561.41849	4.354	Steroids and derivatives	Campesteryl glucoside	37.4	4.31	92.13
409.27537	2.593	Steroids and derivatives	Minabeolide-4	36.8	1.35	85.46
413.19629	0.946	Steroids and derivatives	17-Hydroxypregnenolone sulfate	36.3	-7.15	89.55
477.30608	2.511	Steroids and derivatives	24-methylene-cholesterol sulfate	36	3.50	84.16

Table A5 GC-MS analysis of industrial wastewater samples from UASB influent effluent, and MBR effluent (Chapter 7).

UASB influent			
RT (min)	**Suggested Compound**	**RI**	**Area**
12.14	Phenol	901	2,317,911
12.17	1-Methylethyl Benzene	928	277,354
12.22	m-Ethyl Toluene	1006	401,337
12.30	2,3,3-Trimethyloctane	966	693,822
12.38	3,4,5,6 Tetramethyl Octane	958	188,476
12.40	Decane	1015	379,793
12.65	m/z 59 45 103	-	551,625
12.75	2-(2-hydroxypropoxy), 1-Propanol	1034	178,284
12.80	m/z 59 45 111 103 84	-	624,738
13.07	m/z 59 104	-	2,389,404
13.10	1,2,3-Trimethyl Benzene	1020	1,820,054
13.28	m/z 43 59 117 89 132	-	648,630
13.33	6 methyl, 3- Undecene	1158	809,453
13.35	2-Ethylhexan-1-ol	995	680,877
13.35	m/z 106 121 77 79	-	515,943
13.37	m/z 57 70 83 41	-	326,063
13.38	Formic acid, 2-propylpentyl ester	1116	397,181
13.48	4-Ethyl-1-octyn-3-ol	1111	1,787,829
13.51	Indan	1047	12,106,943
13.65	(2Z)-5-Methyl-2-decene	1059	58,465,881
13.68	Benzyl alcohol	1036	1,836,432
13.92	N-Methyl-2-pyrrolidinone derivative	-	11,056,569
13.95	m-Propyltoluene	1106	112,763
14.09	1,2-DiethyIbenzene	1106	338,952
14.23	o-Cymene	1042	193,643
14.30	o-Cresol	1014	1,336,971
14.69	Cis-Linalool oxide	1164	1,040,652
14.80	4-Ethyl-m-xylene isomer	1119	124,053
14.80	Heptanoic acid	1073	322,596
14.81	Cymene isomer	1042	2,659,286
14.85	p-Cresol	1014	10,066,761
14.87	Hexachlorethane derivative	-	16,009,800
14.99	2-Ethyl-p-xylene isomer	1119	106,990
14.99	Cymene isomer	1042	2,072,079
15.17	1-Undecene	1105	3,843,924
15.20	Bicyclopentylidene	1140	2,378,311
15.35	2-methyl-Decane	1051	281,715
15.37	Octylcyclopropane	1117	7,745,948
15.55	3,7-dimethyl-1-Octanol	1130	11,234,790
15.69	2,6-Dimethylphenol	1127	839,016
15.83	1,2,4,5-Tetramethylbenzene isomer	1133	1,475,217
15.84	p-Mentha-1,3,8-triene	1029	63,614
15.86	1,2-Dimethyl-3-ethylbenzene isomer	1119	170,287
15.90	phenyl alcohol	-	1,392,837
15.94	m/z 43 101 123	-	2,035,023
15.95	alkane substituted benzene isomers		2,192,065
15.97	2-Ethylhexanoic acid isomer	1109	1,612,233
15.97	1,2-Dimethyl-3-ethylbenzene isomer	1119	220,523
16.05	(4Z)-9-Methyl-4-undecene derivative	-	3,264,048
16.12	2,5-Dideoxy-1,3-O-(1-methylethylidene)pentitol	1155	988,830
16.20	Nonyl alcohol derivative	-	3,036,903
16.40	m/z 57 41 83 103 125	-	7,544,499
16.46	(E)-1-Phenyl-1-butene	1100	808,299
16.50	Nonyl alcohol	1159	6,279,773
16.51	2-Ethylphenol isomer	-	762,930
16.57	1,2-Dichlorooctane	1182	3,549,863
16.75	1H-Indene	1160	877,170
16.76	1-[2-(Allyloxy)-1-methylethoxy]-2-propanol	1156	4,943,157
16.81	2,4-Dimethyl-2-decene	1135	5,004,965
16.81	alkane substituted benzene isomers		1,778,747
16.88	2,2'-oxybis-1-Propanol isomer	-	4,258,464
17.28	m/z 107 122 77	-	2,025,204
17.32	Octanoic acid	1173	1,067,325
17.64	Naphthalene	1231	3,611,931
17.66	1-Methylene-1H-indene derivative	1095	219,398
17.84	alpha-Terpineol	1143	1,302,231
17.90	Dodecane	1214	3,496,007
17.90	m/z 59 43 83 141	-	5,549,382
18.06	m/z 44 71 103 163	-	2,727,525
18.24	(1Z)-1-Ethylidene-7a-methyloctahydro-1H-indene	1239	1,400,118

18.37	Cyclic tetramethylene sulfone	0	2,578,062
18.51	Phenoxyethanol	1212	2,006,295
19.39	m/z 43 99 58 72 128 143	-	1,827,248
19.77	2-Methyl-5-oxotetrahydro-2-furanyl acetate (m/z 43 99)	1226	2,737,856
20.15	m/z 88 41 54 120 96 70	-	1,651,749
20.18	Tridecane	1313	309,369
20.24	Benzocycloheptatriene	1251	3,386,267
20.58	m/z 43 187 83 113 143	-	1,451,042
20.64	1-Methylnaphthalene	1345	2,348,156
21.58	4-Methyl-3-[(2E)-2-pentenyl]dihydro-2(3H)-furanone (m/z 99 43)	1353	2,038,847
21.59	Decanoic acid	1372	1,848,795
21.67	Tridecane isomer	-	756,771
21.84	m/z 201 43 83 113 143	-	13,588,505
22.05	Biphenyl	1367	2,030,409
22.05	m/z 154 76	-	126,328
22.10	1-Tetradecene	1403	401,622
22.19	3-Methyl-1H-indole isomer	-	4,187,292
22.24	Tetradecane	1413	5,494,427
22.24	1-Tetradecene	1403	4,083,164
22.31	m/z 135 107 30 55 84	-	2,057,184
22.35	2,3-Dimethyl Naphtalene isomer	1458	786,129
22.50	Diphenyl ether	1443	5,699,326
22.57	2,6-dimethyl- Naphthalene	1458	1,435,353
22.80	Dicyclohexylamine	1540	683,415
22.91	2,3-Dimethyl Naphtalene isomer	1458	2,764,755
23.27	Octyl Cyclohexane	1476	548,601
23.28	2,3-Dimethyl Naphtalene isomer	1458	1,032,630
23.60	2,3-Dimethyl Naphtalene isomer	1458	399,777
23.83	4-Methyl-1H-benzotriazole	0	850,956
24.27	Tetraethylene glycol	1530	1,964,961
24.71	O-Hydroxybiphenyl	1588	7,039,152
24.81	m/z 79 111 190	-	6,816,193
25.35	Dodecanoic acid	1570	4,436,109
25.45	m/z 79 111 191	-	1,610,442
25.47	3-Metyl Pentadecane	1548	1,144,552
25.47	2-Bromododecane	1446	92,621
25.84	m/z 133 160 126 98 88 55 41 69	-	1,561,716
25.89	1-Hexadecene	1602	4,507,889
25.98	Hexadecane	1612	5,982,527
26.24	m/z 119 70 201 297	-	2,049,281
26.67	m/z 79 111 175 190	-	1,380,918
26.67	m/z 84 98	-	687,750
26.84	m/z 84 98	-	617,847
26.91	m/z 55 173 99 84 111 155	-	4,457,889
27.70	Heptadecane	1711	238,521
28.31	N-Phenyl, Benzenemethanamine	1665	3,907,326
28.45	4-Phenyl-1,3-oxazolidin-2-one	1605	1,608,588
28.77	m/z 123 95 138 165 193	-	10,611,792
28.86	3-Methylheptadecane	1746	2,011,552
29.00	m/z 72 114	-	1,838,400
29.15	Pentaethylene glycol	1804	5,342,901
29.24	1-Octadecene	1801	2,683,007
29.33	Octadecane	1810	5,432,095
29.81	m/z 59 113 69 41 103	-	3,275,085
30.40	Caffeine	1795	3,017,055
30.67	Diisobutyl phthalate	1908	1,177,649
31.16	m/z 84 98	-	4,567,503
31.92	10-Methylnonadecane	1945	988,406
32.04	m/z 72 100 128	-	436,056
32.19	m/z 123 101 95 58 86 165 193	-	1,820,850
32.24	9-Nonadecene	1918	52,573
32.24	m/z 79 97 238 191 157	-	879,333
32.32	m/z 72 100 128	-	704,859
32.32	Eicosane	2009	1,158,225
32.36	Pentafluoropropionic acid, octadecyl ester	1971	3,378,222
33.42	Hexaethylene glycol	2079	2,450,742
33.79	m/z 59 113 69 103	-	1,237,812
33.82	Oleic acid, methyl ester	2085	226,593
34.72	alkane	-	259,644
35.08	alkane	-	311,754
35.11	Eicosyl trifluoroacetate	2210	2,214,707
35.41	Benzethonium Chloride (m/z 58 116)	0	6,567,057
35.42	m/z 58 116	-	379,803
35.50	Bis(2-ethylhexyl) fumarate	2224	987,999
36.13	m/z 55 112 86 97 198 226	-	3,296,952

38.82	2-Hexadecanoyl glycerol	2498	3,226,635
42.15	alkane	-	903,618
43.12	m/z 134 91	-	493,236
45.55	3.beta.-Hydroxy-5.beta.-cholestanol derivative	-	1,547,456
45.94	Cholesterol derivative	-	3,934,004
47.94	gamma-Sitosterol derivative	-	1,957,923
50.93	m/z 57 316 191 367 423	-	671,964

UASB Effluent	**(MBR influent)**		
RT (min)	**Suggested Compound**	**RI**	**Area**
12.04	Phenol	901	21,175,635
12.08	m-Ethyltoluene	1006	2,562,234
12.09	m/z 43 58	-	1,319,466
12.17	Isopropylbenzene	928	190,291
12.22	o-Ethyltoluene	1006	315,336
12.22	p-Fluoroaniline	967	11,707,470
12.25	m/z 59 103	-	1,533,720
12.36	Decane	1015	519,158
12.47	1-(2-Methoxy-1-methylethoxy)-2-propanol	967	3,145,860
12.58	m/z 59 103	-	9,462,225
12.67	m-Fluoroaniline	967	8,136,300
12.72	2-(2-hydroxypropoxy), 1-Propanol	1034	4,272,960
13.02	m/z 59 104	-	10,462,560
13.10	1,2,4-Trimethylbenzene	1020	1,227,482
13.17	m/z 99 44	-	1,980,090
13.22	m/z 59	-	3,031,602
13.24	m/z 99 44	-	3,313,935
13.28	m/z 58 99 44 91 135	-	6,623,085
13.32	5-Methyl-2-decene	1059	2,320,056
13.34	Ethylhexanol isomer	-	2,693,846
13.38	1-Butoxy-2-ethylhexane	1226	446,633
13.46	m/z 59 41 73	-	1,205,505
13.51	Indane	1047	5,261,134
13.65	(2Z)-5-Methyl-2-decene	1059	47,564,126
13.74	m/z 99 44	-	10,753,080
13.76	2-Methyl-Phenol	1014	23,647,560
13.82	(2Z)-5-Methyl-2-decene isomer	1059	11,320,586
14.01	N-Methyl-2-pyrrolidinone derivative	-	71,761,322
14.11	m/z 140 47 75 105	-	1,516,218
14.17	m/z 105 91 119 140	-	74,309
14.19	o-Cresol (co-elution)	-	1,809,855
14.24	1-Isopropyl-2-methylbenzene	1042	109,098
14.25	2-Methyl-Phenol isomer	1014	21,830,430
14.32	3-Methyl-Phenol	1014	52,443,675
14.28	2-Methyl-Phenol isomer	1014	74,274,105
14.60	Benzylthiol	1097	7,488,669
14.65	m/z 59	-	3,765,120
14.77	m-Cresol (co-elution)	-	4,409,784
14.82	p-Cresol	1014	69,482,580
14.82	1-Isopropyl-2-methylbenzene isomer	-	229,873
14.88	Hexachlorethane derivative	-	23,384,249
14.88	Benzenemethanethiol	1097	1,963,838
14.99	1-Isopropyl-2-methylbenzene isomer	-	2,273,455
15.13	2,6-Dimethylphenol isomer	-	9,028,605
15.19	1-Undecene	1105	3,420,318
15.38	3-Methyl-3-nonanol	1107	5,529,675
15.39	7-Methyl-1-undecene	1140	6,731,955
15.56	m/z 43 112 119 154 134	-	836,094
15.63	2,6-dimethyl-Phenol	1127	9,809,295
15.90	1,2,3,5-Tetramethylbenzene	1133	4,671,486
16.21	Nonyl alcohol isomer	-	5,205,299
16.23	2,3-Dimethylphenol	1127	47,236,995
16.35	m/z 59 103	-	19,097,925
16.40	m/z 69 55 141 176 93	-	11,362,841
16.46	2-Methyl-1-phenyl-1-propanol	1190	1,051,005
16.49	2-Ethylphenol	1114	9,819,915
16.51	alkene/alcohol	-	8,432,339
16.58	m/z 43 68 105 140	-	5,540,301
16.73	3,4-Dimethylphenol	1127	96,961,998
16.76	m/z 59 103	-	1,646,175
16.76	6-Methyl-1-octanol derivative	-	3,053,879
16.82	2-Methyl-2-nonen-4-one	1136	5,138,807
16.80	trans-3-Caren-2-ol	1136	1,528,529
16.86	m/z 59 103	-	21,962,445
17.17	Methyl benzyl sulfide	1144	2,046,564

17.19	m/z 91 105 138 123 77	-	222,771
17.24	2,3-Dimethyl Phenol	1127	43,557,498
17.35	Levomenthol / 5-methyl-2-(1-methylethyl)-Cyclohexanol	1164	11,799,150
17.49	2,6-Dimethylphenol	1127	11,883,195
17.49	2,5-Dimethylbenzenethiol isomer	-	2,073,792
17.63	Naphthalene	1231	3,724,116
17.65	1H-Indene isomer	-	275,346
17.86	3,4-Dimethylphenol	1127	8,572,935
17.91	alcohol	-	5,160,041
17.96	2-phenoxy-ethanol	1212	18,974,595
18.10	2-Ethyl-5-methylphenol	1227	14,892,210
18.30	unknown	-	9,064,410
18.39	Dimethyl hexanedioate	1151	2,456,685
18.39	m/z 41 56 120 143	-	7,778,063
18.46	m/z 79 45 64 158 94	-	3,771,393
18.49	2-phenoxy-ethanol isomer	-	44,571,960
18.61	unknown methyl ester	-	1,487,730
18.63	2-Ethyl-6-methylphenol (isomer)	1227	1,539,540
18.65	m/z 78 106 55 98 162 129	-	261,381
18.65	3-Methyl-4-ethylphenol	1227	19,538,910
18.69	m/z 43 190 73 112	-	1,904,646
18.75	m/z 56 43 107 69 136	-	17,277,600
18.75	(3E)-7-Methyl-3-undecene isomer	-	3,249,255
18.88	2-Ethyl-6-methylphenol (isomer)	1227	659,505
18.92	2-Ethyl-5-methylphenol	1227	13,753,140
18.98	Hexanedioic acid, monomethyl ester	1241	28,970,610
18.99	2-Ethyl-6-methylphenol (isomer)	1227	347,490
19.37	2,4,6-Trimethyl Phenol	1241	13,817,343
19.40	m/z 58 72 42 99 128 143	-	2,815,457
19.53	unknown	-	4,023,360
19.55	2,3,6-Trimethylphenol	1241	814,854
19.56	m/z 121 136 88 77	-	16,745,700
19.66	3,5-Dimethyl-1-hydroxymethylbenzene	1263	4,971,495
19.68	m/z 42 70 56 84 133 142 162 177	-	2,922,014
19.84	1-(2-butoxy-1-methoxy)-2-Propanol isomer	1265	4,684,875
19.86	m/z 66 91 117 148	-	10,831,875
19.97	1-(2-butoxy-1-methoxy)-2-Propanol isomer	1265	5,032,875
20.07	Methyl phenyl disulfide	1295	574,539
20.13	m/z 88 41 120 70 54 112	-	28,824,135
20.24	1-Methylnaphthalene isomer	-	3,792,132
20.25	m/z 44 58 117 75 100	-	5,054,190
20.40	Tripropylene glycol isomer	1328	8,801,475
20.52	Tripropylene glycol	1328	8,739,075
20.62	1-Methylnaphthalene isomer	-	1,834,749
20.74	m/z 44 58	-	7,349,565
20.78	m/z 83 112 197 232	-	6,895,050
20.89	m/z 44 59 117 75 100	-	11,438,640
20.92	m/z 57 41 204 87	-	2,729,718
21.08	m/z 44 59 117 75 100	-	21,180,390
21.08	m/z 55 84 112 142	-	11,338,542
21.66	m/z 43 83 113 143	-	331,230
21.72	m/z 30 56 84	-	20,977,155
21.84	m/z 43 201 83 113 143	-	11,876,795
22.04	Phenylbenzene	1367	5,100,795
22.08	m/z 41 55 69 83 154 97 111 128	-	165,151
22.19	m/z 130 138 111 77	-	12,690,390
22.19	3-Methylindole isomer	-	3,992,316
22.24	1-Tetradecene	1403	3,605,817
22.25	m/z 91 170 123	-	5,649,552
22.27	m/z 30 41 56 84 141	-	3,674,910
22.32	m/z 30 56 84	-	40,341,600
22.42	m/z 91 123 45 79	-	1,088,427
22.49	m/z 141 51 77 115 170 142	-	98,358
22.49	Phenoxybenzene	1443	12,620,397
22.56	2,3-Dimethylnaphthalene	1458	948,540
22.76	Dicyclohexylamine isomer	1540	13,817,115
22.90	1,8-Dimethylnaphthalene isomer	-	2,427,311
23.17	m/z 159 101 41 114	-	1,452,851
23.61	m/z 45 64 110 174 78 141	-	642,898
23.85	m/z 55 45 159 101 83 126	-	1,482,108
24.00	m/z 135 105 184 77	-	1,000,071
24.07	m/z 136 45 91 77 105 184	-	1,061,106
24.12	m/z 159 101 41 114	-	2,531,391
24.21	m/z 105 184 138 153 77	-	496,629
24.52	Di-tert-butylphenol	1555	12,616,472

24.71	o-Hydroxybiphenyl	1588	994,614
25.06	m/z 55 111 143 83	-	7,660,245
25.88	1-Hexadecene	1602	2,209,747
25.98	Hexadecane	1612	967,461
26.24	m/z 55 99 173 84 111 135 155	-	9,592,620
26.24	m/z 119 201 297	-	1,754,730
26.32	m/z 173 55 99 84 111 155	-	127,913,520
26.48	m/z 44 59 103	-	44,464,755
26.65	m/z 91 45 123 79 202	-	945,849
26.90	m/z 55 99 173 84 111 135 155	-	19,592,805
26.91	m/z 173 55 99 84 111 155	-	170,012,841
27.00	m/z 91 137	-	907,623
27.67	m/z 45 55 83 101	-	2,731,232
27.74	m/z 122 42 70 96	-	12,753,330
27.82	m/z 57 71 43 85 233	-	1,010,742
27.85	4-Phenyl-1,3-oxazolidin-2-one isomer	-	11,277,720
28.30	4-Phenyl-1,3-oxazolidin-2-one isomer	-	359,953,764
28.30	Benzylaniline	1665	25,954,455
28.45	m/z 142 174 202 78 64 121	-	804,408
28.48	4-Phenyl-1,3-oxazolidin-2-one isomer	-	78,635,655
28.53	Hexathiepane	0	2,240,870
28.53	m/z 130 68 115 103 154 197	-	735,660
28.99	m/z 72	-	27,965,910
29.14	alkane	-	1,216,599
29.24	1-Octadecene	1801	1,336,924
29.31	1-Butyl 2-isobutyl phthalate	1973	1,333,485
29.58	m/z 45 111 55 143 83 155	-	17,557,185
30.39	Caffeine	1795	21,400,905
30.67	Diisobutyl phthalate	1908	981,438
31.52	unknown	-	700,611
31.91	Hexadecanoic acid	1968	1,058,396
31.97	Eicosane	2009	1,441,803
32.03	m/z 72 100 128	-	4,511,925
32.09	1-Butyl 2-isobutyl phthalate	1973	426,506
32.19	m/z 123 101 95 86 58 165	-	8,547,960
32.31	m/z 72 100 128	-	4,404,255
32.33	m/z 213 57 119 71 85 43	-	1,003,995
32.36	1-Heptadecanol	1954	1,977,104
33.84	Cyclic octaatomic sulfur	0	1,837,107,595
35.04	alkane amide	-	927,114
35.11	Eicosyl pentafluoropropionate	2170	1,305,656
35.40	Benzethonium Chloride	0	2,391,330
35.50	m/z 70 57 100 55 83 112	-	2,069,055
36.13	m/z 55 112 86 97 141 198	-	14,023,860
36.23	m/z 55 41 69 156 83 97 120	-	1,861,425
37.68	alkane	-	1,885,323
38.48	unknown	-	1,371,578
38.82	Hexadecanoic acid, 2-hydroxy-1-(hydroxymethyl)ethyl ester isomer	2498	3,903,767
39.12	Hexadecanoic acid, 2-hydroxy-1-(hydroxymethyl)ethyl ester isomer	-	1,609,295
39.61	Phthalic acid, di(6-methylhept-2-yl) ester	2575	7,129,154
40.01	alkane	-	1,845,798
41.10	2-methylhexacosane	2641	1,825,145
42.15	Hexacosyl pentafluoropropionate	2767	3,116,540
43.18	2-methyloctacosane	2840	710,465
44.16	alkane	-	1,018,553
45.55	3.beta.-Hydroxy-5.beta.-cholestanol derivative	-	1,255,503
45.94	Cholesterol derivative	-	1,920,431
46.04	alkane	-	937,391
50.93	m/z 57 316 191 367 423	-	3,012,570

MBR Effluent			
RT (min)	**Suggested Compound**	**RI**	**Area**
12.39	Decane	1015	260,459
13.38	(2Z)-5-Methyl-2-decene	1059	53,407,276
14.88	unknown	-	16,400,919
15.18	1-Undecene	1105	2,435,655
15.38	Octylcyclopropane	1117	4,217,540
15.54	3,7-Dimethyl-1-octanol	1130	5,461,943
15.64	m/z 114 58 41 70 86	-	2,210,601
16.06	(2E)-9-Methyl-2-undecene	1158	3,598,689
16.20	Nonyl alcohol	1159	3,093,870
16.36	m/z 43 86 57 72	-	148,169
16.40	(5E)-7-Methyl-5-undecene	1158	5,262,620
16.50	Nonyl alcohol	1159	5,991,593
16.58	Octyl acetate	1183	3,620,532

16.76	1-butyl-2-pentyl-, trans-Cyclopropane	1178	931,041
16.82	N,N'-Bis(2,6-dimethyl-6-nitrosohept-2-en-4-one)	0	1,717,574
17.75	m/z 42 86 99 56 129 71	-	596,475
17.77	2-Methyl-2-propyl-1,3-oxazolidine	1068	1,446,738
17.86	(Iodomethyl)benzene	1208	1,039,656
17.92	unknown	-	6,941,370
18.14	m/z 42 99 86 129 71 56	-	2,629,940
18.25	(1Z)-1-Ethylidene-7a-methyloctahydro-1H-indene	1239	889,691
18.40	m/z 58 42 72 99 143 128	-	2,196,882
18.55	m/z 72 44 85	-	738,357
18.60	m/z 86 56 42 101 129	-	113,982
18.76	m/z 86 56 42 133 101 169	-	495,419
19.08	m/z 82 54 93 108 39	-	179,823
19.40	m/z 58 72 42 99 128 143	-	1,793,006
19.68	m/z 42 70 56 84 142 133 162 177 114	-	1,188,218
20.59	m/z 43 187 83 113 143	-	853,880
20.89	m/z 121 57 94	-	1,033,211
20.91	m/z 43 116 57 88	-	2,103,663
21.65	alkane	-	568,079
21.66	unknown	-	757,904
21.84	m/z 43 201 83 113 143	-	8,082,830
22.14	1-Tetradecene	1403	2,362,692
22.15	4-Methylpentyl methylphosphonofluoridoate	0	260,559
22.21	m/z 99 71 77 57 43 112	-	3,884,768
22.23	Tetradecane	1413	1,715,866
22.31	m/z 30 84 41 56 141	-	5,207,477
22.54	m/z 113 156 128 85 141	-	1,888,577
22.80	m/z 112 106 42 70 77 147 155	-	344,919
23.12	m/z 41 111 55 93 69 139 196	-	125,450
23.12	m/z 136 85 140 112 127	-	2,509,178
23.19	2,6-Di-tert-butylphenol	1555	3,311,558
23.25	Octylcyclohexane	1476	626,798
23.93	m/z 175 91 119 64 147 203 218	-	7,420,569
24.39	Methyl p-tolyl sulfone derivative	-	4,975,455
24.49	Di-tert-butylphenol	1555	4,460,872
24.66	m/z 99 141	-	3,051,429
24.77	m/z 72 128 114 99 55 41 145 156	-	371,942
24.91	m/z 88 111 69 41 157	-	2,502,275
25.03	m/z 42 191 69 165	-	1,610,030
25.08	m/z 42 104 133 191 165	-	7,099,019
25.28	m/z 57 129 72 142 85 101	-	9,458,372
25.46	3-Methylpentadecane	1548	1,276,220
25.66	m/z 43 97 113 140 69	-	221,810
25.87	1-Hexadecene	1602	2,502,173
25.97	m/z 105 57 77 185 169 121	-	3,442,404
25.97	Hexacecane	1612	2,729,860
26.06	m/z 111 55 71 154	-	2,099,279
26.16	m/z 138 96 134 181 111	-	5,014,415
26.25	unknown	-	1,463,453
26.28	m/z 138 135 96 124 107 41	-	6,237,191
26.36	(Z)-3-Hexadecene	1620	168,174
26.37	m/z 105 69 56 126 141 184	-	3,370,157
26.59	unknown N compound	-	3,361,610
26.68	m/z 217 57 232 189	-	2,232,567
26.81	Benzophenone	1603	5,351,450
27.01	m/z 180 138 166 237	-	4,793,478
27.07	3,5-Di-tert-butyl-1,2-benzenediol derivative	-	318,206
27.33	m/z 96 141 69	-	14,568,657
27.42	m/z 119 191 109 135 43 198	-	6,050,550
27.47	m/z 57 177 219 163	-	379,851
27.83	Heptadecane	1711	631,118
28.52	4-Phenyl-1,3-oxazolidin-2-one derivative	-	3,850,167
28.84	m/z 164 210	-	14,918,322
28.85	3-Methylheptadecane	1746	1,160,748
29.02	unknown N compound	-	66,593,885
29.11	m/z 86	-	294,543
29.24	1-Octadecene	1801	1,083,570
29.24	m/z 120 79 107 43 181 155	-	4,808,493
29.30	Octadecane	1810	1,758,619
29.52	m/z 43 191 234	-	562,871
29.54	Phosphoric acid, tris(2-chloro-1-methylethyl) ester	0	4,461,129
30.04	m/z 95 43 148 123 204 189	-	3,444,251
30.40	Caffeine	1795	3,238,349
30.47	m/z 135 179 107	-	328,356
30.49	m/z 179 243 135 213 258	-	6,281,772

30.62	m/z 187 135 107 43 91 205 221	-	2,767,656
30.71	m/z 69 41 111 55 141 95 83 125 197	-	453,578
31.22	m/z 236 138 180	-	4,430,114
31.31	m/z 114 43 72 141 212 182	-	3,925,380
31.47	7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione isomer	-	12,006,998
31.68	m/z 69 125 41 55 75 112 205	-	1,044,089
31.70	m/z 205	-	11,782,545
31.77	m/z 86 72 156 100 43 200 128	-	5,309,874
31.91	alkane	-	982,991
31.92	Hexadecanoic acid	1968	541,046
31.92	m/z 170 96	-	5,782,394
32.10	m/z 174 145 93 77	-	161,591
32.23	m/z 43 55 97 83 69 111	-	99,090
32.31	Eicosane	2009	978,397
32.36	1-Heptadecanol	1954	1,390,950
32.45	m/z 121 263 149 57 107 248 278	-	3,768,423
33.91	m/z 72 100 239	-	3,188,121
34.31	m/z 72	-	2,651,249
34.48	m/z 83 55	-	3,151,565
34.69	alkane	-	228,174
34.90	m/z 224 82 141 238 127	-	8,062,541
34.97	m/z 142 184 213 83 252 129	-	4,174,646
35.05	Hexadecanamide	2021	446,294
35.06	alkane	-	511,419
35.24	m/z 44 102 161 236	-	42,725,439
36.04	m/z 58 116	-	36,215,846
37.40	(Z)-13-Docosenamide derivative	-	1,215,717
37.69	alkane	-	563,069
38.17	m/z 102 44 58 236 135	-	8,748,824
38.28	Benzethonium Chloride derivative	0	4,344,099
38.66	m/z 58 209 293	-	3,733,607
38.70	m/z 91 117 207	-	647,135
38.79	Hexa(methoxymethyl)melamine	2499	3,192,783
38.83	m/z 98 239 55	-	1,095,543
38.88	alkane	-	944,261
39.03	m/z 134 107 123 77 97 145 161 254	-	2,428,686
39.13	1,16-Hexadecanedicarboxylic acid	2523	926,322
39.55	m/z 191 145 261 406 388	-	4,683,074
39.62	Phthalic acid, di(6-methylhept-2-yl) ester	2575	1,170,029
39.74	m/z 261 191 145	-	11,389,214
39.87	m/z 86 264 44	-	11,309,498
40.02	alkane	-	1,079,765
40.21	m/z 86 264 58	-	2,802,209
41.11	Squalane	2619	995,271
42.15	alkenenamide	-	3,128,729
42.57	m/z 86 162 135 44 264	-	13,696,491
43.15	m/z 286 77 56	-	571,869
43.18	2-methyloctacosane	2840	579,983
43.82	m/z 123 191 95 165 55 384	-	2,408,274
44.17	alkane	-	665,474
50.94	m/z 57 316 191 367 535	-	2,777,445

Table A6 LC-Q-ToF analysis of industrial wastewater samples from UASB influent and effluent, and MBR effluent (Chapter 7).

m/z	RT (min)	UASB inf	UASB eff	MBR eff	Chemical class	Suggested Compound	Score	Mass Error (ppm)	Isotope Similarity
354.28597	0.03	2578	6096	6927	Fatty acyls - fatty acids	Arachidic acid(d3) (eicosanoic acid (d3))	38	3.65	94.44
271.16694	0.35	8058	0	0	Fatty acyls - fatty acids	7,10,13-hexadecatrienoic acid	40.8	-4.02	97.97
421.30737	0.54	33220	59	41	Prenol lipids	19-(3-methyl-butanoyloxy)-villanovane-13alpha,17-diol	37.2	27.05	97.41
486.36890	0.54	7277	15208	0	Steroids and derivatives	(22R)-1alpha,22,25-trihydroxy-26,27-dimethyl-23,24-tetradehydro-24a,24b-dihomo-20-epivitamin D3	42.8	-1.88	89.84
329.24209	0.55	4907	5067	1628	Fatty acyls - octadecanoids	9-hydroperoxy-12,13-dihydroxy-10-octadecenoic acid	43.1	28.40	86.02
151.03527	0.57	31516	49706	49407	Aryl	diphenyl sulfide	35.9	-6.46	86.63
283.17617	0.58	11992	16135	7619	Polyketides	4-Prenyldihydropinosylvin	46.1	24.50	95.23
506.37969	0.58	0	4031	5398	Prenol lipids	Acacic acid	45.9	-8.82	95.28
216.95052	0.59	8011	7808	8354	Aryl	1-iodo-2-methoxybenzene	36.8	-1.53	84.95
366.28608	0.60	12384	6268	983	Fatty acyls - fatty acids	6-hydroxy-nonanoic acid	42.5	3.06	89.99
239.96672	0.60	35582	33993	37298	(unclassified)	4-nitrophenyl phosphate(2−)	39.5	-0.56	86.85
261.13803	0.61	6166	1913	0	Fatty acyls - fatty acids	Phaseolic acid	37.2	14.00	95.99
182.19208	0.62	0	5267	114	Fatty acyls - fatty amides	dodecanamide	37.8	8.78	98.47
271.16688	0.62	11465	3749	0	Fatty acyls - octadecanoids	4-oxo-9Z,11Z,13E,15E-octadecatetraenoic acid	41.3	-11.97	96.04
338.23439	0.62	932	81574	0	Steroids and derivatives	testolic acid	42.2	5.64	94.74
338.27570	0.63	238	7714	12644	Fatty acyls - eicosanoids	15R-hydroxy-5E,8Z,11Z,13Z-eicosatetraenoic acid	37.3	21.02	95.55
608.10353	0.63	0	4149	8745	Polyketides	Delphinidin 3-caffeylglucoside	40	-21.73	94.12
352.24980	0.64	0	182180	254832	Fatty acyls - eicosanoids	5-J2-IsoP	42.2	4.67	94.76
736.49830	0.64	5263	2848	0	Glycerophospholipids	PS(O-16:0/14:1(9Z))	43.3	-19.40	96.57
322.23866	0.65	0	4377	7835	Fatty acyls - fatty esters	(9Z)-3-hydroxydodecenoylcarnitine	40.9	2.77	96.37
405.07986	0.66	2655	5931	9948	Polyketides	5,7,3',4'-Tetrahydroxy-3,6,8,5'-tetramethoxyflavone	38.4	-7.05	97.27
350.29121	0.66	5663	1960	0	Fatty acyls - fatty acids	Phloionolic acid	49.3	3.33	96.63
260.87293	0.66	8421	11609	9868	Organophosphorous	Trimetaphosphoric acid	39.2	-3.03	97.20
834.60882	0.67	3627	5361	4833	Sphingolipids	GlcCer(d16:2(4E,6E)/24:0(2OH))	39.5	9.08	88.87
447.29375	0.69	42547	14209	5573	Steroids and derivatives	(22E,24E,26E)-1alpha,26b-dihydroxy-22,23,24,25,26,26a-hexadehydro-26a,26b-dihomo-27-norcholecalciferol	38.5	15.69	95.55
514.31736	0.77	3778	9246	0	Steroids and derivatives	polypodine B	37.1	10.77	92.05
307.20269	0.78	5316	2296	0	Prenol lipids	Acutifolane A	42.4	5.27	90.42
218.90486	0.78	6183	8909	7931	Purines and derivatives	5-iodouracil	35.8	-5.14	84.78
196.06382	0.79	2824	10076	11252	Organophosphorous	2-(N-morpholino)ethanesulfonic acid	40.5	0.06	97.99
674.50470	0.81	8588	4119	0	Prenol lipids	bacteriohopane-32,33-diol-34,35-dicarbamate	42.3	-8.79	95.66
322.27497	0.81	0	2845	5042	Fatty acyls - fatty amides	N-palmitoyl threonine	50	2.56	82.29
272.25996	0.82	8498	3986	0	Fatty acyls - fatty acids	2R-aminohexadecanoic acid	50.1	5.73	94.32
347.00312	0.82	5100	5986	0	Polyketides	Ellagic acid (antioxidant)	39.8	-4.48	95.12
311.23453	0.82	36244	16656	8507	Steroids and derivatives	Desogestrel	50.3	-7.78	93.46
732.54280	0.85	11087	5410	320	Glycerophospholipids	PA(19:1(9Z)/18:1(9Z))	41.3	-15.37	80.29

282.20787	0.86	37877	27222	16407	Fatty acyls - fatty acids	all-trans-7-hydroxyhexadeca-2,4,8,10-tetraenoic acid	50.1	5.68	87.13
343.99488	0.86	17069	23424	0	Coumarin	N-(6-Oxo-6H-dibenzo[b,d]pyran-3-yl)-2,2,2-trifluoroacetamide	45.9	2.11	97.84
421.30732	0.87	45537	13419	9971	Steroids and derivatives	Homocholic acid	42.5	26.92	97.15
790.58479	0.90	17959	7809	96	Glycerophospholipids	PG(P-20:0/17:2(9Z,12Z))	37.4	-14.06	89.49
311.16956	0.95	14844	16399	2349	Glycerolipids	1-dodecanoyl-sn-glycerol	46.2	23.85	89.41
848.63031	0.95	28969	12374	173	Glycerophospholipids	PG(20:1(11Z)/20:1(11Z))	44.6	-8.67	94.50
353.20093	0.98	6169	1531	0	Fatty acyls - fatty acids	5-hydroperoxy-7-[3,5-epidioxy-2-(2-octenyl)-cyclopentyl]-6-heptenoic acid	44	11.21	94.09
491.19307	0.99	1	5855	2	Steroids and derivatives	Estrone 3-glucuronide	52	1.79	92.16
776.55740	1.01	7568	2707	0	Glycerophospholipids	PG(18:1(9Z)/17:2(9Z,12Z))	47	18.17	91.31
144.96397	1.02	5856	5260	5221	Inorganic acids	sulfenic acid	37.8	4.95	94.71
616.46261	1.03	5269	1507	0	Glycerophospholipids	PE(P-16:0/13:0)	48.2	-11.75	94.50
325.18496	1.07	2505	13999	1406	Fatty acyls - fatty alcohols	docebenone	42.1	12.39	94.52
491.37395	1.08	11312	4374	0	Saccharolipids	DAT(16:0/24:0(2Me[S],4Me[S]))	35.1	20.19	95.13
112.98454	1.08	1731	3563	0	Carboxylic acids	Trifluoroacetic acid	37.8	-9.17	99.24
1022.75581	1.15	19107	5281	1	Sphingolipids	Galalpha1-4Galbeta-Cer(d18:1/26:1(17Z))	40.7	8.83	95.36
674.50258	1.17	5294	1252	0	Glycerophospholipids	PE(16:0/16:0)	55.5	-13.50	94.29
644.49305	1.18	6226	1870	0	Glycerophospholipids	PE-NMe(O-14:0/O-14:0)	36.6	-9.49	93.20
339.19979	1.24	3384	10508	1647	Fatty acyls - fatty acids	3,4-dihydroxy-4-methylhexadecanoic acid	50.3	18.10	94.96
790.58361	1.26	6789	2315	0	Glycerophospholipids	PE(21:0/20:5(5Z,8Z,11Z,14Z,17Z))	53.8	11.26	83.80
746.55690	1.28	6478	2308	0	Glycerophospholipids	PA(18:2(9Z,12Z)/20:0)	33.9	-17.20	87.02
702.53064	1.30	6587	2485	0	Glycerophospholipids	PA(O-18:0/18:3(6Z,9Z,12Z))	33.8	-18.38	87.40
658.50441	1.32	6676	2624	0	Prenol lipids	(+-)-Trihydroxy-decipiadiene	37.6	0.46	88.61
614.47761	1.33	6645	2605	0	Glycerolipids	DG(16:1(9Z)/0:0/16:1(9Z)) (d5)	37.8	-0.55	89.43
570.44960	1.36	7235	2606	0	Prenol lipids	(5S,6R)-beta-carotene 5,6-epoxide	34.3	-18.17	89.58
339.20055	1.64	7	5190	5	Fatty acyls - fatty acids	3,4-dihydroxy-4-methylhexadecanoic acid	48.2	20.61	92.52
297.08570	1.68	6246	2218	25	Benzene and substituted derivatives	2-Aminobenzoic acid	41.1	4.08	97.03
173.07865	3.14	31212	16373	713	Alcohols and polyols	triethylene glycol	43.5	1.45	99.84
217.10503	3.80	9580	4835	1008	Alcohols and polyols	tetraethylene glycol	41.2	-0.64	99.72
187.06042	3.82	6620	1706	0	Carboxylic acids	2-Oxosuberate	44.6	-5.36	99.20
231.08398	3.82	6093	2166	34	Carbohydrates and derivatives	Ethyl beta-D-glucopyranoside	42.3	-1.49	97.73
357.07937	3.83	6524	358	0	Organosulphur	Methyl-N,N-diethylthiocarbamate (organic thiocarbonic acid derivatives)	38.2	-2.97	91.00
157.08361	4.01	91094	53370	7140	Alcohols and polyols	Polypropylene glycol (m w 1,200-3,000)	41.5	-0.06	99.28
353.14840	4.02	31906	22951	89	Prenol lipids	19-Oxo-all-trans-retinoic acid	42.2	-9.40	94.23
243.06182	4.07	106	12125	13270	Nucleosides and analogues	Uridine	44.4	-1.79	98.34
307.25899	4.34	13682	731	10	Fatty acyls - fatty acids	15-methyl-heptadecanoic acid	53.5	-6.19	95.07
308.26567	4.35	6504	344	1	Fatty acyls - fatty alcohols	2,4-Nonadien-1-ol	40.8	8.26	93.80
329.24086	4.36	11279	503	0	Fatty acyls - fatty acids	Oleic acid(d2)	37.9	4.44	94.53
261.13121	4.37	77674	29200	1270	Aminopyrimidine	pirimicarb	39.7	-4.14	98.14
275.11022	4.42	24065	6194	66	Amino acids and analogues	Histidinyl-Proline (dipeptide)	51.3	-4.91	96.76
160.13322	4.53	26907	7905	33	Fatty acyls - fatty acids	3-amino-octanoic acid (metabolite of octanoic acid)	52.4	0.06	99.43
171.01159	4.66	83270	23733	290	(unclassified)	p-Toluenesulfonic acid	43.9	-3.17	99.08

249.15758	4.75	80341	34629	110	(unclassified)	cyclo(L-leucyl-L-leucyl)	39.2	-1.28	95.86
305.15762	4.86	72256	19859	654	Alcohols and polyols	Hexaethylene glycol (Lignans, neolignans and related compounds)	46.5	1.92	99.55
319.13645	4.94	31080	7229	73	Benzene and substituted derivatives	Pizotifen	41.5	-0.22	88.75
172.09714	4.94	47016	14687	4381	Amino acids and analogues	N-Acetylleucine (leucine and derivatives)	42.3	-4.51	99.24
333.11542	5.01	6476	1353	0	Saccharolipids	alpha-tyvelopyranosyl-(1->3)-alpha-D-mannopyranose	58	-0.59	96.89
309.11851	5.04	5658	1431	0	Carbohydrates and derivatives	α-tyvelopyranosyl-(1→3)-α-D-mannopyranoseα-tyvelopyranosyl-(1→3)-α-D-mannopyranose	55.3	-1.91	99.41
181.01346	5.12	10334	3172	0	Keto acids	Maleylacetoacetic acid (an intermediate in the metabolism of tyrosine)	51.3	-3.95	99.74
165.01874	5.13	9577	4441	96	Benzene and substituted derivatives	4-O-Methylgallic acid	47	-3.24	99.15
233.00623	5.14	14040	12885	43	Keto acids	2-Hydroxy-6-ketononatrienedioate	46.5	-3.10	98.97
300.99388	5.15	5319	5312	0	Alkyl nitrate	Erythrityl Tetranitrate	37.1	9.72	91.11
250.20113	5.26	19384	2383	438	Alcohols and polyols	3-methylbutane-1,2-diol	42.9	-0.76	93.88
349.18342	5.30	32510	7696	524	Alcohols and polyols	Heptaethylene glycol	45.3	0.40	99.42
393.20949	5.69	12427	3286	611	Amino acids and analogues	Ala-Leu-Ala-Pro	42.2	-3.66	97.56
195.09167	5.72	8153	4633	3656	Benzene and substituted derivatives	pyocyanine (produced by Pseudomonas aeruginosa)	51.3	-0.04	97.85
407.18877	5.79	7322	1758	50	Polyketides	lehualide H (Isolated from the marine sponge of the genus Plakortis)	53.5	6.53	89.05
185.02709	6.01	24065	7695	701	Benzene and substituted derivatives	2-(Methylthio)phenol	38.7	-5.02	97.63
437.23579	6.04	5540	1762	730	Alcohols and polyols	nonaethylene glycol	43.4	0.16	98.16
264.19607	6.14	59036	31087	22868	fatty acyls - fatty amides	Hydroxy-alpha-sanshool	41.8	-0.09	99.59
186.98893	6.15	7278	2506	0	Pyridine and derivatives	3-carboxypyridine-2-carboxylate	51.9	1.35	92.18
240.08489	6.17	8896	3729	0	(unclassified)	Pantothenic acid	46.4	-2.07	97.79
185.02712	6.38	8716	2774	0	Benzene and substituted derivatives	2-(Methylthio)phenol	56.2	-4.78	98.42
390.16993	7.21	14539	4268	35	Prenol lipids	Gibberellin A34	46.3	-8.57	98.30
874.24552	7.21	5761	1336	0	Polyketides	Kaempferol 3-(6'''-rhamnosyl-2'''-(6-malyl-glucosyl)-glucoside)	39.1	10.00	80.58
235.07539	7.22	9976	6918	422	Amino acids and analogues	Cysteinyl-Hydroxyproline	51.8	2.94	95.84
419.14369	7.22	51197	18760	43	Polyketides	Villinol	41.7	-0.73	94.89
198.07652	7.23	0	12879	231	Amino acids and analogues	anticapsin (bacterial metabolite, antimicrobial)	39.4	-3.33	89.78
855.25467	7.23	14027	1630	0	Lignans and derivatives	Sesaminol glucosyl-(1->2)-[glucosyl-(1->6)]-glucoside	42.7	-2.08	96.06
273.16718	7.23	5858	1610	730	Polyethers	3,6,9,12,15-pentaoxaheptadecane	39.2	-1.58	97.81
288.04630	7.24	10066	10782	733	Fatty acyl glycosides	2-(α-D-mannosyl)-D-glycerate (E. coli metabolite)	41.7	-1.77	94.72
392.98205	7.25	8111	8935	149	Quinones and derivatives	topopyrone A (isolated from a fungal strain Phoma sp.BAUA2861)	36.2	9.95	81.68
356.03379	7.26	7966	9352	357	(unclassified)	isoxicam (NSAID drug)	38.7	3.77	91.19
159.10183	7.65	9112	5291	0	Fatty acyls - fatty acids	8-hydroxy caprylic acid	51.4	-6.72	99.23
202.98441	7.70	6057	1323	0	Benzene and substituted derivatives	5-nitrosalicylate	38.9	4.38	92.51
202.18009	7.73	7663	1698	23	Fatty acyls - fatty acids	11-amino-undecanoic acid	59.3	-0.35	99.23
352.02193	7.78	656	9954	10664	Polyketides	Avenanthramide C (avenanthramides, phenolic alkaloids)	44.7	-3.06	94.27
201.00687	7.80	6170	2775	0	(unclassified)	Imidazole acetol-phosphate (monoalkyl phosphates)	39	-0.88	96.01
199.04296	7.85	48346	12849	821	Organosulphur	1-(2-Thienyl)-1-butanone	54.8	-3.13	97.88
173.08112	8.01	45147	25587	162	Fatty acyls - fatty acids	Suberic acid	49.2	-4.69	99.40
188.12800	8.18	6423	1672	40	Fatty acyls - fatty acids	8-Amino-7-oxononanoate (Biotin metabolism KEGG)	45.3	-0.63	99.28
157.08612	8.59	9937	1210	0	Alcohols and polyols	cis-4-Hydroxycyclohexylacetic acid	56.1	-5.69	91.37

154.08737	9.03	0	48218	1139	Alkaloids	Arecoline	38.4	-4.34	97.21
399.15112	9.03	9897	3210	0	Amino acids and analogues	N6-L-homocysteinyl-N2-L-valyl-L-lysine (tripeptide)	45.5	-1.37	97.01
331.16379	9.04	0	16487	71	Benzene and substituted derivatives	isoxaben	38.1	-7.66	98.69
576.22686	9.04	5740	847	0	Carbohydrates and derivatives	α-L-Rhap-(1→2)-[β-D-GlcpNAc-(1→3)]-α-L-Rhap-Opr	47.3	-0.92	93.72
201.11250	9.16	11344	1635	0	Fatty acyls - fatty acids	9,10-dihydroxy-2-decenoic acid	51.8	-3.64	99.19
339.23597	9.28	55	17918	19360	Fatty acyls - fatty acids	2-mercapto-octadecanoic acid	52.2	9.95	88.76
326.19615	9.41	8815	4869	3242	Nucleosides and analogues	5'-[(3-aminopropyl)-amino]-5'-deoxyadenosine	38.9	8.10	98.92
352.24822	9.42	349	18566	19625	Sphingolipids	Capnine	41.3	-9.64	93.80
326.19582	9.43	5933	3543	0	Amino acids and analogues	glyoxal-lysine dimer (cyclo-dimerisation of L-lysine and glyoxal)	50.1	-0.42	99.05
324.18141	9.43	0	27794	18731	Nucleosides and analogues	5'-[(3-aminopropyl)-amino]-5'-deoxyadenosine	36.6	7.53	88.61
209.06132	9.57	13169	2768	0	Unsaturated hydrocarbons	(Z)-1,3-Tridecadiene-5,7,9,11-tetrayne (enynes)	51	3.14	98.65
313.21292	9.59	4184	5809	5525	Fatty acyls - fatty esters	(E,E)-3,7,11-Trimethyl-2,6,10-dodecatrienyl butyrate	42.1	-6.76	97.80
768.14813	9.74	0	4741	5164	Nucleosides and analogues	FADH	45.9	-8.65	93.89
313.21296	9.79	9494	12487	11262	Fatty acyls - fatty esters	(E,E)-3,7,11-Trimethyl-2,6,10-dodecatrienyl butyrate	43	-6.62	98.52
409.23402	9.84	276	21203	23050	Glycerophospholipids	PA(16:0/0:0)	43.5	-4.98	94.96
267.06719	9.89	19	5257	5727	Amino acids and analogues	L-Cystathionine (intermediate of cycteine synthesis)	43.1	7.03	90.16
193.08957	9.96	18178	4813	0	Organosulphur	R-3-(Methylthio)-1-hexanol (thioethers)	38.3	-5.51	97.82
315.10358	10.06	21270	5673	2529	Amino acids and analogues	4-Hydroxy-L-threonine (E.coli, saccharomyces cerevisiae metabolite)	47.1	-3.47	83.48
226.14430	10.07	29694	24879	19744	Fatty acyls - fatty amides	N-Ethyl trans-2-cis-6-nonadienamide	54.3	-3.15	97.23
339.23592	10.16	46	19174	19692	Fatty acyls - fatty acids	2-mercapto-octadecanoic acid	52.5	9.80	88.75
324.18129	10.25	5672	4812	0	Benzene and substituted derivatives	N-[(4-Hydroxy-3-methoxyphenyl)methyl]octanamide	48.9	-1.28	84.96
352.24836	10.33	539	58879	56927	Sphingolipids	Capnine	37.6	-9.25	93.84
215.12818	10.36	8940	1570	0	Fatty acyls - fatty acids	Undecanedioic acid	47.6	-3.26	99.14
314.19699	10.50	7342	7649	6549	Carboxylic acids	Butoctamide hydrogen succinate	50	-0.97	98.85
325.21269	10.59	6691	2566	0	Fatty acyls - fatty acids	20:4(5Z,13Z,16Z,19Z)	49.1	-7.25	90.46
241.04888	10.89	13612	3524	0	Organophosphorous	D,L-cyclohexanephosphinothricin	37.8	1.57	90.93
409.23408	10.91	37	10089	10971	Glycerophospholipids	PA(16:0/0:0)	44.7	-4.84	96.69
298.20121	10.97	8968	6514	4943	Fatty acyls - fatty acids	Dinor-7-NO2-CLA	49.9	-0.80	97.28
466.13693	10.98	6235	6425	5173	Alkaloids	Dichotomide X (natural product found in Stellaria dichotoma var. lanceolata.)	40.5	-6.10	95.83
316.21205	11.00	107475	79794	61562	Carboxylic acids	Butoctamide hydrogen succinate	46.6	0.64	99.10
314.19741	11.01	299264	267010	206342	Carboxylic acids	Butoctamide hydrogen succinate	48.5	0.35	98.60
261.10998	11.14	117459	151725	143198	Polyethers	tetraglyme	40.4	-7.83	97.20
298.20204	11.18	12342	8420	6030	Fatty acyls - fatty esters	3-hydroxynonanoyl carnitine	40.7	-1.09	96.26
329.23296	11.24	6625	907	0	Fatty acyls - fatty acids	9,10,13-TriHOME(trihydroxyoctadecenoic acid metabolite of linoleic acid)	51.8	-1.19	99.13
298.20192	11.28	5175	3561	0	Fatty acyls - fatty esters	3-hydroxynonanoyl carnitine	39.5	-1.46	99.28
280.19146	11.34	6732	4760	0	Pyrrolidine derivative	scalusamide A	39.8	-1.27	98.70
229.14399	11.49	11242	1524	0	Fatty acyls - fatty acids	Dodecanedioic acid	53.1	-2.36	99.43
241.04856	11.62	9708	2204	0	Organophosphorous	D,L-cyclohexanephosphinothricin	44.3	0.11	90.11
186.95616	11.73	8299	11211	0	(unclassified)	etidronic acid(2−)	38.4	2.79	95.20
298.20201	11.75	17221	12734	9398	Fatty acyls - fatty esters	3-hydroxynonanoyl carnitine	42.5	-1.17	97.63
337.16465	11.78	0	5475	5698	Fatty acyls - fatty alcohols	18-hydroxy-18-oxo-dinorleukotriene B4	40.1	-2.98	96.87

298.20195	11.84	5198	3930	0	Fatty acyls - fatty esters	3-hydroxynonanoyl carnitine	41.3	-1.36	96.24
329.23259	12.08	6343	2819	0	Fatty acyls - octadecanoids	Sativic acid	40.5	-2.17	93.86
383.09734	12.11	5549	3159	0	Alcohols and polyols	3-O-p-Coumaroylquinic acid	40	-3.04	95.88
843.07047	12.12	239	20916	14033	(unclassified)	(R)-methylmalonyl-CoA(5−)	40.4	-4.43	84.54
255.15917	12.12	5080	6737	0	Macrolide	aspergillide A (L1210))	44.9	0.08	99.63
209.15412	12.12	9366	12931	11049	Fatty acyls - fatty acids	11-Hydroxy-9-tridecenoic acid	48.2	-2.55	97.89
243.15955	12.16	6540	1185	0	Fatty acyls - fatty acids	2-methyl-dodecanedioic acid	53.4	-2.57	99.36
283.20207	12.20	18897	17636	15186	Quinolizines	Cadiamine	46.3	1.61	99.56
280.19123	12.20	5589	4071	0	Pyrrolidine derivative	scalusamide A	41	-2.09	93.54
337.16519	12.20	408	7347	7726	Fatty acyls - fatty alcohols	18-hydroxy-18-oxo-dinorleukotriene B4	42.6	-1.40	94.31
453.28904	12.25	15026	5964	3383	Steroids and derivatives	3a,7a,12b-Trihydroxy-5b-cholanoic acid	39.5	7.99	94.76
255.15952	12.27	5107	2853	0	Amino acids and analogues	L-pyrrolysinium	45.1	2.66	98.48
241.14396	12.29	9157	7876	6160	Pyranones	6-Heptyl-5,6-dihydro-2H-pyran-2-one	53.4	-2.94	96.71
327.16534	12.31	10168	9966	7348	Prenol lipids	Merulin C, (rel)- (natural product found in Endophytic fungi)	44.5	-4.05	95.60
283.19079	12.34	3679	5482	5021	fatty acyls - fatty esters	Ethyl trans-2-methyl-2-pentenoate	38.2	-2.46	80.40
283.20177	12.35	12291	14215	12404	Quinolizines	Cadiamine	49.5	0.54	99.10
433.12834	12.49	7223	635	0	Benzene and substituted derivatives	Garcimangosone C	41.4	3.56	92.71
437.07080	12.50	5012	147	0	Carbohydrates and derivatives	2-O-sinapoyl-D-glucaric acid	37.6	2.91	91.64
365.14097	12.50	5890	978	6348	Polyketides	Hildgardtene	37	4.74	89.40
353.19946	12.66	4405	25856	0	Fatty acyls - lineolic acids	Corchorifatty acid A	57.2	-3.83	98.90
421.18743	12.74	3045	5745	722	Prenol lipids	3'-Hydroxy-HT2 toxin	45	1.46	89.97
255.06446	12.79	6835	1858	0	Fatty acyls - fatty acids	2-hydroxy-decanedioic acid	37.4	1.98	89.37
365.14132	13.01	5238	303	0	Indoles	bisindolylmaleimide III	53.4	1.38	85.23
768.63413	13.05	31261	73686	0	Glycerophospholipids	PE(19:0/21:0)	52.8	9.43	91.60
397.22602	13.41	3987	5876	672	Fatty acyls - eicosanoids	ent-12-D2c-IsoP	36.9	8.07	93.50
377.16163	14.58	5225	244	0	Prenol lipids	(1E,4Z,6a,8b,10a)-8-(2-Methylbutanoyloxy)-10,15-dihydroxy-3-oxo-1,4,11(13)-germacratrien-12,6-olide	54.4	2.79	89.40