Vertical distribution of heavy metals in seawater column during IBA construction in land reclamation – re-exploration of a large-scale field trial experiment

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Abstract

Data from large-scale field trial experiments simulating the application of incineration bottom ash (IBA) for land reclamation were re-explored, to understand the spot-specific leaching characteristics and re-adsorption of heavy metals associated with various reclamation scenarios. Data showed that IBA leaching changed significantly as a function of seawater depth rather than time. The application of a chute had a minor effect on the total metal leached amounts; however, it would magnify the gradient of leaching concentrations across depths. Metal re-adsorption occurred within half an hour after IBA dumping, which however was significantly alleviated when a chute was applied. It may be ascribed to various degrees of contact with seawater of IBA, seawater movements and particle resuspension. Batch leaching tests from the laboratory under different L/S ratios were conducted as the references to “effective” leaching behaviors in the large-scale experiments, suggesting that the batch leaching test with the liquid to solid ratio = 10 provide a closer estimation of IBA leaching concentrations during land reclamation. As the current study took account of major field factors during land reclamation, including seawater depth (m), IBA loading (ton), IBA dropping method, particle dispersive area (m^2), and settling time (min), these findings are valuable for the risk assessment of IBA utilization in land reclamation.

Keywords: IBA, vertical distribution, land reclamation, heavy metal leaching potential, ecotoxicity

1. Introduction

It is estimated that 440 million tons of incineration bottom ash (IBA) was generated worldwide in 2016 (Lynn et al., 2017). IBA carries similar properties to natural aggregates making it one of the promising alternatives to construction materials (Dou et al., 2017). IBA is considered non-hazardous waste based on leaching criteria (EU) at pH range between 7-12 (Klymko et al., 2017). National legislations have been implemented to regulate utilization of IBA in EU countries like The Netherlands and France (Liu et al., 2015; Tang and Brouwers, 2018). Many studies have been carried out to evaluate the potential use of IBA for various applications, including IBA as aggregates (Ferraris et al., 2009; Jurič et al., 2006; Lam et al., 2010) and IBA as raw materials to synthesize other novel materials (Chen et al., 2016; Song et al., 2015; Zhu et al., 2018). Among these, IBA utilization for land reclamation attracts attention in a bid to close the waste loop, especially for land-scarce countries like Singapore, the Netherlands and Japan (Yin et al., 2018). Yet, for such an application, no field projects have ever been implemented so that, there is a knowledge gap between laboratory data and real field measurements.

Heavy metals refers to any metallic element that has a relatively high density ($>4 \text{ g/cm}^3$), however, being a heavy metal has little to do with density but concerns chemical properties which is frequently toxic or poisonous even at low concentration (Duruibe et al., 2007). Health hazard is associated with a number of heavy metals including As, Be, Cd, Cr, Cu, Pb, Hg, Mo, Se, Ag, Tl, and Zn (Förstner and Wittmann, 2012). In marine system, some of them such as Zn, Cu and Co are absolutely essential for normal growth and development of marine organisms; yet, at sufficient high concentrations, heavy metal becomes toxic to living organisms (Bryan, 1971). Tremendous research works have been performed to quantify the heavy metal ecotoxicity on marine species (Arnold et al., 2005; Debelius et al., 2009; George, 2017; Gissi et al., 2018). For

certain metals, very tiny amount may already present observed toxic effects to the marine biota. For instance, Mance et al. (1984) proposed an environmental quality standard (for the protection of saltwater organisms) of 5 µg/L for copper ion in the seawater. A much lower value of 0.0175 µg/L for As has been benchmarked by U.S. Environmental Protection Agency's human health criterion (fish consumption) (Neff, 1997). Trace metals from the IBA exhibit high leaching potential, therefore it is vital to understand the leaching behaviors of IBA during its application in land reclamation.

Challenge to understand IBA behaviors associated with land reclamation As a matter, during land reclamation settling of IBA, which is dependent upon grain size, the shape and density of the grains, is not homogeneous and simultaneous. The IBA fraction with highest terminal velocity arrives at bottom first and continuously overlain by another one with less terminal velocity until all IBA settles. Thus, IBA is subject to different degree of exposure to seawater during dumping – the first-arrival fraction (denser particles) on the bottom are likely to be less mixed/ contacted with seawater as it will be covered by the lighter fractions, while the inner fraction would be partially masked by the exterior fractions. It is postulated that, the various degrees of mixing with seawater and the limited time of exposure for IBA may eventually yield different leaching kinetics (and capacity as well) from standard leaching methods in the laboratory.

Challenge in laboratory hazard identification There exist significant margins of uncertainties on the IBA properties from the laboratory standard leaching tests, which is dependent of the types of leachants, liquid to solid (L/S) ratio, pH and operation procedures, etc. (Yin et al., 2018). Although many laboratory-based leaching methods, such as batch leaching, column leaching and pH-static leaching, etc. have been well developed to simulate the IBA

leaching potential and to understand its associated hazards, factors considered in these operation procedures are rather limited and thus hardly conveyed the *in-situ* environmental conditions (Yin et al., 2018). In this regard, Our earlier publication (Chan et al., 2018) has concluded that there exists distinct heavy metal leaching potential between the large-scale column trial experiments and the standard laboratory leaching tests.

However, there is one big concern from most laboratory-leaching studies that spot-specific release of IBA into the aqueous phase may be compromised by the size and operations from laboratory setups. It does exist in the field while would pose significant impacts on ecotoxicity study and exposure assessment of sea biotas in the IBA application zone (Chou et al., 2009; Pal and Maiti, 2018; Yang et al., 2015; Yin et al., 2010). To comprehensively understand the IBA leaching behavior associated with land reclamation, we re-explored the 6 large-scale field trial experiments which were carried out with erected big columns on the ground surface ($h \times d = 10/7/5 \text{ m} \times 3 \text{ m}$). Approx. 3.2 tons (wet weight) of IBA was dropped on top of the column for each of experiment. Simultaneously, comparative laboratory batch leaching tests (L/S ratio = 2, 5 and 10) were carried out with the same IBA to the field trial experiments, to understand the differences through which useful information for guidance of future IBA utilization in land reclamation will be achieved.

2. Methodology

2.1. Sampling of IBA

Six IBA samples (approx. 3.2 tons/sample) were collected from a local metal recovery plant in Singapore, which had been subjected to approx. 10% (w/w) removal of ferrous and non-ferrous metals. IBA sampling device (Fig. S1a) was used to receive IBA directly from drop-

hopper above and then truck-delivered to the field trial site for the dumping experiment. 20 kg of sub-sample of IBA was collected directly from sampling device before field trial experiments and used for laboratory analysis. The volume of IBA used for field trial experiments (3.2 tons) was calculated in terms of batch leaching results of the IBA sub-samples from the laboratory – whereby most metal leaching concentrations based on the field trial experiments should be near or above the detection limit as measured using inductively coupled plasma – mass spectrometer (ICP-MS). The trials were herein designed at $L/S = 13, 18.3, 26 (<30)$. Mineralogical studies were performed in IBA, using X-ray diffraction (XRD) analyzer, to develop a better understanding in the leaching behavior of IBA (Fig. S2).

2.2. Column trial experiments

The large-scale column experiments were performed in an attempt to get a measure of the release of the substances of interest during the stage of land reclamation when IBA is dumped from barges with bottom doors that open. The load of IBA falls through the water column to the bottom of the sea and is soon overlain by more IBA and/or by sediment dumped from other barges. A particular load of IBA is thus only exposed directly to the seawater during its fall from the barge to the seabed and for a relatively short time after that until it is covered by another load of IBA or sediment. Not all parts of the falling load experience the same degree of contact with the seawater – the middle or inner parts of the load are likely to be somewhat shielded from water contact by the outer parts. It is therefore assumed that the restricted water contact and short contact time combine to produce an “effective L/S ” for the release of a given substance from a given type of IBA being dumped. The hypothesis of the experiment is that the “effective L/S ” for a given type of IBA is dependent on the water depth at the place of dumping and that the

“effective L/S” for a given type of IBA can be used to establish a relationship between the release of a given substance from the IBA dumped at a certain water depth and the results of a laboratory leaching test performed on the same IBA, in terms of mg of the substance per kg of IBA. In the practical land reclamation, L/S ratio is hardly controlled due to various seawater depths encountered during land reclamation. However, we’ve adopted 3 different heights (depths) of seawater column, i.e. 10 m, 7 m and 5 m in the large-scale column experiments, covering a good range of seawater depths in the practical land reclamation. As such, we would be able to understand the IBA leaching characteristics associated with different seawater depths.

Three tubular units made of fiber-reinforced plastic with the same diameter at 3 m and respective heights at 2 m, 3 m and 5.5 m, through different combinations, were used to assemble 3 different column heights, which were put up in the order of 10.5 m column (using 3 tubular units) first, then 7.5 m column (using 2 tubular units of height at 2 m and 5.5 m) follow by 5.5 m column (using single tubular unit of height at 5.5 m only) (Fig. 1). Two rounds of dumping experiments were performed for each column height and denoted as CT1 & 2 for 10.5 m column, CT3 & 4 for 7.5 m column, and CT5 & 6 for 5.5 m column as illustrated in Table S1. After dumping of IBA, liquid samples were collected at designated locations by use of a customized sampling device (Fig. 1a). Two dumping methods, i.e. with a chute (CT2, CT4 & CT6) and without (CT1, CT3 & CT5), were employed to unveil the influence of various dumping methods for IBA placement during land reclamation. Chute was positioned right underneath the IBA dumping device while ~1.0-1.5 m above the bottom of the column. It aimed to simulate the typical condition that a chute would be installed (vertically) downwards in the seawater from the barge; while the IBA would be dropped (by gravity) via bottom doors of the barge followed by the attached chute to the seabed for a relatively short time. After that it is overlain by another

load of IBA or sediment dumped from other barges. In addition, the initial seawater movement effects induced by wind and the ocean current were eliminated (considering stagnant state).

Seawater was pre-filled into the column until its designated level, i.e. 10, 7, and 5 m for 10.5, 7.5, and 5.5 m column setup, respectively. Seawater sample was analyzed as blank. IBA was then dumped into the filled column via a crane-levelled dumping device with its bottom (originally closed) around 0.2-0.5 m below seawater surface (Fig. S1d). It is a simulation of the actual activities of dumping reclamation materials from the bottom of barges. After dropping the IBA, the dumping device was immediately removed by positioning a sampling device into the seawater (Fig. 1 b, e). The actual time for the first sampling started at about 2 minutes after dumping as time was needed for moving away the dumping device of IBA and then positioning the sampling device into the column. Seawater samples (approximately 5 L each) were taken at different positions (A-E) of heights (H1-H4 for CT1 & 2; H1-H3 for CT3-6) at T = 2, 17, 32, and 62 minutes after dumping of IBA (Fig. 1e). Sampling time was selected based on expected logistic constraints (time needed for sampling process) and by taking account of the estimated settling time for IBA. Design and layout of sampling device was illustrated in Fig. 1a. After the experiment, seawater and IBA were taken out of the column and collected for treatment before disposal. The column was conditioned before next round of experiment. Total number of seawater samples (360) and seawater blanks (12) collected were in total of 372. All samples were filtered through 0.45 μm filter paper at the same day of collection and stored at 4.0 $^{\circ}\text{C}$ before metal analysis. pH and conductivity were measured with a pH meter D-50 (Horiba) and a InLab®738-ISM (Mettler-Toledo) conductivity probe, respectively. Filtered samples with proper dilutions were analyzed using ICP-MS for the concentration of trace elements ($\mu\text{g/L}$).

2.3. Batch scale leaching tests

IBA samples were tested for grain size distribution with Wet Sieving BS 1377 Part 2 1990. Moisture content was determined with oven drying at 105° C for 24 hours. Total organic carbon (TOC) and total carbon (TC) were determined with a TOC analyzer (Analytik Jena Multi N/C 2100/2100S) (Table S2). Baked IBA was crushed to < 4 mm (BB 100 crusher, Retsch), was then mixed with seawater at L/S = 10 and incubated in a rotating tumbler for 24 h, based on standard leaching method EN12457-2. The leachate was collected and filtered through the 0.45 µm filter paper. Element analysis of IBA (size < 150 µm by a rotor mill (ZM 200, Retsch)) was achieved by mixing digestion using HCl/HNO₃/HF, according to US EPA Method 3052. The digested liquid was first filtered through 0.45 µm nylon membrane filter followed by certain dilutions. Both the leachate and digested liquid were analyzed with APHA 3125B method using ICP-MS (Thermo Scientific iCAP).

2.4. Statistical analysis

Normality tests for characteristics of IBA used in the large-scale field trial experiments (CT1-6) were performed in terms of their size distribution, density, TC, TOC, heavy metal content, metal leaching concentrations (L/S = 10) by using Anderson-Darling statistic, suggesting that the results could be generally considered as normally distributed data as summarised in Figs. S3 and S4. We hereby assume that all IBA samples in the field trial experiments are not statistically significantly different between each other with respects of their element contents and leaching potential under identical conditions, allowing to compare their performances excluding their intrinsic heterogeneities.

3. Results and Discussion

3.1. Study of heavy metal distribution as a function of depth and time

Figs. 1-3 show vertical concentration distributions of heavy metals at different time, with application of a chute (Figs. 1-3 e-h) or not (Figs. 1-3 a-d), respectively. Distribution of metals exhibited characteristics dependent of seawater depth, time and the dumping method.

Figs. 1-3

3.1.1. Effects of the chute application

Metal leachability in seawater followed an order of Ba > Cu > Sb, Cr > Ni > Pb > Ag, As, Cd, Hg, Se, Tl and Zn (Fig. 6). Such an order was roughly kept among all 6 experiments. The leachability ranking of most metals exhibited a good agreement between large-scale column experiments and batch leaching tests from the laboratory (see Fig. 6). Since the major differences between large-scale column experiments and laboratory batch leaching tests lie in their various reaction time and the L/S ratio while they did not change the rough ranking order of metal leachability, the dominant factor affecting the metal leaching potential has to be associated with the IBA intrinsic properties (Yin et al., 2018). Based on XRD analysis of selected IBA samples in the study (Fig. S2), SiO₂ and Ca-based minerals are found to be the dominant components that is agreeable to literatures (Gonzalez et al., 2017; Rocca et al., 2012; Wei et al., 2017). Because of the presence of glassy matrix of IBA together with Ca, Fe and Al containing mineral phases, heavy metals are subjected to complexations and metallic inclusions (Wei et al., 2011), which may limit their availability for leaching (Rocca et al., 2012). Each metal release from the IBA matrix is also functions of pH, the L/S ratio, its specific distribution and the partitioning coefficient between IBA and seawater. Highest released concentrations of Ba were likely due to

(1) its high affluence in IBA, (2) less pH sensitive as compared to other elements. High Cu release was associated with its activity of Cu^{2+} as well as the high mobility of Cu-dissolved organic matter complexes (Olsson et al., 2009). Albeit high amounts of Zn and Pb in the IBA, both metals exhibited limited leaching concentrations suggesting their inhibition of release under seawater (Yin et al., 2017; Yin et al., 2018). The application of a chute in the column trial experiments (CT2, 4 & 6) presented much higher concentration gradients across depths, e.g. surface vs. bottom, as compared to those not. For CT1 (10 m seawater without a chute) (Fig. 1a), concentrations of most leachable metals, such as Ba, Cu and Cr, were found comparable to those at depth of -3, -7 and -9 m in the seawater column, independent of time (note that, most samples at “0” m seawater level were unavailable in CT1 except for time = 2 min). By contrast, metal concentrations at the same seawater depths in CT2 with application of a chute were increased with depth, as much as twice in the end for Ba.

Data from CT3-6 unveiled that, IBA leaching potential at the surface seawater was generally much lower than the other depths underneath it, and less than no chute application at the surface as well (Figs. 3 and 4). In the meanwhile, concentration gaps across depths got significantly larger to be up to an order of magnitude like Ba when a chute was applied (Figs. 2 & 3, e-h). It suggests the significant impact imposed by the chute – in general minimizing the IBA leaching potential into the surface seawater, which is benign to land reclamation particularly where a sand bund is constructed. This is because contaminants transport via surface seawater overflowing will be greatly reduced. Note that, however, its impacts on the deeper seawater was much more complicated (likely worse in certain scenarios). For instance, metal release next to bottom seawater in CT4 (Fig. 2, e-h) indicated higher Ba, Cu and Cr concentrations than their counterparts in CT3 without a chute. Moreover, at deeper depths (-4 m and -6 m), most of the

highly leachable metals (i.e. Ba, Cu, Cr, Ni and Sb) presented even higher concentrations with application of chute (CT2, Fig. 1, e-f). From ecotoxicity perspective, these results are not in favour of the application of a chute, as both the acute and chronic toxicity ascribed to synergy of higher strength IBA leachate can be dramatically promoted in deeper seawaters (Gao, Y. et al., 2018; Ghosh et al., 2010). It suggests that IBA leaching associated with land reclamation is rather complicated which would be dominated not only by the dumping method but the dumping depth.

3.1.2. Effects of seawater depth

Seawater depth is critical to affect IBA leaching from two aspects, 1) degree of IBA contact with seawater, and 2) severity of seawater disturbance due to IBA dropping and subsequent resuspension. IBA possessed a bulk density approximately 1.5 ton/m³ analogous to natural aggregates (Table 1). The spent time for different IBA fractions (0-2 mm, 2-8 mm, 8-20 mm and 20-50 mm) to fall down onto the bottom for 10, 7 and 5 m seawater were calculated based on the equation (*Stokes' law*):

$$w = \frac{2(\rho_p - \rho_f)gr^2}{9\mu} \quad (1)$$

Where w is the settling velocity, ρ is density (the subscripts p and f indicate particle and fluid respectively), g is the acceleration due to gravity, r is the radius of the particle and μ is the dynamic viscosity of the fluid. The settling time for each fraction of IBA for the field trial tests was calculated as shown in Table 1.

Table 1

The fine fraction of IBA (<2 mm) may require an average time about 6.3, 4.5 and 3.2 seconds to settle down onto the seabed in the 10, 7 and 5 m seawater column, respectively (Table 1). Contrastively, the other fractions may take in only less than a second. It is noteworthy that one third (by weight) of the particles had particle sizes less than 2 mm. Indeed, the fine fraction is critical to the overall IBA leaching as it possessed higher surface area meanwhile experienced the most degree of contact with seawater, while their original total metal contents were even higher (del Valle-Zermeño et al., 2017). Echoed by the metal leaching magnitudes from CT1 as compared CT3 and CT5, more metals (Ba, Cu and Sb) were thus released (discuss more lately in section 3.2.1).

As mentioned, the seawater depth could also affect the IBA dispersion and resuspension potential (Gao, G.D. et al., 2018). Since there were two scenarios of IBA dumping in the study – with a chute or without, we herein separately give discussion. Clearly, small turbulence in the surface layer (farthest from particle rebound/resuspension) and insufficient IBA hydration led to minimal leached amounts of heavy metals, no matter with a chute or not (Siegel et al., 2009). Firstly, data from CT1, 3 & 5 without a chute were investigated. It showed that metal distribution patterns at deeper seawaters (>“0” m) in CT5 were significantly different from those in CT1 and CT3, whereby significant concentration gradients appeared (Fig. 3, a-d). As suggested by Fig. S5, IBA spread more as it fell deeper, so that IBA in CT1 who experienced the longest travelling distance had the largest coverage area on the bottom, followed by that in CT3 and then by CT5. The strength of tidal currents determines the resuspension of particles from the seabed (Gao, G.D. et al., 2018). In this regard, downward current (induced by IBA dropping) close to the bottom of the column in CT1 would be stronger than that in either of CT3 or 5. As it rebounded, the countercurrent would move back much quicker and stronger in CT1 according to the law of

action-reaction (Fig. S5). The countercurrent resuspended part of the IBA particles settled until it encountered the smaller and lighter IBA particles that was later arrived, causing severe turbulence at the meeting spot. Because of the different energy carried from both downward current and countercurrent in each column as earlier mentioned, such turbulence ranked from strongest to weakest with an order of CT1 >CT3 >CT5. As such, higher release of heavy metals took place in CT1 ascribed to stronger mechanical stripping and higher degree of contacting (Fig. 1) (Juanico et al., 1995; Yanful and Verma, 2000).

Generally, turbulence induced by IBA dumping became limited by the application of a chute due to the confined IBA spreading space (Fig. S5) (Chan et al., 2018). Meanwhile, the chute and the seawater inside may absorb a big proportion of countercurrent energy, leading to a restricted turbulence zone. Noted that, however, the rebound effects may achieve “resonance” effects under specific column dimensions (which was also a function of countercurrent strength). As reflected in CT4, the metal release was even comparable to that in CT3 (Fig. 2).

3.1.3. Effects of time

Time effects was further investigated with reference to specific metal distributions at different depths. Within monitored period of time, the primary release pattern in terms of various metals at time = 2 min were more or less well maintained thereafter. This is especially true in all cases when a chute was used (Figs. 2-4, e-h, respectively). Without a chute, however, certain metal concentrations tended to be decreased with increased time, such as Cu, Cr and Pb at all measured depths from 2 to 17 min in CT1, Cu at “0” m and Cr at all measured depths from 17 to 32 min in CT3, and Sb at “0” m from 2 to 17 min in CT5. Opposite findings, for instance 25% of Ba concentration increase (8 to 10 mg/kg) from 2 to 62 min in CT3, however, complicated the

time effects. Nevertheless, these local differences observed were minor as compared to the overall stable shape of concentration distribution among most metals. That is to say, metals release from IBA into the seawater column should be instant and rapid until achieving their isothermal equilibrium. Such an equilibrium may be kept so long as no presence of another disturbance – for instance an extra load of reclamation material dropping to break the equilibrium again.

3.2. Studies of total heavy metal release

From a broader point of view, one of the most concerns lies in the overall metal leaching capacity of IBA into the seawater column in proximity. As such, weighted averages of measured values of all samples collected at the same time ($5 \text{ planar points (A-E)} \times 4 \text{ seawater depth (H1-4)} = 20 \text{ samples}$ for CT1-2, and $5 \text{ planar points (A-E)} \times 3 \text{ seawater depth (H1-3)} = 15 \text{ samples}$ for CT3-6) are plotted in Fig. 4 and 5.

Metal concentrations in the whole seawater column were compared under two scenarios, without a chute (CT1, CT3 and CT5) and with one (CT2, CT4 and CT6), as shown in Fig. S5. Similar trends of leaching potential among different heavy metals were noted between column experiments with a chute and without, indicating the dominant influence by the IBA intrinsic properties rather than the chute application. The release of most heavy metals for column experiments with a chute was less than that without a chute, suggesting inhibited seawater contact and thus a smaller effective “L/S” ratio. Ranking L/S ratios with an increased order for the first scenario (Fig. 4a), most metals (As, Ba, Cd, Cr, Cu, Hg, Pb, Sb, Se, Tl, Zn) presented an increased release, likely due to extended exposure path and prolonged travelling time (Table 1). Also, ascribed to strong pH buffering capacity of seawater (meaning that pH variation among

various seawater columns were not obvious), metal leaching potential would be dominant by their respective partitioning coefficients (constant values). Therefore, the presence of more seawater (in the proximity) yielded more metal release (Yin et al., 2017; Yin et al., 2018). As for the second scenario (Fig. 4b), effects due to increased L/S ratios were compromised by the usage of a chute, whose influences appeared to be mixed. Nevertheless, significant leaching inhibition was found for a number of heavy metals at L/S = 26 as compared to L/S = 18.2 (while comparable or lower than L/S = 13), including Ag, Ba, Cr, Cu, Hg, Ni, Pb, Sb, Se and Tl (Fig. 4b). In this regard, a chute may be valuable to reduce total leached amounts of most metals from IBA if their spot-specific concentration distributions were not a concern (Figs. 1-3).

Fig. 4

3.2.1. Heavy metal re-adsorption potential

It is necessary to investigate the transition of metal concentrations over time to illustrate the IBA leaching kinetics and potential trends. Metal concentrations represented by weighted average of all samples collected at the same time were again plotted vs. time (Fig. 5). Most metal concentrations leveled off within half an hour, suggesting a rapid isotherm for IBA leaching. It is relevant to the higher settling speed of major IBA particles whereas tides or seawater movement which is commonly occurred in the field were avoided in the current field trial experiments. Interestingly, certain metals demonstrated decreased concentration over a certain period of time until being further leveled off (e.g. Cu in CT1, CT3 and CT5, and Ba in CT4-6), indicating occurrence of re-adsorption (Shieh and Roethel, 1989). Re-adsorption usually happens under, 1) the presence of competitive ions; 2) the presence of extra precipitates induced by change of ambient geochemistry (e.g. pH); and 3) the presence of complexation surface (Moghal et al.,

2014; Qiu et al., 2018; Wang et al., 2009). As seawater were extremely abundant surrounding IBA in all designated experiments, the competitive ions (born from IBA) would be greatly diluted (Yang et al., 2016) while seawater significantly buffers the changes of environmental chemistry in the solution induced from IBA (Cyronak et al., 2018; Fajar et al., 2015; Hain et al., 2015). As such, influences induced by the first two circumstances dimed out. On the contrary, complexation surface did exist due to seawater resuspension coerced with IBA fine particles, which would re-adsorb the metal ions dissolved to form bigger size particles and then settle down again, resulting in decreased overall metal concentrations. Re-adsorption seemed lesser in CT2, CT4 (except for Ba) and CT6, however, likely attributed to the limited resuspension (Fig. S5).

Fig. 5

3.2.2. Comparison of field trial experiments to batch leaching tests in the laboratory

Comparison was performed between field trial experiments and batch leaching tests in the laboratory, aiming to establish useful correlations for guidance of IBA safe application in land reclamation. First of all, standard batch leaching tests with various L/S ratios = 2, 5 and 10 from the laboratory were carried out while the data are compared in Fig. S6.

Except for Ag (below detection limit), Cu, Ni, Pb and Zn (below detection limit), the leaching potential of the other metals was significantly enhanced with increased L/S ratios, as much as 2 orders of magnitude higher at L/S = 10 than those at L/S = 2 (Fig. S6). While Cu, Ni and Pb presented comparable concentrations independent of L/S ratios, suggesting that the metal availability may be the only limiting factor for their leaching.

Fig. 6 was further plotted to unveil the “effective” L/S ratio based on field trial experiments (only field trial experiments without a chute were compared with the average results from batch leaching tests). With an exception of a few metals Ag, Ba, Cd, and Zn, the rest 9 metals (except Pb concentration at L/S = 26 in CT1), regardless their slight variation in concentrations with higher L/S ratios (= 13 to 26), always had lower concentrations than their counterpart measurements in batch leaching tests at L/S 10. It may suggest that, IBA leaching in the field during land reclamation would largely achieve its “saturated” concentration at the “effective” L/S = 10, echoed by batch leaching tests from the laboratory. This finding is essential to establish the proper standard leaching test from the laboratory to monitor the IBA leaching potential in the field. Yet, it is acknowledged that the adoption of “effective” L/S = 10 may underestimate the leaching potential of Ag, Ba, Cd and Zn, so that further studies have to be performed to specify their “effective” L/S ratios.

Fig. 6

4. Conclusions

Large-scale field trial experiments were performed for the first time to simulate IBA leaching behaviors when it is used for land reclamation. Not a surprise, due to different degrees of contact with seawater as well as various particle settling velocities during IBA dumping, the metal concentration indicated significant gradients across depths, which was further magnified with application of a chute. Such gradients exhibited interestingly minor changes as a function of monitored time. As such, the ecotoxicity assessment associated with IBA for land reclamation become more sophisticated beyond deliverables from batch leaching tests, which has to take account of depth effects of seawater. IBA leaching kinetics was generally rapid to achieve

equilibrium in minutes. Yet, instant turbulence in the seawater column after dropping IBA would incur subsequent IBA particle resuspension, resulting in re-adsorption of certain metals.

Data from large-scale field trial experiments suggested different IBA leaching behaviors as compared to batch leaching tests from the laboratory. Overall, metal leaching potential showed no significant variation with respects of their ranking orders, following the same as Ba > Cu > Sb, Cr > Ni > the other metals. Concentration variation of different metals was capped within an order of magnitude between the two types of leaching tests. With much higher L/S (= 13-26) ratios from field trial experiments though, the leaching concentrations of most metals (except for Ag, Ba, Cd, and Zn) were noted lower than those from batch leaching tests at L/S = 10. Based on the current study, batch leaching tests at L/S = 10 as opposed to L/S = 2 & 5, seemed a better (conservative) estimation of IBA leaching potential during land reclamation in terms of the total metal release.

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420 **Tables and Figures**

421 Table 1. Calculation of time for particle settlement onto the seawater bottom in respects of different grain sizes of IBA (0-2 mm, 2-4
422 mm, 4-20 mm and 20-50 mm, respectively).

Field trial exp.	SW conductivity (mS/cm)	SW salinity (ppt)	Viscosity, μ (10^{-3} kg/m $\cdot$ s)	Density, ρ (10^3 kg/m 3)		g (m/s 2)	Settling velocity, w (m/s)					Estimated settling time, t (sec)			
				SW	IBA		<2mm	2-4 mm	4-20mm	20-50mm	<2mm	2-4mm	4-20mm	20-50mm	
CT1	43.30	31.3	1.065	1.022	1.80	9.8	1.59	14.32	229.2	1950	6.28	0.70	0.044	0.0051	
CT2	42.80	30.8	1.064	1.021	1.80	9.8	1.59	14.34	229.5	1952	6.27	0.70	0.044	0.0051	
CT3	43.20	31.2	1.065	1.022	1.79	9.8	1.57	14.14	226.2	1925	4.46	0.50	0.031	0.0036	
CT4	42.00	30.2	1.063	1.021	1.79	9.8	1.58	14.18	226.9	1930	4.44	0.49	0.031	0.0036	
CT5	44.60	32.3	1.067	1.022	1.79	9.8	1.57	14.10	225.6	1919	3.19	0.35	0.022	0.0026	
CT6	44.70	32.4	1.068	1.023	1.79	9.8	1.56	14.08	225.3	1917	3.20	0.36	0.022	0.0026	

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427 Figure 1. Heavy metal leaching concentrations (mg/kg dry IBA) in the seawater column as a function of seawater depth in CT 1 (a-d)

428 & 2 (e-h) at time of 2 (a, e), 17 (b, f), 32 (c, g) and 62 min (d, h), respectively.

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432 Figure 2. Heavy metal leaching concentrations (mg/kg dry IBA) in the seawater column as a function of seawater depth in CT 3 (a-d)

433 & 4 (e-h) at time of 2 (a, e), 17 (b, f), 32 (c, g) and 62 min (d, h), respectively.

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437 Figure 3. Heavy metal leaching concentrations (mg/kg dry IBA) in the seawater column as a function of seawater depth in CT 5 (a-d)

438 & 6 (e-h) at time of 2 (a, e), 17 (b, f), 32 (c, g) and 62 min (d, h), respectively.

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442 Figure 4. Different metal leaching concentrations in the field trial experiments by using a chute

443 (a) or not (b) under L/S ratios = 13, 18.2 and 26, respectively.

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447 Figure 5. Different metal leaching concentrations (on average from different collection locations) in the
448 whole seawater column as a function of time during IBA field trial experiments in CT1 (a), CT2 (b),
449 CT3 (c), CT4 (d), CT5 (e) and CT6 (f), respectively.

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453 Figure 6. Comparison of leaching data between batch leaching tests (average value of metal leaching concentrations) and field trial

454 experiments (average value of metal leaching concentrations of all time and locations for CT1, CT3 and CT5) based on various L/S

455 ratios.

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