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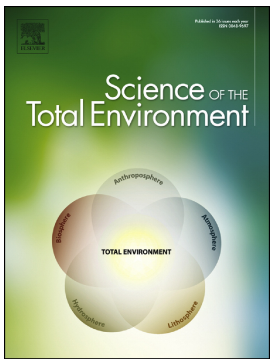

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Journal Pre-proof

Influence of pH, depth and humic acid on metal and metalloids recovery from municipal solid waste landfills

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Abstract:

Key words: Landfill, metal recovery, leaching, pH, organic acids

1 INTRODUCTION

The growing resource use has, for many people, strengthened social foundations, incomes and welfare. However, it has also produced negative effects; the world faces resource shortages. To provide the necessary resources to meet demand (European Commission, 2010), the transition towards resource-efficiency is required. The global demand for metals has accelerated to an extent where it is widely considered a threat to economical and societal functioning (Watari et al., 2021). Therefore, waste management recently moves towards a Circular Economy by recycling pre-consumer manufacturing scrap/residues and End-of-Life products (European Commission, 2018a). Reduction and re-use are the most effective ways to save natural resources, and as the UK's recycling rate has increased from 44.5% in 2015 to 45.5% in 2020 (DEFRA, 2020), there has been a gradual decrease in the amount of waste sent to landfills. Nevertheless, the total amount of waste has been showing consistent growth (DEFRA, 2020). Therefore, turning waste into a resource is a crucial key to a circular economy.

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Landfills are still a major route for waste disposal throughout the world. It has been estimated there are around 500,000 landfill sites across Europe (EURELCO, 2016) and approximately 22,000 historic landfill sites in the UK, of which 90% were closed before 1996 (Wagland et al., 2019). Landfills contain substantial amounts of materials, including metals, thus being a new potential resource base that can become part of the Circular Economy (Wagland et al., 2019). Metal(loid)s are an irreplaceable component, used in various technological applications such as mobile devices, computers, vehicles and medical technologies. Therefore, sustainable supply of metals is essential. Ensuring supply from secondary raw materials, reducing reliance on raw material supply, is undoubtedly part of a resilient and circular economy. Enhanced landfill mining (ELFM) is a potential approach to meeting expected global demand of metals by mining disposal of metals. Krook et al., (2012) define landfill mining as "a process for extracting materials or other solid natural resources from waste materials that previously have been disposed of by burying them in the ground." However, it is mainly to remediate the site, and its success and practice in materials recovery have been limited by economic infeasibility and the performance of technology, i.e., what quality levels (Kook et al., 2012; Wagner and Raymond, 2015). The concept of ELFM, which started to develop in 2008 (Jones et al., 2013; Canopoli et al., 2018), focuses on maximising the valorisation of waste as materials (WDM) and energy (WtE), which supports sustainable materials management by recovering and recycling of waste generated through the creating of the consumer product (Jones et al., 2013). However, there is uncertainty regarding the economic feasibility and environmental consequences of ELFM (Pastre et al., 2018).

In-situ landfill mining could enable the recovery of metals without excavation through the recovery of metals from landfill leachate (Kurniawan et al., 2021). Challenges remain in recovering metals to high efficiency and yield. A primary challenge for metal(loid)s recovery from leachate is the low concentration of many metals influenced by several factors such as landfill age, type and pH. The critical factors that affect the leachability of heavy metals are pH and chemical mechanisms such as precipitation, adsorption and ion-exchange and biological processes such as microbiomes which can dissolve metals (Dijkstra et al., 2004; Saveyn et al., 2014; Gutiérrez-Gutiérrez et al., 2015; Gu et al., 2018; Roy et al., 2021). The sorption characteristics of metals in landfills are important with recovering metals from landfills, and the presence of organic matter influences this sorption process (Spark et al., 1997; Sapsford et al., 2017). Natural organic matter in landfills originates from food, wood, paper, yard trimmings. Natural organic matters in landfills are converted to humic substances (HS) via humification (Mallick, 2017). Organic matter is biodegradable in the leachate at the early stage of landfills and becomes non-biodegradable at the late stage of landfills such as HA. Thus, HS are the main organic compounds in landfill leachate, and HA represents the most active HS fraction (Zhou et al., 2015). It is widely recognised that humic acid [HA] affects metal speciation behaviour (Qu et al., 2019), solubilisation and adsorption of hydrophobic pollutants, mineral growth and dissolution, redox behaviour in soil (Scott et al., 1998; Liu et al., 2018; Qu et al., 2019). Therefore, knowledge about HA's roles and interactions with pH is essential for recovering metals from landfill environments. Several studies have investigated the characterisation of HA in landfill leachate and distribution of heavy metals with HA (Bozkurt et al., 1999; Boru˚vka and Dra´bek, 2004; Klavinsa et al., 2006; Gutiérrez-Gutiérrez et al., 2015). However, information about HA's interaction, heavy metals, and pH in landfill environments is still insufficient. Thus,

this study aims to investigate the leaching characteristics of major metals in landfill environments under the influence of pH changes using the batch leaching technique. The recovery should target valuable metal(loid)s that have relatively higher concentrations in landfill environments or be extensively used in our life or listed as critical raw materials. In this work, 12 metal(loid)s including Lithium and Cobalt, which are critical raw materials and strategically important for the European economy but have a high risk associated with their supply (Blengini et al., 2020), were selected to investigate the metal release performance and correlation of HA with metals from the MSW in different pH and depth. Visual MINTEQ software was used to explain pH-dependent leaching characteristics of metals and predict HA effects on metal mobility.

2 MATERIALS AND METHODS

2.1 Sample collection and preparation

A total of thirty drilled municipal solid waste (MSW) core samples were collected from four MSW landfills located in the UK at depths between 3 and 55 m. Different cores were drilled vertically across the landfill area, and samples were taken by a specialised private company hired by the landfill sites operator (Table 1). The samples were stored in a cold room at 4°C until analysis. The samples sorted manually into metal, paper, textile, wood, glass and other materials, and weighed.

Table 1. Waste composition of the samples collected from the studied landfill site (Canapoli et al, 2020)

	Samples no.	Depth (m)	Years	pH	Waste sample (g)	Paper/ cardboard (g)	Metals (g)	Glass/ ceramic (g)	Textile (g)	Wood (g)	Soil/fine fraction (g)	Other (g)
	2	3-9	<10		11561	2493	356	69	1463	1776	3647	1757
Average				7.43	5781	1247	178	35	732	888	1824	879
SD				0.03	2148	1511	215	49	895	505	2013	241

	3	23-30.5	>10		12762	1405	768	21	569	1092	6490	2417
Average				7.58	4254	468	256	7	190	364	2163	806
SD				0.02	1338	366	373	8	329	283	1628	571
	3	48-55	>10		12892	1148	245	151	331	1321	5147	4549
Average				7.64	4297	383	82	50	110	440	1716	1516
SD				0.03	2264	491	93	35	98	294	1426	971

2.2 Leaching tests

The batch leaching tests were carried out following BS EN 12457:2002. Briefly, 50 g of composite waste sample was mixed with 500 ml deionised waste to evaluate the level of metals release from the waste in a wide range of pH values in the controlled site. Before the leaching test, the samples were ground to a size of <1.5mm using a Retsch SM 2000 grinder. The analysis was carried out for six pH values; 2, 4, 6, 7, 8, 10. The pH was adjusted using 1.8 M nitric acid solution or 1 M sodium hydroxide solution. All leaching tests were made in duplicates. The tests were conducted in a 1500 mL cylindrical jars with ribbed cap. The experiments were performed with liquid-to-solid ratio 10:1, which represents typical field conditions (Bestgen et al., 2016) (L/S, where L is deionised water, and S is solid waste, mL g). The jars were manually agitated for 3 repetitions of 5 minutes with 10-minute intervals between repetitions. The mixture was then allowed to settle for 30 minutes and then was pressure filtered through clean 0.45-µm pore size filtration membranes and then collection of the leachate. The leachate was collected in polyethene bottles and stored in a cold room at 4°C until metal analysis and performed analysis within three weeks.

2.3 Humic acid analysis

A stock solution of HA was prepared by dissolving 1 g of HA in 1 L of deionised water for investigating the impact of the presence of HA in leachate on the leachability of metals. HA content was determined by ultraviolet light absorbance at 254 nm. The values were converted

using a calibration curve. For that purpose, serial dilutions of the concentrated HA stock solution were prepared: 1, 2, 5, 7, 10, 15, 20, 50, 100 mg. Samples for UV_{254} were filtered through 0.45 µm membrane filter. UV_{254} was measured through a 1 cm quartz cell. The test was conducted in duplicate.

Table 2. Common properties of HA (Adapted from Chamoil, 2013, Sillanpää, 2015)

Elemental composition (% by weight)	HA	Functional group distribution (% of oxygen is indicated in functional groups)	HA
Carbon	50-60	Carboxyl (-COOH)	14-45
Hydrogen	4-6	Phenol (-Ph)	10-38
Oxygen	30-35	Alcohol (-R-OH)	13-15
Nitrogen	2-4	Carbonyl (-C=O_	4-23
Sulphur	1-2	Methoxyl (-O-CH_3)	1-5
Solubility in strong acid	Not soluble		

2.4 Metal analysis

The metals content was analysed by inductively coupled plasma mass spectrometry (ICP-MS) (Elan 9000 Perkin-Elmer SCIEX) after microwave-assisted acid digestion following the extraction procedure used in previous studies (Gutiérrez-Gutiérrez et al., 2015; Cipullo et al., 2018; Wagland et al., 2019). Briefly, Li, Al, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Pb, and Hg were determined by pre-digesting 30 mL leachate with 1.5 mL concentrated trace metal grade nitric acid for leachate samples. For solid samples, 0.5 g of samples was mixed with 6 ml of HCl and 2 ml nitric acid in Teflon tubes and left overnight. The vessels for leachate samples were placed in the Mars Xpress microwave (CEM system, EPA 3015-8). Then, the vessels were cooled, and the solution was filtered through Whatman No. 2 paper and made up to 50 ml with deionised water. As for the solid samples, they were placed in a microwave digester (Multiwave 3000, Anton paar) for 45 minutes at 800 W, and then the solution was filtered through Whatman No. 2 paper, and

the liquid diluted to 100 ml. A blank digest was carried out in the same way. The microwave is an efficient and fast digestion technique method. Calibration standards were spiked with several certified standard solutions. The concentration ranges were 0.05, 0.1, 0.15 and 0.2 mg/L/ for the elements.

2.5 Geochemical modelling

Visual MINTEQ ver. 3.1 software program was used to estimate the chemical species and the equilibrium mass distribution of dissolved metals in leachate according to different pH and HA value. Data inputs included pH, alkalinity, temperature, and dissolved organic carbon (DOC). A temperature of 25°C was used for all the model calculations. A sensitivity analysis of the model was performed, which responses to changes in the fraction of active SOM by independently varying SOM in the range 10-100%. The Stockholm Humic Model was selected to evaluate metal(loid)s binding to humic acid due to its known success in describing metal and DOC complexation (Baker, 2012). Typically, fulvic acid (FA) is more abundant than humic acid (HA). However, to better understand the effects of humic acid has on metal(loid)s leaching, of the active the total solid organic matter (SOM), humic acid set as 90% and fulvic acid formed as 10%. The input values used included total concentrations of metals Li, Al, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Pb, and Hg and ionic strength was also considered.

2.6 Statistical analyses

Multivariate analysis was performed using SPSS 26 software to identify statistically significant variance between the dependent variable tested and effect on the metal(loid)s leachability. A multivariable study was conducted considering the correlation matrixes. In these matrices, each individual square contains the ordinal coefficient of Spearman which varies between 1 and -1 and

the significance level of estimated correlation for each pair of variables (Bisquerra. 1989). Significance level was set at 0.05.

3 RESULTS AND DISCUSSION

3.1 Influence of depth

The concentration of metal(loid)s in the waste samples (according to depth) are provided in Table 3. Among all metal(loid)s, Hg had the lowest concentration, and Al was the highest. Significant efforts have been made to reduce Hg content at source, thus reducing the content of Hg in waste deposited in landfill. Therefore Hg is not expected to be present in high concentrations in MSW (Cheng and Hu, 2011). The concentrations of metal(loid)s tend to have a higher concentration at 3-9 m than other depths, indicating greater depth may reduce hydraulic permeability and increase waste densities. This is likely due to higher proportions of non-degraded organic materials distributed variably in the surface waste layers; higher organic carbon may increase soluble metals while organic matter bound to soil particles may enhance the retention of metals (Frank et al., 2017). The concentration of Mn and Cd at 3-9 m was remarkably higher than other metals; the composition and distribution of the sample may cause it.

Table 3. The concentration of metal(loid)s in the MSW according to depth

	Li (mg/L)	Al (mg/L)	Cr (mg/L)	Mn (mg/L)	Co (mg/L)	Ni (mg/L)
3-9 m	0.17	111	0.39	23.1	0.096	0.52
23-30.5 m	0.11	106.5	0.26	4.9	0.051	0.45
48-55 m	0.14	132.5	0.38	4.0	0.075	0.34
	Cu (mg/L)	Zn (mg/L)	As (mg/L)	Cd (mg/L)	Pb (mg/L)	Hg (mg/L)
3-9 m	5.31	14.75	0.20	27.05	25.18	0.044
23-30.5 m	6.28	3.75	0.04	0.0078	17.67	0.021
48-55 m	1.60	2.97	0.10	0.0083	2.53	0.015

Therefore, metal(loid)s in the surface layer from the old MSW landfill have a higher concentration because degradation occurs slower than at deeper depths. This finding is in agreement with the findings of Reinhart et al. (2002), suggesting lower layers undergo limited waste stabilisation. Previous studies also found the composition of organic fine materials to increase with depth (Mor et al., 2006; Quaghebeur et al., 2013; Lozano-García et al., 2016). It consequently increases the complexation of metal(loid)s in organic waste residuals, and therefore metals are firmly bound to the compost matrix and organic matter, limiting their solubility with increasing depth (Smith, 2009). The composition of waste each landfill received, distribution of the waste, and landfill area background can influence the accumulation of certain metals and its content. There were observed significant negative correlations between depth and Li, Pb, Hg ($p < 0.05$), As and Cd concentration ($p < 0.01$). This is likely influenced by the metal content of the waste dispose and the binding of these metals within the landfill depths. The mobility of metals within solid waste are influenced by metals' complexation and by adsorption onto molecules of the waste (Adelopo et al., 2018). The concentration of Zn, Pb and Cu at 48-55 m was relatively lower than at 3-9 m and 23-30.5 m, implying Zn, Pb and Cu released in the upper layers may be immobilised by holding the metals through enhancing the formation of metal complexes in MSW that is over 10 years. It may indicate that Zn, Pb and Cu form strong complexes within stabilised organics. The strong metal sorption properties of compost produced from MSW have less opportunity for recovering metal in deeper depth landfill environments. The results demonstrate that waste composition influenced the composition of metals that can be recovered within a different layer of waste and aged. The amount of metals recovered in the surface layer of the landfill may be potentially increased, as shown in Table 4.

Table 4. Percentage change of metals at different depths relative to 3-9 m

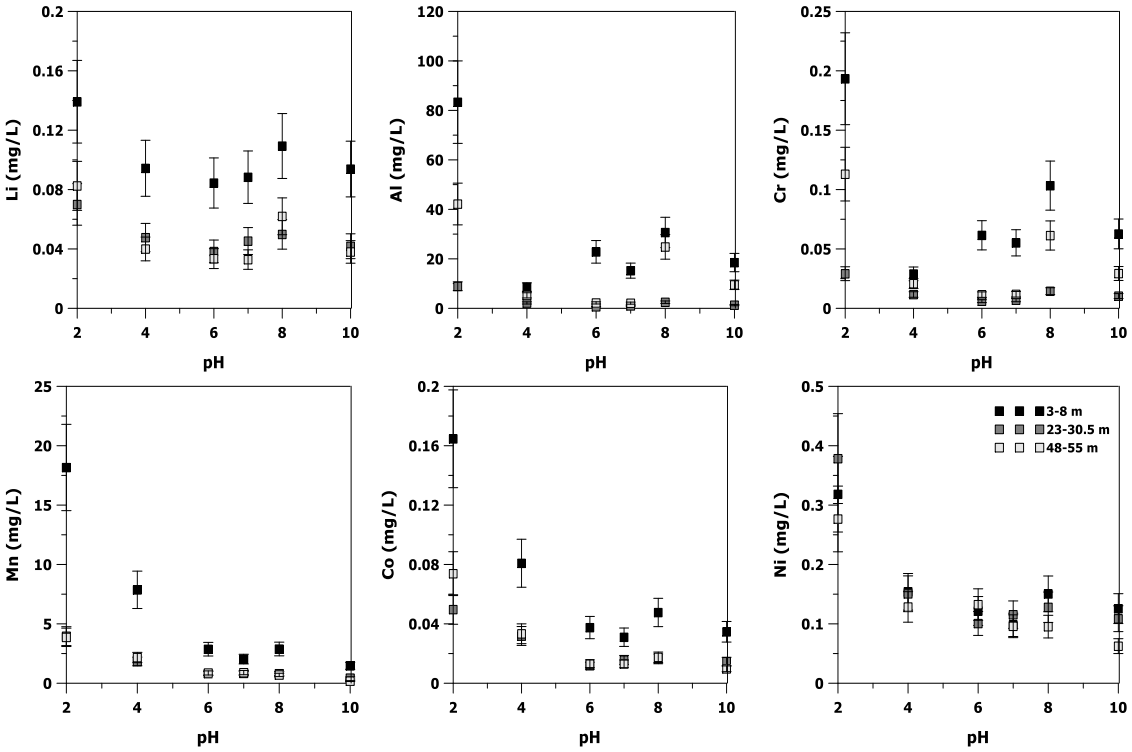
	Li	Al	Cr	Mn	Co	Ni
Change of 23-30.5 m	53.61	4.23	49.03	373.04	50.33	14.34
Change of 48-55 m	20.92	-16.23	2.67	472.73	1.78	51.71
Average	37.26	-6.00	25.85	422.88	26.06	33.02
Variance	267.17	104.57	537.44	2484.51	589.21	349.11
	Cu	Zn	As	Cd	Pb	Hg
Change of 23-30.5 m	-15.52	293.33	365.65	348178.97	42.56	106.30
Change of 48-55 m	232.81	397.19	111.07	325146.49	894.08	199.77
Average	108.65	345.26	238.36	336662.73	468.31	153.04
Variance	15416.71	2696.60	16202.26	132623748.9	18127.6	2184.25

However, depth was not found to influence significantly the concentration of metal(loid)s recovered. This finding is consistent with the previous study of Gutiérrez-Gutiérrez et al. (2015) who reported that there is no clear pattern between metal concentrations and the depth of the waste. As waste would undergo different stages of degradation over various landfill ages, and composition, it is not appropriate to compare heavy metal contents sampled at different depths. Through waste materials disposed of in the landfill are the primary sources of metals in the landfill environment and leachate. Thus, further research is required to identify the factors controlling metals distribution, oxygen, which affects the redox at the site and the effect of waste composition on metals content for increasing economic viability in recovering metal.

3.2 Influence of pH

It is well known that pH plays a key role on the behaviour and speciation of metal(loid)s (Riba et al., 2004). Extracting metals from landfills and their leachate cannot be regarded as environmentally friendly and operational cost-effective; therefore, it is crucial to recovering certain high value and amount metals. Thus, we need to find a pH value or range that maximises recovery of a wide range of metal(loid)s, especially those of high added value or demand such as Li and Co. (Tang and Steenari, 2016). Therefore, the release of metal(loid)s was examined in a

broader pH range between pH 2 and 10 (Fig. 1). It was noted that the release of metal(loid)s was found to be higher in the lower pH range, especially at pH 2 (Fig. 1). According to the values of Pearson correlation coefficient, Mn, Co, Ni and Zn show a strong negative correlation ($p< 0.01$) with pH. The leaching amounts of metals tended to decrease from roughly 99% to 32% with increasing alkalinity of the leaching solution, although some metal elements were increased at alkaline conditions. The decrease of metal leaching amount in alkaline conditions may be caused by precipitation or sorption processes (Dijkstra et al., 2006). The effect of pH on metal leachability also differs among different metal(loid) species. However, the maximum amounts are released at pH 2 for all metals. Table 5 shows the recovery rates for the metals from the concentration of the initial metals found in the waste solid.



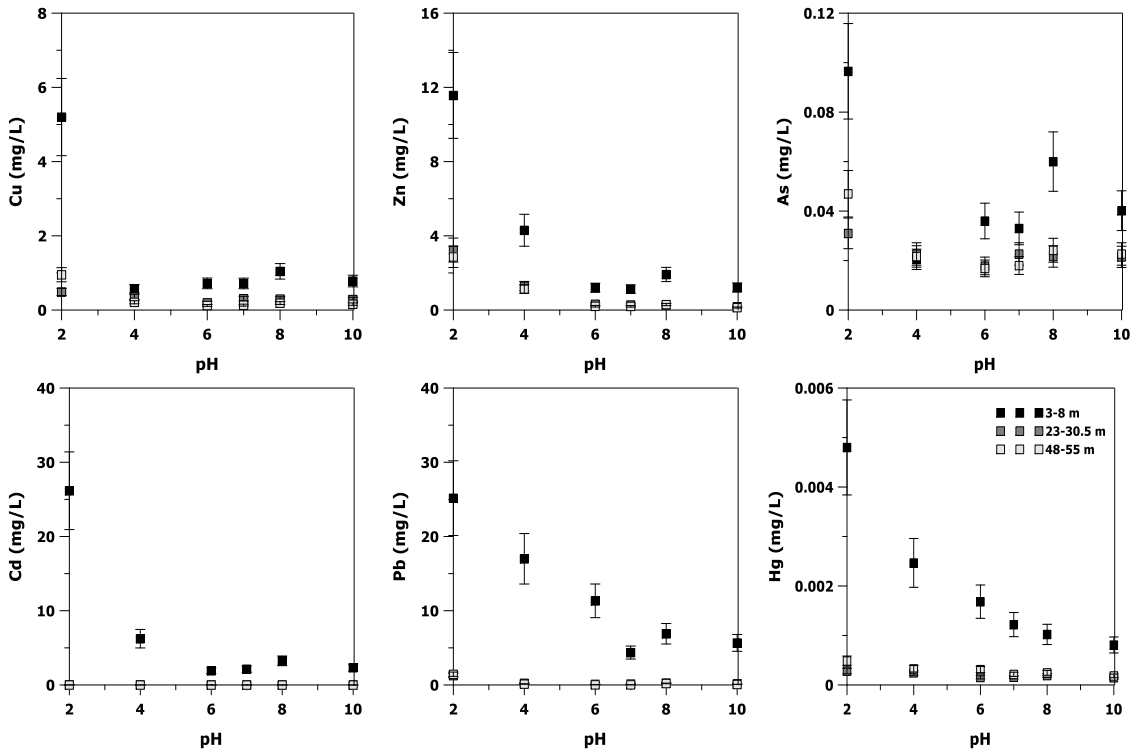


Figure 1. The leached concentration values of 12 metals in MSW landfills, following the depths (3-9, 23-30.5, 48-55 m) and pH values (2, 4, 6, 7, 8, 10)

The limited release was increased in at pH 8, except for Hg. At high pH of 8-10, solubility of metal(loid)s can increase to a certain extent since metals can form stable and soluble complexes with hydroxyl and dissolved organic carbon or are released from the dissolution of sulphide minerals (Ho et al., 2012). The concentration of heavy metal tends to increase again in alkaline condition, which is related to the formation of soluble metal hydroxides (Fig.1) (van der Sloot et al., 2003; Cappuyns and Swennen, 2008; Krol et al., 2020).

Table 5. Recovery rates of metals at pH 2 and at different depths (3-9, 23-30.5, 48-55 m)

	Li (%)	Al (%)	Cr (%)	Mn (%)	Co (%)	Ni (%)
3-9 m	83.5	75.07	50.22	78.64	89.91	61.41
23-30.5 m	64.52	8.37	11.29	81.23	98.03	83.46
48-55 m	59.86	31.82	30.13	95.87	98.66	80.98
Average	69.29	38.42	30.55	85.25	95.53	75.28
Variance	104.58	763.32	252.63	57.52	15.87	97.18
	Cu (%)	Zn (%)	As (%)	Cd (%)	Pb (%)	Hg (%)
3-9 m	97.96	78.42	47.46	96.74	99.93	10.99

23-30.5 m	7.77	86.22	70.99	91.42	7.20	1.33
48-55 m	59.67	96.63	48.79	89.98	57.11	3.34
Average	55.13	87.09	55.75	92.71	54.75	5.22
Variance	1365.9	55.65	116.51	8.44	1436.1	17.33

The results are inconsistent with Krol et al. (2020), who reported a significant decrease in the concentration of Ni and Cr at pH 8 and Cu at pH 9. The results showed that As and Cr release was low at neutral or slightly acidic pH. However, they showed the highest leachability at pH 2; it caused by the dissolution of iron oxides that are the main components that bind to them in soils (Krysiak and Karczewska, 2007, Gersztyn et al., 2013). They notably showed the second-highest concentration at pH 8, which may be attributed to the mechanism of pH-related anion desorption, replacement of oxy-anion forming elements and their bound in the sorption complexes by hydroxide ions. The most important mechanism of As and Cr, which are oxyanion forming elements, is to be due to the dissolution of the organic components, including HA (Gersztyn et al., 2013). The characteristics of Cu solubility is in alignment with the findings of Cappuyns and Swennen (2008), who reported Cu is characterised by a lower solubility in the pH-range 2-6. The release of Al followed an amphoteric leaching pattern (Fig. 1), which is similar to results reported in previous studies (Zhang et al., 2016; Cui et al., 2019). The minimum leaching concentration occurred at pH 7. Cd release amounts decrease as the pH increases at acid condition, but the reduced amounts are not so much above pH 6. It may be due to the precipitation of the metal sulphide phase, resulting in Cd being pyritised (Morse and Luther, 1999). The release amount of Ni was lower at pH 7 for 3-9 m, pH 6 for 23-30.5 m and pH 10 for 48-55 m. The characteristics of Mn and Zn solubility follow the cationic pattern in which the concentration of metal element steadily decrease with pH.

Chromium recovery trend was identical to that of As and Al (Fig. 1). Zn recovery was similar to that of Mn and Cd, which can be observed in Krol et al. (2020). Cu showed that similarity tendency with Pb. Pb are maximum 41 to 50 times more released at the pH 2 compared the leaching amount in the range of pH.

Overall, metal cations are most mobile in acidic conditions as shown in Figure 2. In contrast, anion release increase towards high pH. These results are consistent with the previous study of van der Sloot et al., (2003). However, the release of metals does not always show a similar trend as the leachability of metals can change depending on the type and composition of the tested sample. In the case of Cu and Pb, the leachability curve typically makes V or U shaped (van der Sloot et al., 2003; Cappuyns and Swennen, 2008; Sloot et al., 2010). However, this study Pb does not show a clear upward trend between pH 8 to 10. But it still showed that Pb solubility increase at high pH of 8-10. Al, As and Cr presents a V-shape, similar to results reported in the previous studies (Rubions et al., 2011; Cui et al., 2019). The most pH-dependent metal was Mn in this study. Metals from landfill leachate are typically present in low concentrations; therefore, more effective and selective recovery methods under acidic conditions need to be determined for efficient recovering metal from landfill environments. In this study, the leaching of metal(loid)s from MSW at pH 2 and 4 gave the most efficient metal release and showed high concentration at pH 8.

Metal(loid)s leachability is highest when hydrolysis, fermentation and acetogenic bacteria dominate, due to an accumulation of VFA, and a pH decrease (Fig. 2). Previous studies showed that significant heavy metal leaching occurs during the initial stage of the landfill and pH values have a direct influence on metal mobility (Yao et al., 2014; Yao et al., 2017).

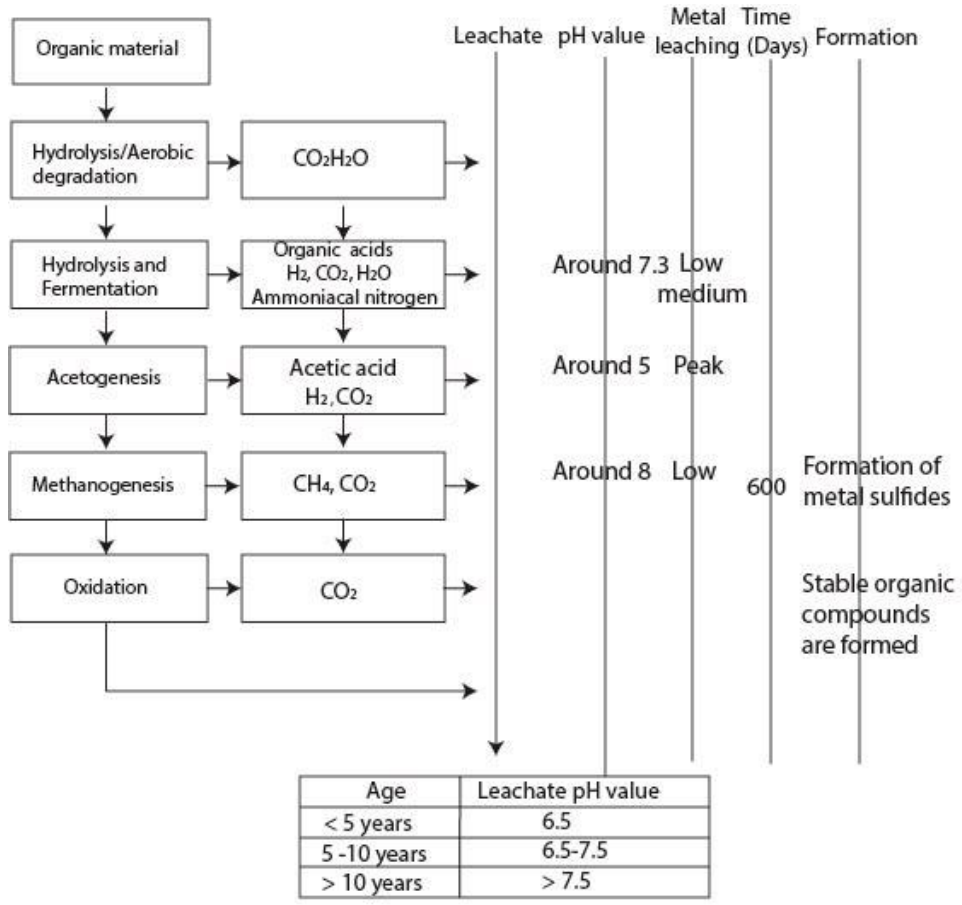


Figure 2. Metal leaching Process in a landfill and leachate pH value (Adapted from Zainol et al., 2012, Adhikari et al., 2014)

However, depending on metal(loid)s, the characterisation of pH may differ, such as Cu having the amphoteric character, thus forming soluble anionic species, and strong acidic conditions can cause environmental problems due to most organisms cannot tolerate the conditions (Breeze, 2018; Król, et al., 2020). For this reason, a suitable pH value for each metal must be determined to fit the entire metal(loid)s recovery process by adjusting the pH value to the desired range and understand the character of metals with pH value. Further research should also develop

alternative methods for recovering metals such as biodegradable extraction agents using organic acids (e.g. humic or acetic acid) to reduce reliance on strong acid.

3.3 Humic acid in the landfill

HA has a high sorption capacity, which makes them capable of holding metals. Therefore, metals may be retained and are not leached out easily. HA leaching tends to increase with the increase of depth (Fig 3). As depth is increased, the humification process increases. HA is weakly acidic with carboxylic-and phenolic-OH groups (Prado et al., 2011).

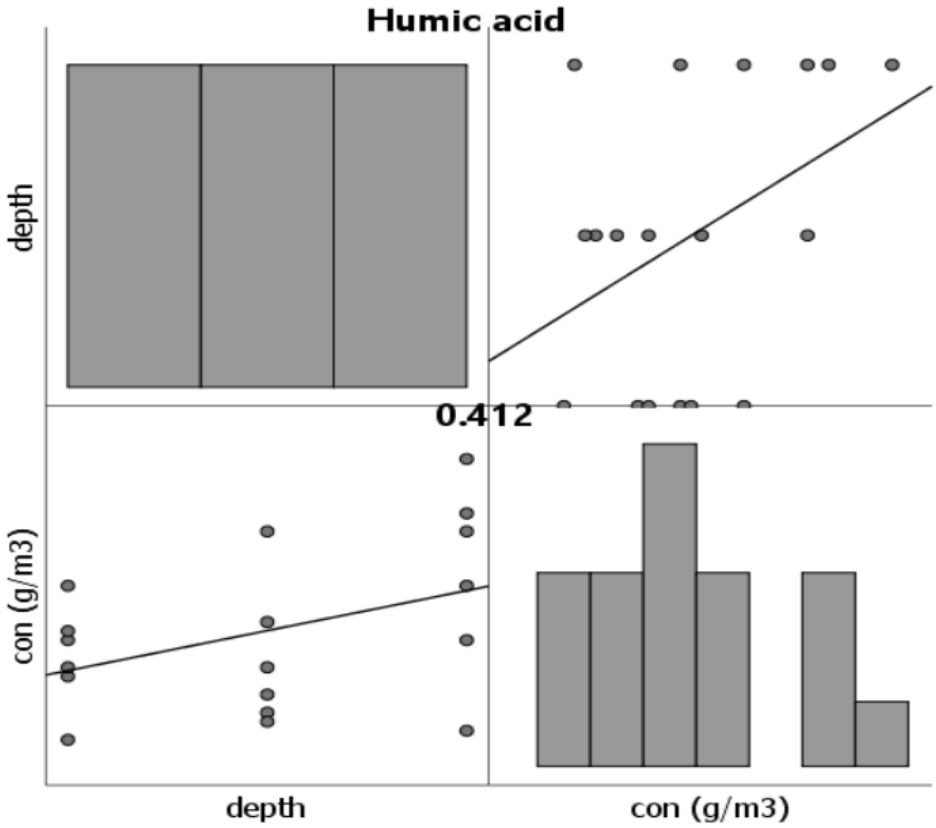


Figure 3. The leached concentration values of humic acid in MSW landfills, according to depths

The correlation between pH, metals, and HA is shown in Figure 4 (Details in supplementary data Figure 1). Four metals among 12 metal(loid)s are illustrated in Figure 4. Li and Co are shown as they are critical raw materials and Al has been shown as there are concerns justifying focused recovery due to high content in the landfill. There was a strong positive relationship between pH and HA, i.e., HA leaching increases in higher pH value. Adsorption of organics on the surfaces would therefore be affected by pH. The amount of HA increased by 2% to 4% at pH 10 compared at pH 2 and increased by 0.4% to 4% as depth increased. The results may indicate that HA is not soluble at acidic conditions and become most soluble from pH 6. It may be due to carboxyl groups on HA be ionised in alkali condition. The ionisation would lead to a negative charge on HA molecules. Thus, HA is more leachable in alkali conditions due to lowered adsorption. This finding is in agreement with Sehaqui et al. (2015), who found that HA adsorption gradually increases with decreasing the pH. HA is known to bind metals to their hydroxyl and carboxyl groups, and either mobilise metals or delay their release (Leung and Kimaro, 1997; Bozkurt et al., 1999; Kochany and Smith, 2001; Klavinsa et al., 2006; Gutiérrez-Gutiérrez et al., 2015). Strong negative correlations were found between HA and Co, Ni, Zn ($p < 0.01$) and Mn ($p < 0.05$).

The Visual MINTEQ has been adopted to describe metals speciation in the leachate (Table 6). As significant numbers of closed landfills exist in the UK and across Europe, the model input used the batch test results at depth 48-55 m, which would be similar to the closed landfills parameters. The Stockholm Humic Model (SHM) was used to assess metal binding to HA. The results show that Li does not much affect by pH. However, all the metals show that high leachability at pH 2.

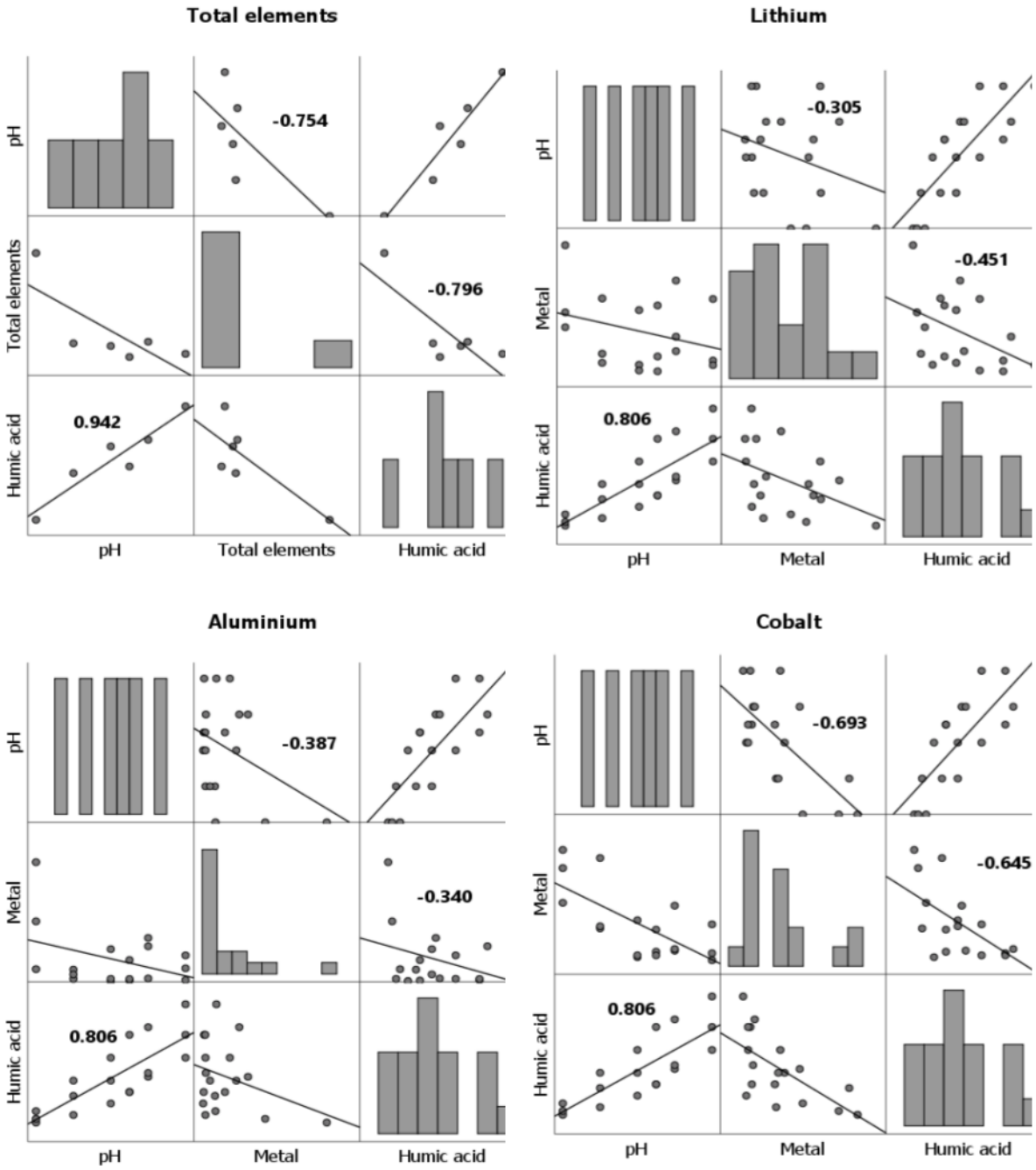
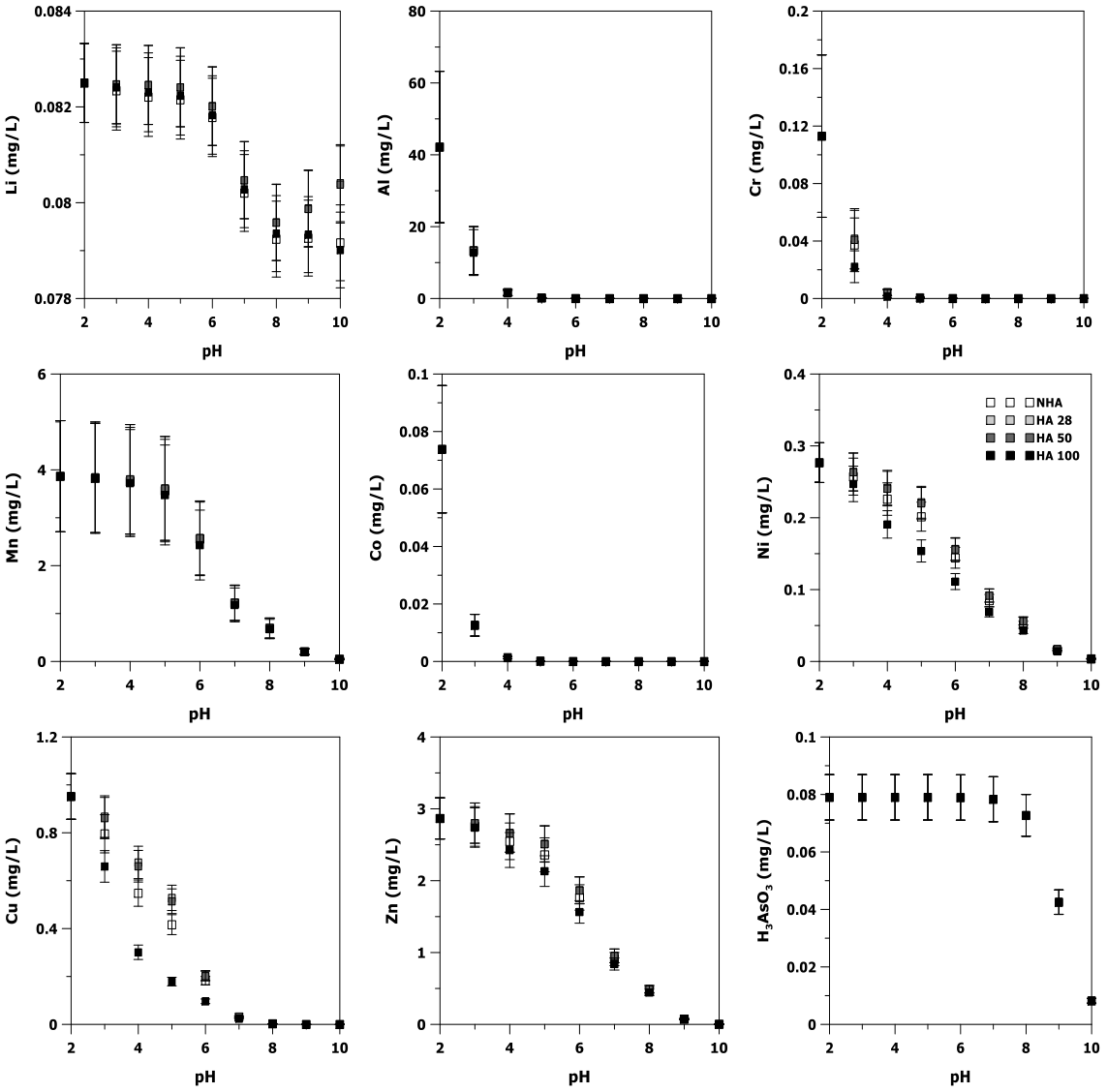


Figure 4. Draftsman's plot resenting the relationship between waste depth (m), pH, metal (mg/L) and HA (mg/L)

The geochemical analyses also showed that HA accelerated metals leaching. This finding is in good agreement with the previous study of Usharani and Vasudevan (2016), where an increase in HA concentration increases the heavy metal leaching from sewage sludge. Cu, Pb, Ni, and Zn were all significantly affected by the presence of HA as their leachability increase roughly 6-17%, especially at below pH 6 (Fig. 5).



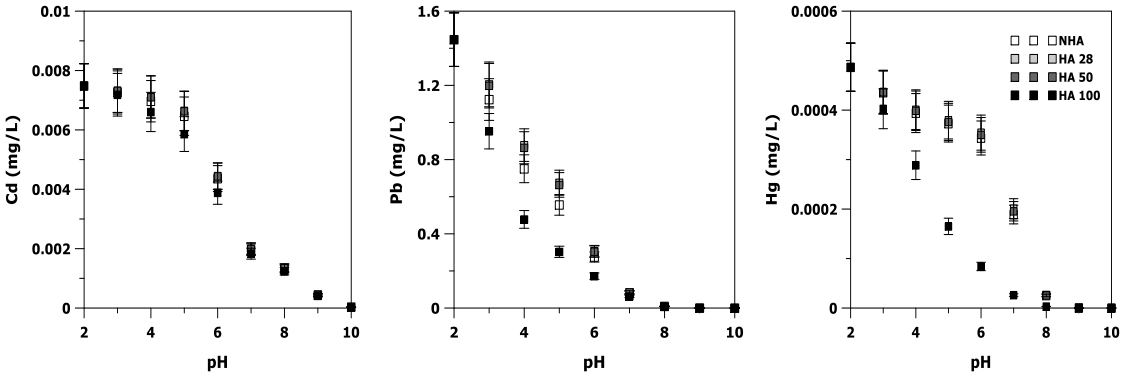


Figure 5. The leached concentration values of 12 metals at different humic acid concentration (0, 28, 50 and 100 mg/L)

Results expressed that a high concentration of HA can leach out metals but can be in lesser concentration depending on the metal, indicating that the visual MINTEQ model could predict free ion/labile species efficiently under different environments, such as the acidic environment. With an increase of HA concentration, the improvement of metal leaching rate is not apparent, which may be due to excessive HA can chelate with metal ions and reduce metals release (1).

$$ROH + Cd^{2+} <\!\!\longrightarrow ROCd^{+} + H^{+} \quad (1)$$

Metal ions can effectively chelate heavy metals, thus delay their release; in aerobic conditions, the HS lose their binding properties. In addition to chelating metals, HA is applied in the bioremediation of environmental contaminants as a redox mediator (Maurer et al., 2012; Liu et al., 2018). HA is redox-active for enhancing microbial reduction of nitrate, implying their great potential for acting as a redox mediator in enhancing multiple microbial reductions, resulting in affecting various biogeochemical processes (i.e., iron cycle, nitrogen cycle, etc.) as well as *in situ* remediations in an anaerobic environment (Zhang et al., 2018). The leaching efficiency of HA shows that be comparatively higher at pH 4 to 6. Most metals can be found at the beginning of the humic phase (Bozkurt et al., 1999; Gutiérrez-Gutiérrez et al., 2015). Therefore, Fig. 3

showed the sharp contrast which metal(loid)s release in acidic conditions and HA release in alkaline conditions. Chelate compounds “hold” metal and, in consequence, it can be immobilised metals in landfills. This is probably due to the distinctive ring structure of chelate compounds, in which metal ion is surrounded by a molecule like, for example, humic compounds (Zhou et al., 2015). Computer modelling revealed that the HA could strongly bind metals. Also, it showed that higher pH is more effective HA binding with metals and metals are more soluble at lower pH. These are caused by the fact that at lower pH values, less acidic functional groups on the DOM molecules were deprotonated and available for metal binding (Stevenson, 1994). However, Li, Co, and As do not much affect by organic matter. Even the HA dominated DOC fractions in leachate, the leaching potentials for FA-metals complexes leaching out were relatively high. The solubility and complexation ability of HA is related to their interactions with metal(loid)s and other environmental conditions. This interaction leads to the formation of metal complexes and chelates, which influence leaching amounts of metal(loid)s, and the main factor influencing the interactions of HA with metals is pH value. According to the modelling results especially, Cu and Pb were bound very strongly in metal ion-humic complexes. In the acid to neutral pH range, HA is a vital biding constituent for metal(loid)s.

Table 6. Recovery of selected metal(loid) species in the leachate sample at 48-55m depth by visual MINTEQ (content: %)

Li		Al		Cr		Mn	
Speciation	Content	Speciation	Content	Speciation	Content	Speciation	Content
Li^{+1}	96.05	$Al(OH)_2^{+}$	0.13	$Cr(OH_{)2}^{+1}$	3.12	Mn^{+2}	20.37
LiF (aq)	0.05	$Al(OH)_3$ (aq)	2.45	$CrOH^{+2}$	0.18	$MnOH^{+}$	0.02
LiCl (aq)	0.46	$Al(OH)_4^{-}$	95.93	$Cr(OH)_3$ (aq)	68.22	MnF^{+}	0.11
$LiSO_4^{-}$	0.062	AlF_2^{+}	0.28	$Cr(OH)_4^{-}$	0.02	$MnCl^{+}$	0.09
$LiHPO_4$-	3.38	AlF_3 (aq)	0.83	$/HA_3Cr_2(OH)_2^{+}$(s)	4.92	$MnSO_4$ (aq)	0.22
		AlF_4^{-}	0.17	$/FA_2Cr^{+}$(aq)	0.07	$MnNH_3^{+2}$	0.01
		$AlHPO_4^{+}$	0.07	$/FA_3Cr_2(OH)_2^{+}$(aq)	23.46	$MnHPO_4$ (aq)	52.97
		$Al_2(OH)_2CO_3^{+2}$	0.08			$MnHCO_3^{+}$	3.75
		$/FA_2AlOH$(aq)	0.04			$MnCO_3$ (aq)	21.86

						/$HAMn^{+}$(s)	0.03
						/$FAMn^{+}$(aq)	0.58
Co		Ni		Cu		Zn	
Speciation	Content	Speciation	Content	Speciation	Content	Speciation	Content
$CoOH^{+2}$	87.89	Ni^{+2}	22.51	Cu^{+2}	0.50	Zn^{+2}	19.98
$Co(NH_3)_5Cl^{+2}$	12.11	$NiOH^{+}$	0.09	$CuOH^{+}$	0.51	$ZnOH^{+}$	0.64
		NiF^{+}	0.07	$Cu(OH)_2$ (aq)	0.05	$Zn(OH)_2$ (aq)	0.40
		$NiCl^{+}$	0.04	$Cu(NH_3)_2^{+2}$	0.08	ZnF^{+}	0.07
		$NiSO_4$ (aq)	0.27	$CuNH_3^{+2}$	0.41	$ZnCl^{+}$	0.26
		$NiNH_3^{+2}$	0.92	$CuHPO_4$ (aq)	6.57	$ZnSO_4$ (aq)	0.26
		$Ni(NH_3)_2^{+2}$	0.01	$CuCO_3$ (aq)	63.61	$ZnNH_3^{+2}$	0.25
		$NiH_2PO_4^{+}$	0.06	$CuHCO_3^{+}$	0.29	$ZnHPO_4$ (aq)	40.32
		$NiHPO_4$ (aq)	19.83	$Cu(CO_3)_2^{-2}$	23.20	$ZnCO_3$ (aq)	24.62
		$NiCO_3$ (aq)	17.91	/HA_2Cu(s)	0.02	$ZnHCO_3^{+}$	5.84
		$NiHCO_3^{+}$	25.63	/$HACu^{+}$(s)	0.09	$Zn(CO_3)_2^{-2}$	1.16
		/$HANi^{+}$(s)	0.56	/HA_2CuOH^{-}(s)	0.03	/$HAZn^{+}$(s)	0.15
		/$FANi^{+}$(aq)	12.10	/FA_2Cu(aq)	1.15	/$FAZn^{+}$(aq)	6.04
				/$FACu^{+}$(aq)	0.82	/FA_2Zn(aq)	0.03
				/FA_2CuOH(aq)	2.63		
As		Cd		Pb		Hg	
Speciation	Content	Speciation	Content	Speciation	Content	Speciation	Content
H_3AsO_3	94.84	Cd^{+2}	13.40	Pb^{+2}	0.88	$Hg(OH)_2$	2.83
$H_2AsO_3^{-}$	5.16	$CdOH^{+}$	0.03	$PbOH^{+}$	0.71	$HgCl_2$ (aq)	8.70
		CdF^{+}	0.04	PbF^{+}	0.02	$HgCl_3^{-1}$	0.98
		$CdCl^{+}$	5.71	$PbCl^{+}$	0.14	$HgCl_4^{-2}$	0.07
		$CdCl_2$ (aq)	0.16	$PbSO_4$ (aq)	0.03	HgClOH (aq)	11.07
		$CdSO_4$ (aq)	0.19	$PbHPO_4$ (aq)	1.09	$Hg(NH_3)_2^{+2}$	9.85
		$CdNH_3^{+2}$	0.37	$Pb(CO_3)_2^{-2}$	22.33	$HgCO_3$ (aq)	0.08
		$CdHPO_4$ (aq)	66.38	$PbCO_3$ (aq)	64.11	$Hg(CO_3)_2^{-2}$	0.03
		$CdHCO_3^{+}$	3.92	$PbHCO_3^{+}$	6.50	$HgOHCO_3^{-}$	0.71
		$CdCO_3$ (aq)	6.73	/$HAPb^{+}$(s)	0.14	/HA_2Hg(s)	2.86
		$Cd(CO_3)_2^{-2}$	0.66	/HA_2Pb(s)	0.05	/FA_2Hg(aq)	62.83
		/$HACd^{+}$(s)	0.12	/$FAPb^{+}$(aq)	2.58		
		/$FACd^{+}$(aq)	2.28	/FA_2Pb(aq)	1.42		

4 CONCLUSION

The leaching performance of metal(loid)s and HA from MSW at various pH was investigated. Batching leaching tests showed that the optimum conditions were pH 2 and HA 28 mg/L for recovering a broad range of metal(loid). Al, Mn, Cu and Zn may suggest recovery opportunities as their contents in MSW are high. Analysis of the mobility of the metals through the MSW suggested that these metals are not being vertically transported completely, and no clear pattern was identified between the release of the metals and depths due to waste would undergo different

stages of degradation over various landfill ages, and composition. However, the metals showed higher concentrations in the surface layer in MSW. The recovery rates at different depths are following: Pb > Cu > Cd > Co > Li > Mn > Zn > Al > Ni > Cr > As > Hg for 3-9 m, Co > Cd > Zn > Ni > Mn > As > Li > Cr > Al > Cu > Pb > Hg for 23-30.5 m, Co > Zn > Mn > Cd > Ni > Li > Cu > Pb > As > Al > Cr > Hg for 48-55 m. For most metals, their concentrations have decreased with increasing pH. Analysed metals increased at pH 8 except Hg. HA are sparingly soluble in acidic pH. HA promote metal mobilise, but an additional amount of humic acid may assist metals removal. High levels of HA can lead to extensive complexation and chelation of metals. Metal recovery in MSW landfill may have high efficiency in the surface layer, at pH 2 and 4, with an appropriate HA concentration. However, the relationship between HA and metals is still unclear. The capability of humic acid for interactions with metals is strongly dependent on pH. Therefore, further work is required to explore the mechanism of the organometallic process because it can govern the mobility of metals, resulting in enhanced sustainability and economic opportunity by recovering metals by understanding these effects on metal mobility.

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Credit Author Statement

Hyeyeon Lee: conceptualization, investigation, writing- original draft. **Frederic Coulon:** supervision, conceptualization, writing- review & editing. **Stuart Wagland:** conceptualization, supervision, funding acquisition, writing- review & editing.

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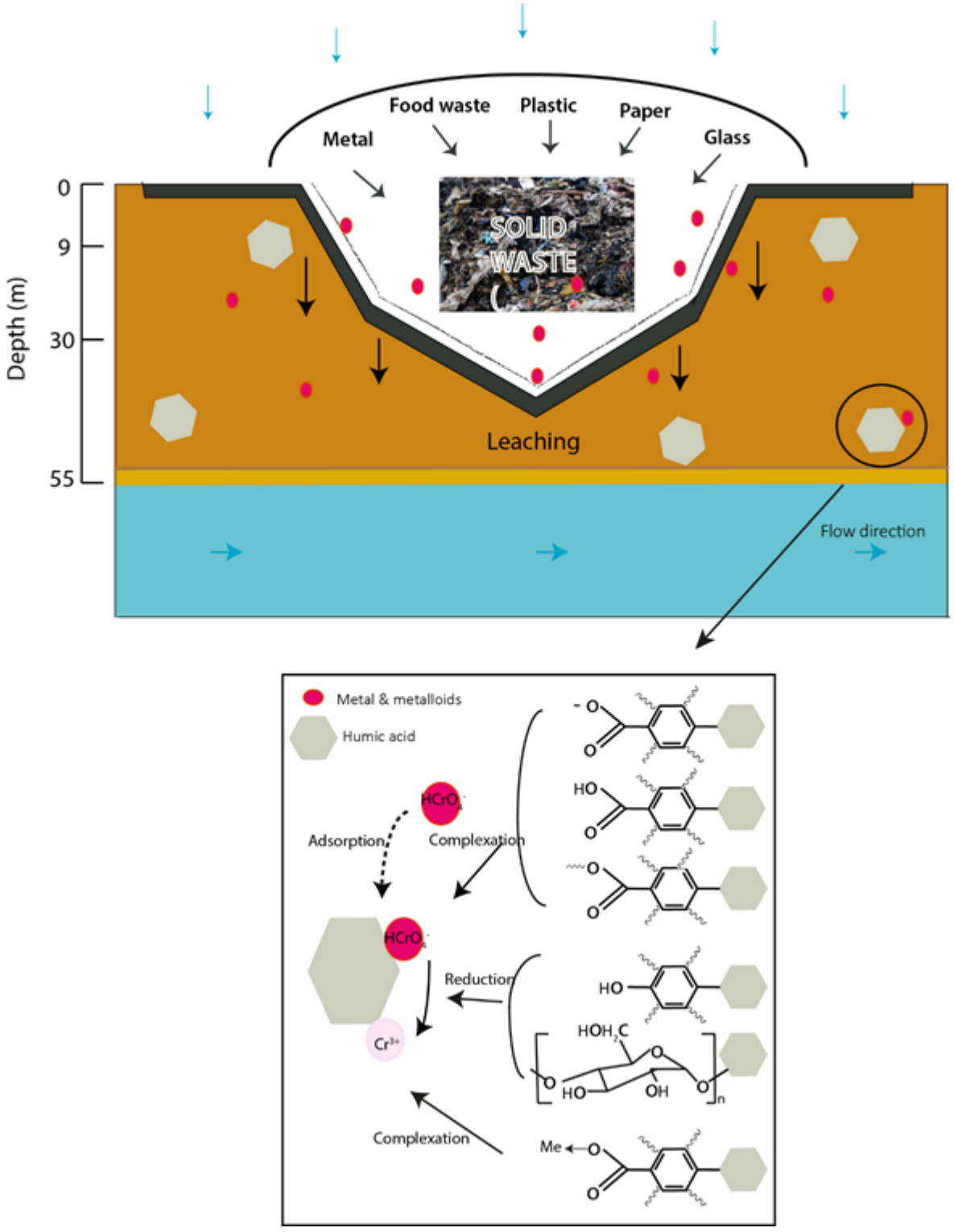
Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:



Graphical abstract

Highlights

- The leachability of metalloids at pH 2 had a humic acid content of 28 mg/L
- High concentrations of Al, Mn, Cu and Zn outline recovery opportunities
- Addition of humic acid would yield further mobility of target metals
- Humic acid-metal interaction is dependent on acidic environments

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Influence of pH, depth and humic acid on metal and metalloids recovery from municipal solid waste landfills

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