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**Insights for contaminant transformation via monitored natural attenuation- Effects of
DOC, time and hydrogeology**

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Abstract

The purpose of this study was to track the long-term trends of contaminants distribution in the old landfill of Singapore through monitored natural attenuation and to explore the main parameters that rule such transition. The distribution of contaminants, including dissolved organic matter (DOM), inorganic species, heavy metals, and organic compounds, was investigated via monitoring wells in the years 1997, 2004 and 2011. The data revealed that the distribution of contaminants possessed selective attention of spots associated with leachate/groundwater movement. DOM presented high affinity to certain constituents in the leachate, suggesting enhanced mobilization potential. However the leachate composition exhibited limited correspondence to the nearby soil, indicating the minor effect induced by the partitioning coefficient. The sulphate detection unveiled that air intrusion took place at later stage, increasing the stability of the landfill. Continuous flushing and physicochemical precipitation facilitated the nutrient removal resulting in overall low concentrations of the contaminants. As hydrogeology in the tropical landfill is critical for the fate and transport of contaminants, it is suggested to be integrated into the long-term monitored natural attenuation.

Keywords: monitoring well, leachate, heavy metals, hydrogeology, DOC

1. Introduction

Landfilling is still one of the popular approaches for solid waste disposal among many developing regions and countries. Old landfills worldwide present several environmental concerns in terms of post-closure, as they incorporate little engineering design to better isolate the waste from the surrounding environment. Even if many landfills have been designed with protection layers, uncontrolled leachate and gas could be released due to defects of the aged liner system (Tong et al., 2015). Landfill leachate contains a variety of pollutants, such as humic acids and heavy metals, etc., which may adversely affect groundwater and surface water quality (Kjeldsen et al., 2002; Regadío et al., 2013). The landfill biogas, mainly comprised of CH₄, CO₂ and some non-methane organic carbon, could result in unpleasant odor, explosion, global warming and deleterious health effects (Barlaz et al., 2002). Herein counteractive measures, such as *in-situ* aeration, reactive barriers, pump and treat, advanced oxidation processes, innovative landfill bioreactor by leachate circulation and the placement of hygienic facilities, and facilitating biodegradation and isolation, are taken to minimize the negative impacts (Bilgili et al., 2007; Jun et al., 2009; Kurniawan et al., 2006; Pleasant et al., 2014; Tigini et al., 2014). However, landfill aftercare, under certain criteria, requires completion times of up to decades or even centuries (Stegmann et al., 2003; Wang et al., 2012).

The long-lasting stabilization period for the landfill is mainly associated with the heterogeneity of waste composition, the slow anaerobic processes as well as potential constraints from the site-specific conditions e.g. the moisture content, the climate and original soil properties in the site etc (Barlaz et al., 2002). To obtain information in old landfills, monitored natural attenuation (MNA) may be performed at an affordable cost (Baun et al., 2003; Dong et al., 2015; Youcai et al., 2000). MNA relies on the natural processes to attenuate the contaminants. Landfill

monitoring is performed for several groups of pollutants, i.e. dissolved organic matter, inorganic macrocomponents, heavy metals, and xenobiotic organic compounds (Baun et al., 2003; Sizerici and Tansel, 2015). Albeit the rapid growth of available information on attenuation processes (Christensen et al., 1994), the database based on long-term monitoring and the constant recording remains limited, as natural attenuation processes are complicated by the large degree of heterogeneity and long lifetime of a landfill as a source for pollution. Researchers have proposed several indicators suggesting the completion of post-closure monitoring period and safe release of the landfill site, for instance the typical parameters such as BOD/COD ratio and total organic carbon on solid sample, the range of views on landfill stability however is extremely diverse (Barlaz et al., 2002; Pohland and Harper, 1986; Prantl et al., 2006; Reinhart and Grosh, 1998; Wimmer et al., 2013).

In this study, the natural attenuation of Long Halus Dumping Ground (LHDG-Phase III) in Singapore was monitored for the years 1997, 2004 and 2011. Evaluation on the transitional distribution of contaminants was made in the specific timeframe. A comparative examination was conducted to understand the natural attenuation with respect to investigated parameters. This understanding is valuable because it may be used to (1) identify the stability of the landfill, (2) locate the parameters affecting the landfill behavior, (3) investigate the ruling mechanisms behind parameters, and (4) evaluate the landfill post-closure strategy in the context of long-term effects, both qualitatively and quantitatively.

2. Methodology

2.1. Background

The LHDG used to be the largest landfill in Singapore and was operated between the early 1970s and later 1990s. Previously known as the Tampines dumping grounds, it occupies some

230 ha of land in northeastern Singapore, flanking both sides of the Tampines Expressway. It has been divided into several distinct phases to receive wastes at different period of time. The key features of the LHDG such as the landfill type, landfill age, the phase area and waste quantity can be found in Table S1 and S2. This study was focused on Lorong Halus Phase III (Fig 1), which lies on the northeastern portion of LHDG landmarked by the Serangoon River and the Tampines expressway running along its northeastern boundary (Meinhardt 2004).

It was originally a mangrove swamp covering about 44 ha. The area climate is classified as tropical rainforest climate, with no true distinct seasons. Completion of the first government incinerator in 1979 resulted in gradual diversion of landfill wastes from municipal solid waste (MSW) to incineration ashes (IA). In addition the rapid economic growth since 1980s saw significant generation of construction and demolition (C&D) waste, meaning that the LHDG-Phase III actually received a mixture of untreated MSW together with IA and C&D waste during its operation period (Meinhardt Infrastructure and Environment, 2004; Montgomery Watson, 1997). Since closure, no significant reclamation activities have been conducted except 2-5 m soil cap. Landfill gas extraction wells were constructed in 2002 for flaring of landfill gases. Previously running on a continuous basis, the extraction system is now operated intermittently as landfill gas production diminishes in tandem with the increasing age of the site.

Fig. 1

2.2. Geotechnical characterization

Geotechnical works were conducted in 1996-1997, 2004 and 2011. In brief, five boreholes (MW23 through MW27) were drilled at LHDG-Phase III in October - November 1996 (Fugro Singapore Pte Ltd). All borings were converted to combined leachate monitoring wells until 1997. Six geotechnical borings (MH16 - MH21) were made in June to September 2004 at the

same region (Setsco Services Pte Ltd), whereas MH16 was later completed as the leachate monitoring well. In 2011, seven boreholes were further drilled to 30m in depth at Phase III again. These were subsequently converted into monitoring wells R1 through R7 (Setsco Services Pte Ltd) (Fig. 1).

Prior to commencement of drilling, a cable detector was used to verify that the location was clear of electrical cables and/or metallic pipes. A hand auger or trial pit was then used to drill the top 1m to ensure the clearance of any underground services. Spiral auger drilling method was used to drill the 100 mm boreholes. All the drillings, soil sampling and loggings were done in accordance with BS5930 (Code of Practice for Site Investigations 1981 and 1999).

The land survey was conducted using a global positioning system/real time kinematic positioning (GPS/RTK) methodology. The indicative locations, elevation and termination depth of borings (monitoring wells) are presented in Table 1. Static water level measurements were performed with a water level meter and referenced to ground elevation.

Table 1

2.3. Soil sampling and analysis

Soil samples were collected using either a standard penetration test (SPT) split spoon or 75mm diameter Shelby Tube sampler. The samples were placed into laboratory-supplied wide-mouth glass sample containers and stored in an ice chest while on site and during transportation to the laboratory. Environmental testing was performed on soil samples according to Dutch standards (2000). All provisions were taken to avoid cross-contamination of samples by ensuring common equipment being properly washed and decontaminated. Leaching test of soil samples (R1 -R7 in 2011) was conducted at liquid-to-solid ratio (L/S) of 10. In brief the reaction bottle was sealed and agitated in a rotary tumbler at 10 rpm for 24 hr. Then, the eluent was filtered

through a 0.45 µm filter membrane and stored at 4 °C for further analysis. Anions were determined by ion-chromatography (Dionex, USA), while NH₃-N concentration was colorimetrically measured based on the salicylate method using a DR2800 spectrophotometer (Hach Company, US). Heavy metal concentrations were determined by ICP-OES/MS (Perkin Elmer, USA). The cumulative oxygen consumption in 4 d (RI₄), a typical parameter related to biostability of landfill wastes, was measured in the WTW Oxi Top system (WTW GmbH, Germany).

2.4. Leachate sampling and analysis

The leachate sampling was conducted at three different periods, (1) in February 1997 for MW23-MW27, (2) September 2004 for MH16, and (3) November 2011 for R1-R7. Prior to sampling, at least of 3-5 well volumes were purged from the wells. The leachate samples were then collected using a disposable HDPE bailer for each location. Samples were immediately sent for environmental analysis. Parameters included pH, bulk ions, BOD, COD, dissolved organic carbon (DOC), and NH₃-N (APHA-AWWA standards), semi-volatile organic compounds e.g. phthalates (USEPA 8270), heavy metals and metalloids (USEPA 3051), total petroleum hydrocarbons (TPH) (USEPA 8440 IR & 8015 GC). It is worth noting that comparison was only made on available data (Table 1). Quality control during sampling and environmental analysis was conducted throughout the monitoring according to respective analytical methods.

3. Results and discussion

3.1. Landfill characteristics in 2011

Landfill leachate is considered as a major concern to the surrounding environment owing to its mobility (Mårtensson et al., 1999). The leachate mobility is controlled by engineering design, waste components, operation procedures and methods, the adopted topography, hydrogeological

properties, etc. The hydrogeological and geological characteristics of LHDG-Phase III were therefore carefully investigated.

3.1.1. Leachate analysis

Leachate samples were collected from monitoring wells (R1 -R7) of LHDG-Phase III. Heavy metals, dissolved organic matter (DOM), organic compounds and bulk anions were analyzed (Table S2). The concentration of organics (as COD) was below 1000 mg L⁻¹ whereas the pH lay in the neutral to slightly alkaline range in compliance to reported values in old landfills (Chen, 1996; Kjeldsen et al., 2002; Kulikowska and Klimiuk, 2008). Given the assumption that leachate is well affiliated to a small scale ($\leq 1 \text{ km}^2$) in the landfill, which is plausible in view of the high precipitation and uncontrolled dumping conditions, spatial distribution of pollutant concentrations was subsequently modeled using the Kriging algorithm simulation (Fig. 2 and 3).

Fig. 2 and 3

In general, most heavy metals, organic compounds and anions in a typical landfill post closure are appeared at a low concentration (He et al., 2006). In this study, the BOD/COD ratio was measured around 0.05-0.1, indicating that the landfill have reached the mature stage (Jung et al., 2011). Interestingly, most contaminants showed higher levels at two spots (Fig. 2). For example, the metal species Ba, Co, Cr, Fe, Ni, and Zn were appeared at high concentrations at the southwest zone of the monitored rectangle. Moving farther from their peaks, their concentration was decreased. By contrast the highest concentration of As and Mo was shown at the other spot close to R5.

Analogous to metal species, spot-specific patterns were noticed with other parameters (Fig.3). The concentration of most constituents appeared higher at the southwest zone. Besides,

SO₄²⁻ displayed its peak concentration at the other spot next to R5 similar to As and Mo. The pH value was noticed to be in line with the latter group as well. Herein two groups of contaminants were identified based on their distribution pattern.

Several reasons are responsible for such distribution. Firstly, the waste components were highly varied whereas their distribution may be heterogeneous, complicating the leaching behavior. Taking account of leachate movement, mixing and exchange of pollutants between plumes may often occur. Alongside the intense precipitation may further disperse the original resources of contamination. As a consequence, the mechanisms in understanding the fate and transport of various contaminants become intangible from these combined effects. DOC affects leachate composition not only via involvement in biological activities, but also its complexation properties (Baun and Christensen, 2004; Xie et al., 2015). Studies have reported that heavy metals are highly affiliated with the organic matter in the leachate (Kalbitz and Wennrich, 1998; Kang et al., 2002; Ward et al., 2005). The mobility of the heavy metals may be enhanced by the complexing capacity of the organic matter leaching from the landfill (Jensen et al., 1999). Hence the correlation of various contaminants with dissolved organic carbon (DOC) was investigated, aiming to reveal the mechanisms using least square linear regression (Fig.4 and 5).

Fig. 4 and 5

Strong positive linearity was identified between DOC and metal species of Ba, Co, and Cr with correlation coefficient of 0.92-0.96 (Table S3). Fe, Ni and Zn showed a moderate linearity with the coefficient of 0.58-0.76, better than As and Mo (Fig. 4). The lower coefficient for Fe, Ni and Zn was resulted due to the less complexation with DOC (Baun and Christensen, 2004; Kjeldsen et al., 2002). While the poor correlation of As with DOC indicates other mechanisms. Ghosh et al. (Ghosh et al., 2006) and Hartley et al. (Hartley et al., 2004) have studied the pH

effects on As leaching, observing that the increased pH may highly promote As solubility. Certain anions like SO_4^{2-} may enhance As leaching as well. In this regards, correlations between As and pH together with SO_4^{2-} were further investigated (Table S3). Interestingly, the correlation coefficient for As vs. pH and SO_4^{2-} was higher as compared to most of the other metals, i.e. 0.85 and 0.62 with regards to pH and SO_4^{2-} respectively, attesting the findings from literatures (Ghosh et al., 2006; Hartley et al., 2004).

Apart from metal species, strong linear correlations were also noticed for BOD, COD, TPH, $\text{NH}_3\text{-N}$ and anions (except for SO_4^{2-}) with DOC, with the coefficients ranging from 0.81 to 0.98. BOD and COD measure the biodegradable and total organics, respectively, which could explain why the high correlation to DOC (Kjeldsen et al., 2002). The lower coefficient for BOD (0.88) may be ascribed to BOD only meant for biodegradable organics, which is solely determined by microbial activity. TPH presented high coefficient of 0.82, attributable for its non-polar characteristics (Christensen et al., 2001). In the case of anions,, a moderate-to-high correlation coefficient was found, complexation seemed a minor effect however, as their affinity to organic matters is considerably low (Christensen et al., 2001). Alternatively, other factors may play a paramount role e.g. leachate movement and physicochemical activity (Christensen et al., 2001). For instance, leachate mound may significantly account for accumulation of inorganic compounds (Fig. S1). Phthalates demonstrated negative correlation (-0.1) likely attributed to their presence as a group of compounds rather than a single element, in both diesters and monoesters, which were further influenced by factors like landfill ageing, waste type and management regime (Jonsson et al., 2003).

R5, the monitoring well at which high concentrations of As, Mo and SO_4^{2-} , and high pH as well was detected, indicated more complicated conditions (Fig. 2 and 3). The existence of high

concentration of SO_4^{2-} was not expected. In a typical landfill a variety of anaerobic processes take place due to anoxic environment in the refuse layer (Xie et al., 2015). Bacteria such as *Desulfovibrio* could reduce the available sulphate to sulphide (Suna Erses and Onay, 2003), hence, sulphate should not exist unless oxygen is present. Since the dumping site has been closed for over two decades, conditions might have developed favoring the presence of oxygen at LHDG-Phase III due to air intrusion via broken layers (Jung et al., 2011). Infiltration in this case may facilitate the oxygen intrusion by several pathways. Infiltration usually occurs after precipitation. This could cause (1) introduction of moisture into the refuse layer; (2) formation of hydraulic head to mobilize, mix and/or dilute the leachate; and (3) evolvement of preferential infiltration channels. Oxygen gas can then be delivered into certain refuse pockets in either dissolved form during infiltration or gas form directly via preferential infiltration channels, resulting in sulphide oxidation. The pH value would thus increase as well (Aziz et al., 2010). As a further effect, it favored As and Co leaching and led to their peaked values (Ghosh et al., 2006; Hartley et al., 2004). In a long term the landfill may undergo several phases in which oxygen from the atmosphere will penetrate deeper into the waste leading to higher redox potential (Kjeldsen et al., 2002).

To attain a clear picture of the underground hydrogeology and the relevant effects, hydraulic conditions were investigated (Fig. S1). The hydraulic gradient showed a range of 0.001-0.018 throughout the monitored area, indicating varied potentials on leachate flow. The hydraulic head originated at R5 (Fig. S1) and spread to its surrounding, whereby higher vectors were distributed specifically from R5 to northwest and northeast. Two distinct zones were thus defined, (1) static zones –with relatively low hydraulic gradient responsible for potential leachate mounding such as the southwest and southeast corners, and (2) advective zones –with relatively high hydraulic

gradient close to the northeast and northwest corners, causing the preferential flow (Milosevic et al., 2012). Since advective condition affects much more the transport of contaminants than the static condition (Viana et al., 2008), low concentrations of contaminants were found at advective zones (Fig. 2 and 3). By contrast contaminant accumulation occurred at static zones, e.g. the southwest corner at LHDG-Phase III. The southeast corner at LHDG-Phase III possessed low hydraulic gradient as well; however, illustrating low concentrations of contaminants were probably due to a limited source of pollution (Fig. S2 and S3). In summary, most of the contaminants were readily subjected to dilution or accumulation largely dependent on leachate movement. Also, it is noteworthy that several possible reasons could induce R5 as the hydraulic head, (1) the broken cap resulted in formation of preferential infiltration (echoed by pH and the sulphate concentration), and (2) the higher ground surface elevation led to the higher leachate level as shown in Fig. S1 (Milosevic et al., 2012).

With limited nutrients in a matured tropical landfill, the presence of contaminants in the leachate is primarily influenced by physicochemical processes rather than biological degradation, in which DOM and hydrogeology, etc. turn into prevailing players. DOM affected the leachate mobility by its strong affinity with metal species, while the hydrogeological conditions profoundly impacted the leachate composition through dilution and transportation. Other than above, ageing may introduce heterogeneous redox potential contributing further to the leachate spacial complexity.

3.1.2. Soil

To further define the natural attenuation, soils were characterized near leachate collection points (vertical distance between the leachate and soil collection = 0.46 ± 1.95 m) (Fig. S2-S5). In principle the contaminants distribution between soil (Table S4) and leachate exhibited a poor

correlation such as Ni (0.24) and Br (0.35) (Fig. S4). In addition, high concentrations of COD and Cl^- were discovered at both the northwest and northeast zones in the soil profile, while were oddly peaked at other locations in the leachate. More interestingly, certain metals such as Pb, Cu, and Cd were detected in soil, but not in the leachate, and vice versa. Hereby the accumulation of contaminants in leachate could be a result beyond adsorption/desorption.

The inconsistency indicates two aspects. First, certain metals presented strong affinity to the soil matrix. Landfill ageing is often accompanied by pH elevation and growing metal stability, so that matured wastes possess higher sorption capacity for metal species (Bozkurt et al., 1999). Secondly, the metal species were prone to complex with organic matter in the leachate, and thus possessed higher mobility to further distort its trace (Baun and Christensen, 2004; Ward et al., 2005). Therefore metals that appeared only in the leachate may be a result of contaminant transport. However, the extraordinarily high correlation between Cu and DOC (0.95) was expected as Cu is known to have considerable affinity with organic matter, as the stability constant of Cu-ligand complex is over 10^{11} (Hartley et al., 2004; Jonsson et al., 2003). Generally the findings in the soil provide limited prediction on contaminants in the leachate. To obtain the full picture of an old landfill both leachate and soil should be investigated.

3.2. Time effects

Limited environmental investigation was conducted in 1997 including pH, Fe, Cl^- , BOD and COD, and the results were compared to those in 2011 (Fig. 6). The hydrogeological condition of the landfill in 1997 was also compared to that in 2011 to unveil the transportation of contaminants (Fig. S1). There was an increase in pH from 6.5-7.1 to 6.7-8.8 from 1997 to 2011, indicating growing stabilization of the landfill (Kjeldsen et al., 2002). It was further evidenced by strong reduction of BOD and COD. It is worth noting that preferential infiltration channels

were speculated at R5, and they may induce air intrusion and further raise the pH (Xie et al., 2015). Air intrusion could establish passive aeration and thus both BOD and COD removal have been greatly promoted (Bilgili et al., 2007). Hydraulic disturbance induced nutrient exchange may also occur at R5 via the preferential infiltration channels, resulting in changes of the BOD/COD ratio. Chlorides as the conservative ions were removed considerably by dilution corresponding to high precipitation. Interestingly, the iron showed a trend of accumulation in the leachate (except for R5).. Comparison data of other metal species were not available though. Fe was reported in large quantity and higher lability according to which the leaching behavior could be tricky over time (Øygard et al., 2004). Moreover, the iron (II or III) carries redox potential, posing additional challenges in terms of adsorption/desorption performance (deLemos et al., 2006). Nevertheless, the limited amount of iron concentration at R5 (in 2011) seemed to be an effect caused primarily by mineral precipitation at higher pH (deLemos et al., 2006).

Fig. 6

Investigation of hydraulic gradients in 1997 and 2011 suggests a change in the hydrogeological condition during 1997-2011 (Fig. S1). The hydraulic gradients climbed from a low range of 0.001-0.007 in 1997 to as high as 0.018 in 2011, indicating a raised hydraulic head in LHDG-Phase III due to natural attenuation. As landfill settles it compacts the refuse, and thus significantly reduces the permeability (Simões and Catapreta, 2013). On the other hand, biological processes may induce contaminants deposition and mineral precipitation, aiding to increase the hydraulic gradient via blocking the flow paths. In addition, the headstream was slightly shifted to its northwest from 1997 to 2011 (Fig. S1), likely ascribed to unequal settlement and the topographic reformation. Yet the flow vector maintained the similar shape suggesting that the original geochemistry has not been severely amended.

Correlations among available parameters (BOD, Cl^- and Fe) as a function of organic matter (as COD) were also plotted in 1997 and 2011 (Fig. 7). Interestingly, Cl^- and Fe in 2011 demonstrated less correlation to COD except for BOD as compared to 1997. The poorer linear correlation between Cl^-/Fe and COD as a function of time indicates increased complexity in the leachate composition. Indeed, the composition of leachate is highly dependent on the degradation stage of the waste (Kjeldsen et al., 2002). Additional influence/disturbance may be involved at the site through pathways such as leachate movement, biogas release, settlement and precipitation etc. As the landfill continues ageing, it would face further amendments with varied inputs and outputs and interactions with external impacts, and eventually it would appear in a hardly traceable fashion.

Fig. 7

3.3. Contaminants Transition

Available data at MH16, including measurements in 2004, and best estimation values from models in respective year of 1997 and 2011 (Fig.2, Fig.3 and Fig. 6), was compared to further understand contaminant transformation (Table 2). Amongst the parameters, four typical groups were categorized: (1) nonreactive variables e.g. Cl^- and Br^- ; (2) reactive variables primarily associated with biodegradation like BOD; (3) reactive variables primarily associated with physicochemical process like Ba, TPH, cyanides and phthalates; and (4) other variables associated with several processes including iron, SO_4^{2-} , $\text{NH}_3\text{-N}$ and COD. Being recalcitrant to biodegradation (Agnello et al.; Barathi and Vasudevan, 2001), organic pollutants such as TPH, cyanides and phthalates were considered non-biodegradable. On the other hand Fe, SO_4^{2-} , $\text{NH}_3\text{-N}$ and COD were considered highly influenced by both microbes and the redox conditions.

Table 2

Transport models of different solutes in leachate have been well established (Brusseau, 1994). In general, the mass transport of nonreactive solute and reactive solute in a porous media are presented in Eq. (1) and (2), respectively:

$$R \frac{\partial C}{\partial t} = \frac{\partial}{\partial x_i} \left[D_{ij} \frac{\partial C}{\partial x_j} \right] - V_i \frac{\partial C}{\partial x_i} \quad (1)$$

$$R \frac{\partial C}{\partial t} = \frac{\partial}{\partial x_i} \left[D_{ij} \frac{\partial C}{\partial x_j} \right] - V_i \frac{\partial C}{\partial x_i} - \mu C \quad (2)$$

where C is the concentration of solute, t is time, x_i and x_j are distance, D_{ij} is the hydrodynamic dispersion coefficient, V_i is the interstitial fluid velocity, and R is the retardation factor which is further defined as $R = 1 + \rho/\theta \cdot K_d$, where ρ is the bulk density of porous media, θ is the fractional volumetric fluid content while K_d is a partitioning coefficient of contaminant between solid and liquid phases, μ is the sink term for biochemical reaction. Since first-order reaction kinetics governs the reactants in the leachate at low levels of COD (Barathi and Vasudevan, 2001), μ is termed as the first-order degradation coefficient.

Considering the monitored natural attenuation at MH16, key factors affecting the contaminants removal rate ($\partial C/\partial t$) follow the advection-dispersion-reaction described in Eq. (1) and (2), which are determined by the hydrogeology of the landfill site, the retardation factor of the pollutants, and biochemical reactions during contaminants transportation. In this regards given the removal rate for monitored contaminants (Table 2) together with known factors mentioned above, the corresponding variation of the other factors could be predicted.

Despite of the prevailing attenuation, the removal rates of BOD and COD were lower than the conservative ion Cl^- in 1997-2004. It is ascribed to the higher retardation factor possessed by organic matter (Yin et al., 2007). COD removal rate was greatly enhanced afterwards, in contrast to BOD removal that maintained a similar rate, indicating that COD removal has been promoted

by factors other than biodegradation (e.g. the retardation factor and/or hydrogeological conditions). Advection potential was reduced over time, evidenced by decreased Cl^- removal rate (from 11.0% in 1997-2004 to 10.2% in 2004-2011). Based on Eq. (2) the increased COD removal rate solely relied on the enhanced retardation. According to Tong et al. (Tong et al., 2015) the molecular weight (MW) of organic matter tends to be higher with landfill ageing. Herein the organic matter with larger MW attained a higher hydrophobicity and thus demonstrated more affinity to solid particles, resulting in higher retardation. Similarly, the accumulated TPH presented higher removal rate at the later stage due to ageing. Apart from the organics, certain inorganics such as $\text{NH}_3\text{-N}$ and cyanide also showed an interestingly higher removal rate over time. $\text{NH}_3\text{-N}$ removal rate was described as first-order removal by air stripping (Marttinen et al., 2002). As such the likely occurred air intrusion in old landfills may lead to the enhanced $\text{NH}_3\text{-N}$ removal (Christensen and Kjeldsen, 1995). Cyanide removal is usually difficult in landfill leachate but the presence of certain metals like increased iron may bind with cyanide to facilitate its removal by precipitation (Ghosh et al., 1999). By contrast, the adverse increase of SO_4^{2-} at the later stage of landfill confirmed the air intrusion that possibly took place in a matured landfill. Appearance of phthalates was interestingly noticed only in 2011, indicating a slow release and presenting another emerging challenge. Other constituents like Br^- and Ba displayed reduction rates comparable to Cl^- , indicating the similar conservative behavior regardless of physicochemical and biological reactions.

4. Conclusion

The monitored natural attenuation was investigated in the old landfill of Singapore, showing a considerable stability with low concentration of contaminants. Landfill leachate presented complex distribution highly relevant to DOC, hydrogeological conditions and time. Overall,

precipitation has derived growing interactions among the different constituents in the leachate while exchanges between the inner and inter regions further mask their traces. In this regards the brought influence of certain parameters may overwhelm the others as a function of time and space, coupled with the site-specific conditions. For instance, monitoring in 1997-2011 showed a shift from biological activities to precipitation-facilitated dilution and transportation due to depletion of biodegradable organic matter. Nevertheless, the latest monitoring at the site has indicated a trend from which the contaminants distribution in leachate presents more correlation among components in the leachate as compared to its adjacent soil. Taking account of the oxygen intrusion at R5, monitored natural attenuation in the LHDG-Phase III demonstrated the characteristics of a matured landfill deemed to its late stage of life whereas the transitory distribution of contaminants over time was complicated yet was explicable with careful synergy of different monitoring parameters.

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Table 1. Summary information of boreholes and monitoring wells at LHDG-Phase III.

Survey year	Borehole /monitoring well #	Coordinates (East, m) (North, m)		Ground surface elevation (m)	Termination Depth (bgs, m)	Refuse depth (m)	Soil sample location (bgs, m)	Soil Parameters	GW level (bgs, m)	GW parameters
2011 (¹ R3C)	^{b,m} R1	40107.0	36457.8	108.40	30.45	15.40	8-9	(COD, F, Cl, Br ⁻	8.4	pH, BOD,
	^{b,m} R2	40227.6	36373.8	108.25	30.45	16.80	12-13	,NH ₃ -N,Cd, Cr,	12.0	COD, TOC, F
	^{b,m} R3	40557.8	36346.3	110.20	24.45	19.00	9-10	Cu, Pb, Zn, Ni)*,	11.7	, Cl, Br ⁻ , PO ₄ ³⁻
	^{b,m} R4	40508.1	36159.3	107.50	30.45	14.00	6-7	SPT-N, density,	7.0	, SO ₄ ²⁻ , NH ₃ -
	^{b,m} R5	40466.6	36502.1	111.44	18.25	18.25	11-11.5	H ₂ O%, OM,	10.7	N, As, At, Ba,
	^{b,m} R6	40490.4	36875.1	109.29	30.45	11.20	8-9	Atterberg limits,	5.5	Cd, Cr, Co,
	^{b,m} R7	40653.9	36874.0	109.31	30.45	11.00	9-10	Particle size	7.7	Cu, Hg, Pb,
2004 (² Meinhardt)	^{b,m} MH16	36467.8	40655.3	111.88	33.45	17.80		analysis, Triaxial	9.4	Mo, Ni, Zn,
	^b MH17	36407.2	40097.7		28.95	14.70		tests (UU, CU)		Fe, EC, TPH
	^b MH18	37264.8	40523.7		19.95	5.40		consolidation		(C6-C9, C10-
	^b MH19	36621.2	40278.2	NA	31.10	12.80		test. *: for	NA	C36), Cynide
	^b MH20	36222.7	40374.5		36.40	19.20		environmental		
1997 (³ MW)	^b MH21	36848.7	40440.7		30.45	14.70	NA	analysis		
	^m MW23	36414.0	40346.2	112.75	16.45	15.00			9.4	pH, Cl, COD,
	^m MW24	36037.5	40560.2	103.38	14.45	NA			3.0	BOD, Fe,
	^m MW25	36789.5	40703.8	102.44	8.45	5.00		NA	1.1	VOC
	^m MW26	36622.7	40377.5	112.17	12.45	11.00			8.8	
	^m MW27	36678.7	40476.3	113.92	17.00	16.00			10.9	

¹: represents the project conductor of the Residues and Resource Reclamation Centre (R3C) of Nanyang Technological University, Singapore;
²: represents the project conductor of the Meinhardt Infrastructure and Environment Ptd Ltd, Singapore; ³: represents the project conductor of Montgomery Watson Engineering Consultants (Singapore) Pte Ltd; ^b: borehole; ^m: monitoring well; GW: groundwater; bgs: below ground surface; NA: not available.

Table 2. Monitored typical parameters of landfill leachate in monitoring well MH16 (N, E) in the year of 1997, 2004 and 2011.

Time (yr)	Parameters											
	pH	COD (mg L ⁻¹)	BOD (mg L ⁻¹)	Cl ⁻ (mg L ⁻¹)	Fe (µg L ⁻¹)	Br ⁻ (mg L ⁻¹)	SO ₄ ²⁻ (mg L ⁻¹)	NH ₃ -N (mg L ⁻¹)	Ba (µg L ⁻¹)	TPH (µg L ⁻¹)	Cyanide (µg L ⁻¹)	Phthalates (µg L ⁻¹)
1997 ¹	6.85±0.1	1450±10	65±1.0	3400±100	32.5±5					NA		
2004	7.00	416	18	554	NA	4.55	10.7	356	1201	5358	11.6	0
2011 ²	7.35±0.1	35±5.0	5.5±1.0	150±10	720±10	1.5±0.1	25.5±0.5	17.5±2.5	310±10	186±2.0	0	2.5±0.1
Rate	Removal	136.35	6.20	375.30						NA		
(1997-04) % removal		9.4%	9.5%	11.0%								
Rate	Removal	NA	53.16	1.74	56.37	0.43	-2.06	47.23	124.33	721.67	1.62	-0.35
(2004-11) % removal		12.8%	9.7%	10.2%		9.4%	-19.3%	13.3%	10.4%	13.5%	14.0%	NA

¹: represents the best estimated values of different parameters at MH16 based on simulated contaminants distribution of LHDG.p3 in 1997 (Fig 7);
²: represents the best estimated values of different parameters at MH16 based on simulated contaminants distribution of LHDG.p3 in 2011 (Fig 2&3).

Figure 1. Map and locations of boreholes and/or monitoring wells at LHDG-Phase III.

Figure 2. Simulated heavy metal distribution from landfill leachate in 2011 (the white blank area represents an area free of contamination; unit in $\mu\text{g L}^{-1}$).

Figure 3. Simulated typical ions, pH and organic matter distribution from landfill leachate in 2011 (the white blank area represents an area free of contamination: unit in mg L⁻¹ except for TPH and phthalate in μg L⁻¹).

Figure 4. Correlation between heavy metals and DOC in the landfill leachate at LHDG-Phase III (curved lines represent the 95% confidence interval of the least squares linear regression).

Figure 5. Correlation of inorganic ions, BOD, COD, phthalates and TPH vs. DOC in the landfill leachate at LHDG-Phase III (curved lines represent the 95% confidence interval of the least squares linear regression).

Figure 6. Simulated distribution of pH, Cl⁻, iron and organic matter in landfill leachate at the same plot of LHDG-Phase III in 1997 and 2011.

Figure 7. Comparison of correlation between BOD, Cl⁻, and Fe concentration vs. 1COD in 1997 and 2COD 2011 at LHDG-Phase III (curved lines represent the 95% confidence interval of the least squares linear regression).

Supplemental Information

Table S1. Critical characters in the Lorong Halus Dumping Ground (LHDG).

Description	Old Dumping Ground	Phase I & III	Phase II(a) & II(b)	Phase IV
Area (hectare)	34.0	56.1	75.3	63
Waste quantity (ton)	3×10^6	3.4×10^6	8.6×10^6	NA ³
Operation period	1970-1974	Phase I (1974-1975) Phase III (1983-1989)	1976-1999	1990-1999
Original conditions	Mangroves swamp	Mangroves swamp	Mangroves swamp	Mangroves swamp
Landfilling types	Municipal landfill	Municipal landfill	Municipal landfill	Municipal landfill
Waste composition	100% MSW ¹	50% MSW (bottom layer) and 50% C&D ² waste (top layer)	30% MSW (bottom layer) and 70% C&D waste (top layer)	NA
Decomposition stage		Advanced		NA
Waste layer depth (m)	4-10	8-15	Up to 40	NA
Sample properties				NA
Leachate		Weak		NA
Gas		Present		NA
Stability		Total/differential settlement		NA

¹: MSW – Municipal solid waste; ²: C&D waste – Construction and demolition waste; ³: NA – not available.

Data adapted from Meinhardt Infrastructure and Environment, 2004.

Table S2. Concentration of different ingredients in the leachate from monitoring wells in 1997 through 2011.

Monitoring well	pH	DOC	As	Ba	Cr	Co	Mo	Ni	Zn	Fe	Cl ⁻	Br ⁻	SO ₄ ²⁻	NH ₃ -N	BOD	COD	TPH	Phthalate
Unit	n.a.	mg L ⁻¹	µg L ⁻¹	µg L ⁻¹	µg L ⁻¹	µg L ⁻¹	µg L ⁻¹	µg L ⁻¹	µg L ⁻¹	µg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	µg L ⁻¹	mg L ⁻¹
R1	6.8	89.0	6.5	1080.0	13.7	3.9	1.4	4.1	3.3	2123.6	260.0	7.5	8.3	186.55	32.2	310	342.1	2.2
R2	7.0	103.0	4.7	1082.7	16.8	7.4	0.5	6.7	5.0	2071.5	682.0	10.8	9.8	445.85	20.4	380	615.7	9.1
R3	6.7	5.2	0.0	419.8	0.0	0.0	1.9	0.0	0.0	1025.2	132.0	1.5	8.6	13.64	5.5	0	153.0	3.6
R4	6.9	103.0	4.9	1078.5	10.0	5.4	0.7	6.0	1.6	809.2	1,165.0	12.3	5.6	349.05	21.6	300	332.4	2.1
R5	8.8	12.2	17.8	7.1	0.2	0.0	39.9	2.0	1.1	239.4	52.5	N.D.	67.9	13.53	7.4	60	200.2	15.3
R6	7.0	6.8	0.0	86.2	0.2	0.0	4.2	0.0	3.0	387.3	77.3	N.D.	36.0	27.10	7.8	0	139.6	0.0
R7	6.8	51.0	7.8	701.1	1.3	3.1	9.8	8.3	2.5	1315.4	329.0	5.5	3.2	141.80	11.6	210	395.9	0.0
MH16	7.0			1201							554		10.7	356	18	416	5358	0
MW23	6.9									25.2	396				61	312		
MW24	6.5									49.8	11730				91	1090		
MW25	7.1									21.6	544		NA		40	216		NA
MW26	6.6									13.4	91				8	34		
MW27	6.8									24.5	177				66	216		

Table S3. Correlations between different ingredients in the leachate from monitoring wells in 2011.

Correlation	pH	As	Ba	Cr	Co	Mo	Ni	Zn	Fe	Cl ⁻	Br ⁻	SO ₄ ²⁻	NH ₃ -N	BOD	COD	TPH	Phthalate	DOC
pH	1.00	0.85	-0.58	-0.30	-0.36	0.96	-0.23	-0.23	-0.54	-0.31	0.89	0.92	-0.32	-0.33	-0.29	-0.24	0.85	-0.35
As		1.00	-0.21	-0.08	-0.07	0.88	0.22	-0.11	-0.20	-0.13	0.45	0.62	-0.10	0.00	0.08	0.07	0.72	-0.01
Ba			1.00	0.86	0.91	-0.64	0.72	0.48	0.81	0.74	0.91	-0.79	0.86	0.84	0.92	0.76	-0.28	0.94
Cr				1.00	0.90	-0.47	0.53	0.70	0.79	0.61	0.78	-0.46	0.88	0.88	0.91	0.79	0.05	0.92
Co					1.00	-0.48	0.80	0.67	0.71	0.80	0.92	-0.59	0.98	0.73	0.97	0.92	-0.04	0.96
Mo						1.00	-0.18	-0.35	-0.56	-0.43	-0.39	0.86	-0.48	-0.43	-0.38	-0.31	0.74	-0.47
Ni							1.00	0.48	0.54	0.62	0.62	-0.52	0.73	0.50	0.83	0.83	-0.11	0.76
Zn								1.00	0.62	0.22	0.59	-0.22	0.64	0.54	0.66	0.75	-0.06	0.58
Fe									1.00	0.24	0.17	-0.68	0.61	0.74	0.76	0.76	-0.17	0.70
Cl ⁻										1.00	0.88	-0.51	0.85	0.50	0.71	0.56	-0.14	0.81
Br ⁻											1.00	0.01	0.94	0.64	0.89	0.66	0.31	0.96
SO ₄ ²⁻												1.00	-0.53	-0.47	-0.54	-0.48	0.68	-0.58
NH ₃ -N													1.00	0.66	0.92	0.88	0.00	0.93
BOD														1.00	0.85	0.57	-0.17	0.87
COD															1.00	0.89	-0.02	0.98
TPH																1.00	0.11	0.82
Phthalate																	1.00	-0.10
DOC																		1.00

We used colored zones to suggest correlations between different groups of contaminants. The colored zones are defined as: 1) the light grey zone represents correlations among metals; 2) the blue zone represents correlations between metals and inorganic ions; 3) the orange zone represents correlations between metals and organic matter/compounds; 4) the green zone represents correlations among inorganic ions; 5) the red zone represents the correlations between inorganic ions and organic matter/compounds; and 6) the yellow zone represents correlations among the organic matter/compounds. Given correlation coefficient 0.8 as the indicator for effective linearity, we set the ratio between the total numbers of correlation coefficients ≥ 0.8 vs. the total number of correlation coefficients as the “interaction index”, and then we could achieve 0.22 (grey), 0.22 (blue), 0.38 (orange), 0.38 (green), 0.3 (red), and 0.4 (yellow).

Table S4. Characterization of soil samples from boreholes in 2011.

Sampling borehole No.	Soil sample location (bgs, m)	GW level (bgs, m)	Leaching test										
			mg L ⁻¹					µg L ⁻¹					
			Cl ⁻	Br ⁻	SO ₄ ²⁻	NH ₄ ⁺	COD	Cd	Cr	Cu	Pb	Zn	Ni
R1	8-9	8.4	19.18	0.00	61.50	0.10	72.00	2.02	4.13	21.35	19.33	43.09	7.49
R2	12-13	12.0	39.96	0.81	884.27	10.50	108.00	2.53	4.44	45.45	20.26	110.26	5.58
R3	9-10	11.7	43.89	0.00	100.58	4.41	157.00	N.D.	3.12	106.13	18.86	23.54	4.71
R4	6-7	7.0	21.04	0.51	230.03	14.80	46.00	2.47	5.77	26.39	13.47	43.95	18.02
R5	11-11.5	10.7	32.31	0.74	223.89	5.76	55.00	0.73	1.10	22.42	3.68	13.48	4.61
R6	8-9	5.5	10.13	0.00	62.39	5.18	43.00	0.13	0.51	14.45	2.78	9.32	6.35
R7	9-10	7.7	119.90	0.66	129.83	1.12	50.00	1.42	0.91	12.42	N.D.	31.53	4.14

bgs: below ground surface; GW, groundwater; N.D.: non detectable.

Figure S1. Groundwater flow vector simulation based on groundwater level of the monitoring wells (MW23-27 and R1-7 in 1997 and 2011, respectively) and the topography at LHDG-Phase III.

Figure S2. Simulated heavy metal distribution from soil next to groundwater samples in 2011 at LHDG-Phase III (unit in $\mu\text{g L}^{-1}$).

Figure S3. Simulated ions and COD distribution from soil next to groundwater samples in 2011at LHDG-Phase III (unit in mg L^{-1}).

Figure S4. Correlation of selected parameters between landfill leachate (y axis) in monitoring wells and the adjacent soil (0.46±1.56 m) (x axis, based on soil leaching data). Curved lines represent the 95% confidence interval of the least square linear regressions.

Figure S5. Correlation of monitored ions/metal species vs. COD in the soil (based on soil leaching data). Curved lines represent the 95% confidence interval of the least square linear regressions.

Graphic abstract:

Highlights

- Leachate composition in old landfill was significantly affected by DOC, hydrogeology and time.
- The distribution of contaminants in the leachate possessed selective attention of spots associated with leachate/groundwater movement.
- The correlation between components in soil and the leachate was limited
- Air intrusion could occur in a matured landfill.