Application of sludge dewatered products to soil and its effects on the leaching behaviour of heavy metals

Ying Qi [a,*], Daniel Szendrak [a], Ronny Tsee Woon Yuen [a], Andrew F.A. Hoadley [a], Gavin Mudd [b]

[a] Department of Chemical Engineering, Monash University, P. O. Box 36, Clayton 3800, Victoria, Australia
[b] Department of Civil Engineering, Monash University, P. O. Box 60, Clayton 3800, Victoria, Australia

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ABSTRACT

The leaching behaviour of eight heavy metals from the dewatered products of sludge and lignite mixtures before and after application to the soil was investigated using batch tests. It was found that for most of the heavy metals the content in the mixtures fell within relevant EPA guidelines for biosolids application. Leaching tests showed that the leached fraction of most of the metals was low. The addition of the sludge–lignite mixtures to soils to increase the soil carbon content by 0.5%, 1% and 2% affected the leaching behaviour of some heavy metals possibly due to the changes in the conditions, such as pH and redox, of the mixtures. For arsenic and chromium, which are present in the environment as various species with different mobilities, the effect of the mixing on their leaching behaviours was the most significant. Cadmium, mercury and lead generally had low mobility. The lignite may have acted as an adsorbent which bonded the heavy metals, e.g. zinc and lead, and hence reduced their leachability. Together with the availability of nutrients in the sludge–lignite mixtures, the addition of sludge and lignite mixtures as a soil amendment is beneficial in improving soil characteristics and presents the potential to be applied to agricultural soils.

1. Introduction

Wastewater treatment plants produce increasingly large amounts of sewage sludge worldwide. The treatment and disposal of the ultimate dry product of the sludge – the biosolids – includes incineration, landfill and agricultural application as soil conditioners or fertilisers. However, the nature and the source of the biosolids mean that they often contain pollutants such as pathogens, heavy metals and organic pesticides that may have an adverse impact on environmental quality, human health and agriculture [1]. New or strengthened legislations and regulations have been introduced in many countries to impose strict limitations on the application and disposal of biosolids [2–4].

Heavy metals are well known for their toxic characteristics and accumulation in plants, animals and eventually human bodies. Among the possible metals arsenic, cadmium, chromium, copper, lead, mercury, nickel and zinc are the most common and are often regulated or given specific guidelines [5,6] due to their potential risks to the environment and human health. Many regulations and guidelines use results from leaching tests to evaluate the potential risks associated with these contaminants.

Lignite from Victoria, Australia, is an abundant and economic energy source. When being mixed with sewage sludge as a filter aid during sludge dewatering, Victorian lignite has been proved to be able to improve sludge dewaterability and significantly increase the sludge solids content [7,8]. Meanwhile, the process produces a mixture of the sludge and lignite solids, which is rich in carbon and nutrients and has the potential to be a soil conditioner. However, the potential of leaching of heavy metals in the sludge solids during soil application presents a major environmental concern.

Low-rank coal lignite, or brown coal, has been investigated as an adsorbent for removing organic components from water [9–12]. With its high ion exchange capacity lignite has also demonstrated to be an effective and cheap alternative adsorbent for removal of heavy metals [13–16]. Moreover, as shown by Schefe and coworkers [17,18], adding lignite as a soil amendment can improve plant nutrient intake and thus reduce the usage of fertilisers. Pusz [19] investigated the application of a brown coal to soils contaminated by heavy metals and found that the use of brown coal led to not only the decreasing content of heavy metals in the soils, but also the reduction of hydrolytic acidity and the improvement of sorptive properties and organic carbon content of the soils.

Soil is also well known for its adsorption and cation exchange properties. The adsorption of heavy metals by soils and its effect on the mobility and fate of the heavy metals has been extensively studied [20–25]. When biosolids containing the sludge and lignite are applied to the soil as soil amendments, not only are the properties

* Corresponding author. Tel.: +61 3 99051428; fax: +61 3 99055686.
E-mail addresses: Emma.Qi@monash.edu, emmaqi@yahoo.com (Y. Qi).

Table 1
Characteristics of sludge, lignite and soils.

Sample description	Sample code	Ash yield (% db[a])	Carbon (% daf[b])	Hydrogen (% daf)	Nitrogen (% daf)
Sludge dewatered product	SD	30.6	35.6	5.2	5.9
Loy Yang lignite	LY	6.6	62.2	4.5	0.59
Sludge–lignite dewatered product, 1:1 dry solids mass ratio	SL 1	19.6	48.2	4.9	4.0
Sludge–lignite dewatered product, 2:1 dry solids mass ratio	SL 2	22.9	45.5	5.0	4.3
Soil residential	Soil A	97.1	1.7	0.2	0.08
Soil industrial	Soil B	94.6	3.0	0.4	0.14

[a] db: dry basis.
[b] daf: dry ash free basis.

of the soil improved, but also the mobility of heavy metals in the mixtures, which is associated with the characteristics of the matrix, may be affected. It has been reported that the mobility of heavy metals in soil is affected by the use of soil amendments [26,27].

The objective of the present study was to investigate the leaching behaviour of the eight heavy metals mentioned above in the mixtures of carbon poor soils and the sludge–lignite mixtures using batch leaching tests and thus deduce the potential for utilisation of the sludge–lignite dewatered products as soil amendments.

2. Materials and methods

2.1. Materials

The solid materials used in this study were lignite (LY), two types of soil (Soil A and Soil B) and dewatered products of pure sludge (SD) and sludge conditioned with the lignite at sludge to lignite solids ratios of 1:1 and 2:1 (denoted SL 1 and SL 2, respectively).

The lignite was Loy Yang coal from the Latrobe Valley, Victoria, Australia. The sludge was anaerobic digested sludge from a municipal wastewater treatment plant in Victoria. Raw sludge (SS) had a solids content between 1.5 wt% and 2.0 wt%. After a dewatering process using a filter press, the solids content of the dewatered sludge (SD) increased to 30%. Soil A was sourced from a suburban residential area and Soil B was from an industrial area in Victoria. Both soils were chosen for their low carbon content and thus the potential for improvement. The main characteristics of the solids are listed in Table 1.

2.2. Methods

2.2.1. Sample preparation

All solid samples were oven dried at 105 °C, then milled and sieved. The portion with a particle size of less than 300 μm was collected for subsequent tests. Samples used for the batch leaching tests consisted of the six materials listed in Table 1 plus a total of twelve samples with different mass fractions of soil and amendments. The two dewatered products of sludge and lignite were added to the two soils as soil amendments. Different amounts of the amendments were added to each soil so that the total carbon contents of the soil were increased by 0.5%, 1% and 2%, respectively, e.g. the total carbon contents of Soil A with the amendments were increased from 1.7% daf to 2.2, 2.7 and 3.7% daf, respectively. This range of the added total carbon was selected based on the work by Schefe et al. [17], who suggested that higher doses of carbon may actually inhibit plant growth.

During the sample preparation process including milling, contact with metal parts was minimised to avoid contamination. Table 2 presents a list of the samples used in the leaching tests.

2.2.2. Leaching tests

Batch leaching tests were carried out based on the standard method DIN 38414-S4 [28] by mixing distilled water and the solid at 10:1 liquid:solid ratio for 24 h. 15 g of each solid sample was added in a 250 mL conical flask and mixed with 150 mL distilled water.

The flasks, sealed with Parafilm, were placed in a shaker machine and agitated for 24 h at 25 °C. The pH of each mixture before and after the 24 h shaking was measured. The mixture was then transferred to a centrifuge tube and centrifuged at 4500 rpm for 30 min. The supernatant was filtered through a 6 μm filter paper and collected in a plastic container containing 1 mL nitric acid (HNO$_3$) for preservation. The samples were then submitted to a NATA accredited external laboratory and stored at below 4 °C prior to heavy metal analysis within 72 h. The tests for samples 1–6 were carried out in triplicate to examine repeatability. Relative standard deviations of the analysis were between 3% and 7%, except for two cases of 12% and 18%. This result is acceptable for quantitative trace analysis at ppb level. These results are used to calculate the deviations of the leaching test results, which are shown as error bars in the figures in Section 3. Where there is high consistency, the error bars are barely visible.

2.2.3. Water and solid sample analysis

Heavy metals in the water samples from leaching tests were analysed by a NATA accredited external laboratory using ICP-AES. The detection limits for all the elements were 5 μg/L, except for Hg, which was 0.1 μg/L. For solid analysis, a small portion (50–100 g db) of each solid sample was sent to an external laboratory for solid analysis. Nitrogen (N), hydrogen (H) and carbon (C) were analysed using a Leco CHN analyser. Potassium (K), phosphorus (P), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni) and zinc (Zn) were analysed using ICP-AES. Arsenic (As) was determined by hydride generation and AAS, while mercury (Hg) was determined by cold vapour generation and AAS.

3. Results and discussion

3.1. Heavy metals and nutrients in soils and biosolids

Analytical results for the eight heavy metals in the solid samples 1–6 and in the sludge solids that did not go through a dewatering

Table 2
Description of samples for leaching tests.

Description	Sample code
Sludge, dewatering product	SD
Lignite	LY
Sludge–lignite dewatering product (1:1)	SL 1
Sludge–lignite dewatering product (2:1)	SL 2
Soil residential	Soil A
Soil industrial	Soil B
Soil A and sludge–lignite (1:1) at 0.5% C	Soil A + 0.5%C SL 1
Soil A and sludge–lignite (1:1) at 1% C	Soil A + 1%C SL 1
Soil A and sludge–lignite (1:1) at 2% C	Soil A + 2%C SL 1
Soil A and sludge–lignite (2:1) at 0.5% C	Soil A + 0.5%C SL 2
Soil A and sludge–lignite (2:1) at 1% C	Soil A + 1%C SL 2
Soil A and sludge–lignite (2:1) at 2% C	Soil A + 2%C SL 2
Soil B and sludge–lignite (1:1) at 0.5% C	Soil B + 0.5%C SL 1
Soil B and sludge–lignite (1:1) at 1% C	Soil B + 1%C SL 1
Soil B and sludge–lignite (1:1) at 2% C	Soil B + 2%C SL 1
Soil B and sludge–lignite (2:1) at 0.5% C	Soil B + 0.5%C SL 2
Soil B and sludge–lignite (2:1) at 1% C	Soil B + 1%C SL 2
Soil B and sludge–lignite (2:1) at 2% C	Soil B + 2%C SL 2

process (SS) are presented in Table 3. The concentration of each element in a mixture of soil and amendment is also calculated for samples 7–18 based on its content in the soil and the amendment and the corresponding solid mass fractions in the mixture. The results for two of the mixtures that have the highest possible level of the metals (Soil A + 2% C SL 2 and Soil B + 2% C SL 2) are also shown in the table. The results are compared with the guidelines prepared by the EPA Victoria, Australia [5] and by New Zealand Water Environment Research Foundation (NZWERF) [6] for biosolids application. The contents of carbon and nutrients N, P and K in the solids are also presented.

In the guidelines by the EPA Victoria, Contaminant Grades (C_1 or C_2) are classified based on biosolids contaminant concentrations. C_1 biosolids have sufficiently low contaminant levels that specific management controls on end use are not needed. In the NZWERF guidelines Grade a and Grade b are similarly classified. All results for heavy metals in Table 3 are below the guideline levels for Grade C_2 and Grade b biosolids. The data that exceed the guideline level for Grade C_1 or Grade a biosolids are highlighted in bold italic.

It can be seen that all pre-mixed solids fell into Grade C_2 category, except for the lignite and Soil A which were Grade C_1 solids. The high levels of Cu and Zn in the sludge and Cd in the sludge and Soil B prevented these materials in their unmixed state from being acceptable in the higher grade. However, after mixing the sludge-containing amendments with Soil A, the mixtures could meet the guidelines for Grade C_1. Only the mixtures with Soil B were still Grade C_2 due to the high Cd level. According to the guidelines by EPA Victoria, processes such as composting, lime stabilisation or soil blending may result in a final product that meets the C_1 provisions despite the initial biosolids material being C_2. In this instance, provided the final product is re-sampled and conforms to the C_1 criteria, the final product can be classified as C_1.

Comparison of the results for the original sludge solids (SS) with that after a dewatering process (SD) showed that after the dewatering process elements such as As, Cd and Hg mostly remained in the dewatered product, while a portion of Cr, Cu, Pb, Ni and Zn was removed together with the sludge water during the process. It should be noted that Zn was present in the sludge solids (SS) at a very high level (860 mg/kg, db), but was reduced to a very low level (8 mg/kg, db) after the dewatering process (SD). This resulted from the removal of the soluble portion of the metal during dewatering when the solids content increased from around 2 wt% to 30 wt%. However, when the lignite was used as a filter aid for sludge dewatering, the concentrations of Zn in the dewatered products (SL 1 and SL 2) were increased, close to that in the original sludge solids (400–500 mg/kg, db). Presumably during sludge dewatering the lignite acted as an adsorbent and thus fixed Zn in the solid products. The contents of Cr, Cu, Pb and Ni in the dewatered sludge solids were also reduced to different extents compared to that in the original sludge.

From the results for C, N, P and K in Table 3 it can be seen that the two soils had the lowest C and N contents and the second and third lowest levels of P and K compared with the other solids. It can be expected that the addition of the sludge–lignite dewatered products as soil amendments will improve the soil properties significantly. The calculated results for the contents of N and P in the mixtures of Soil A or Soil B and the amendment SL 2 were more than 2–3 times of that in the soils, while the total carbon was 2% higher.

3.2. Leaching test method DIN 38414-S4

The method used for the leaching tests (DIN 38414-S4) is originally a German standard procedure for the determination of leachability of sludge and sediment [28] and it has served as the basis for the European standard leaching method EN 12457-4 [29].

Table 3
Heavy metals and nutrients in soils and biosolids compared with guidelines for biosolids application.

| | | SS | LY | Soil A | Soil B | Dewatered product | | | Soil and amendment mixture[a] | | Guidelines (EPA Victoria, Australia [5]) | | Guidelines (NZWERF [6]) | |
						SD	SL 1	SL 2	Soil A + 2%C SL 2	Soil B + 2%C SL 2	Grade C_1	Grade C_2	Grade a	Grade b
Heavy metals (mg/kg, db)	As	6.1	0.52	2.7	0.37	6.6	4.0	5.0	2.8	0.59	20	60	20	30
	Cd	***2.0***	0.04	0.41	***1.5***	***2.3***	***1.2***	***1.5***	0.46	***1.5***	1	10	1	10
	Cr	130	9.0	–	85	70	38	62	2.9	84	400	3000	600	1500
	Cu	***600***	5.0	50	35	***500***	275	***325***	63	49	100	2000	100	1250
	Pb	61	2.0	<0.1	24	2.0	1.0	1.0	0.047	23	300	500	300	300
	Hg	0.75	0.20	0.04	0.05	1.0	0.90	1.0	0.085	0.095	1	5	1	7.5
	Ni	76	3.0	0.40	11	26	6.0	10	0.85	11	60	270	60	135
	Zn	***860***	6.0	66	15	8.0	***458***	***548***	89	40	200	2500	300	1500
Nutrients (% db)	C	–[b]	62.2	1.7	3.0	35.6	48.2	45.5	3.7	5.0	N/A[c]	N/A	N/A	N/A
	N	–	0.59	0.08	0.14	5.9	4.0	4.3	0.28	0.34	N/A	N/A	N/A	N/A
	P	–	0.0034	0.056	0.036	2.8	1.4	1.8	0.14	0.12	N/A	N/A	N/A	N/A
	K	–	0.066	0.075	0.15	0.044	0.37	0.36	0.09	0.16	N/A	N/A	N/A	N/A
% db	Fe	–	0.80	0.17	0.20	1.9	0.35	0.43	0.18	0.21	N/A	N/A	N/A	N/A
mg/kg, db	Mn	–	6	21	54	130	75	88	24	56	N/A	N/A	N/A	N/A

[a] Calculated.
[b] Not determined.
[c] N/A: not applicable.

This method is a very common procedure for the assessment of heavy metal leachability [30–32]. Comparison with other methods such as the EPTox Test by US EPA [33], which uses an acetic acid solution for extraction, have shown that the method can provide comparable or supplementary results for the determination of the leaching behaviour of heavy metals [3,34,35]. Chrysochoou et al. [3] found that the DIN 38414-S4 method proved to be the most statistically reliable due to the high liquid to solid ratio and the strong mechanical agitation compared to the extraction by ammonia nitrate, soil saturation extraction and the pH static test. The great reproducibility of the batch leaching procedure has also been recognised by Jackson et al. [36] for extraction of waste constituents in solids.

According to Arain et al. [37], while the acid extraction may indicate which metals are more mobile and therefore the most bio-available, the results from leaching tests using methods such as DIN 38414-S4 enable the evaluation of the potential environmental risks associated with the pollutants.

It should be pointed out that the leached fraction of a metal measured using this method in this study is not the total water soluble fraction or acid extractable fraction of the metal in the solids. The leaching tests were carried out by a single mixing of the solids and water, where the leaching process reached equilibrium, rather than by sequential extraction to full metal recovery. The leached proportion would be influenced by the total content of the soluble forms in the solids and generally lower than the total leachable fraction of the metal. Therefore, in the following discussion, the term 'leached fraction' rather than 'leachable fraction' is used to identify the fact. The results give an indication of the mobility of the metal in the solids. Comparison of the results also provides information on the effect of the characteristics of the matrix on metal leaching behaviours.

3.3. Leaching behaviour of heavy metals in soils and biosolids

Understanding of the leaching behaviour of heavy metals is very important for assessing the environmental impact of different disposal options for waste materials, including their application to soils. In this study the leaching behaviour of eight heavy metals in soils and sludge–lignite soil amendments were investigated using batch leaching tests.

When the sludge–lignite solids were added to the soils to increase the carbon and nutrient contents of the soils, other properties such as pH and inorganic composition also varied. pH is well reported to be a very important parameter that influences both the mobility and fate of heavy metals in soils [22,26,27,38] and their sorption by lignite [14–16] and other natural carbonaceous materials [39,40]. Soil minerals containing Fe and Mn are also considered to play an important role in precipitation and adsorption of As and Cr [41–43].

Fig. 1 shows the pH values of the water slurries of the soils, amendments and their mixtures. Concentrations of Fe and Mn in the solids are included in Table 3.

The acidity of the soils and the biosolids is in the order of Soil B > SL 1 and SL 2 > Soil A. When the near neutral Soil A was mixed with the two amendments with slightly lower pH, the slurry pH decreased with increasing fraction of the amendments. For the weak acidic Soil B, the addition of increasing fraction of the amendments resulted in the increase of pH of the slurry. After 24-h agitation, the pH of the leachates from the soils and the soil–amendment mixtures slightly decreased mainly due to the dissociation of minerals from the soils and the buffering effect. The pH of the leachates of the amendments and the lignite remained unchanged. The contents of Fe and Mn in the mixtures of soils and amendments increased only marginally compared to that in the soils.
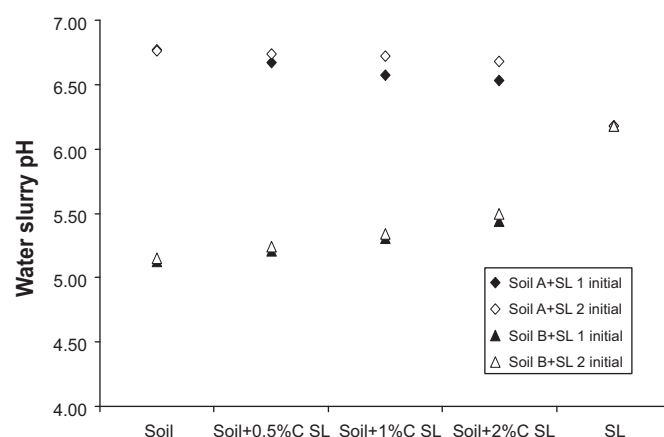

Fig. 1. pH of water slurries of soils, amendments and their mixtures.

The effect of application of the amendments to the soils on the leaching behaviour of the metals, which is related to the change of solids properties, can be evaluated by comparing the leached fraction of a metal in the solids mixtures to the predicted results calculated based on the leached fractions in each solids without mixing using Eq. (1).

$$\text{Predicted leached fraction in solids}\,(A+B)\,\% = \frac{C_A m_A L_A + C_B m_B L_B}{C_A m_A + C_B m_B} \times 100 \qquad (1)$$

C_A and C_B are the concentrations of a metal in Solid A and Solid B, mg/kg, db, respectively; m_A and m_B are the mass fractions of solid A and solid B in solid (A+B), respectively; and L_A and L_B are the leached fractions of the metal from Solid A and Solid B, respectively.

3.3.1. Leaching behaviour of arsenic

Fig. 2 shows the concentrations of As in the six pre-mixed solids and the fractions that can be leached from each solid. Measured results and calculated values of the percentage of As leached from Soil A and Soil B after being mixed with the amendments SL 1 and SL 2 are compared in Fig. 3.

Based on the results in Fig. 2 and assuming that the leaching behaviour of the metal remained unchanged when the soils were mixed with the amendments, the leached fractions of As in each mixture would be similar to the calculated results shown in Fig. 3.

However, as can be seen, all measured results were higher than the calculated results. The main reason could be related to the variation of the pH and redox conditions of the soils before and after the addition of the amendments. pH and redox potential are the two
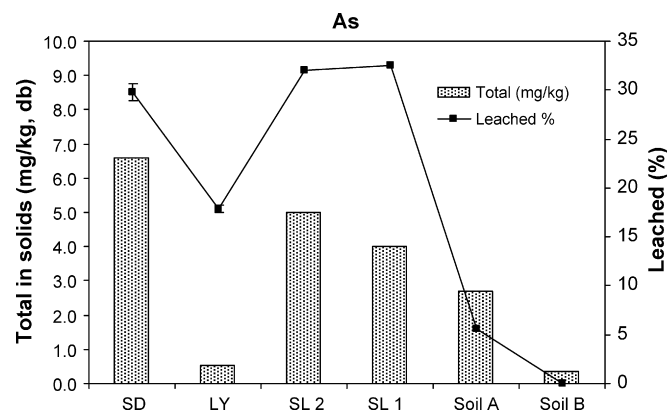

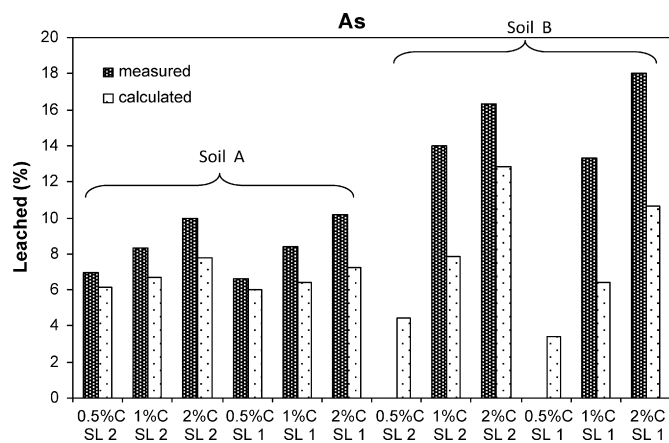**Fig. 2.** Arsenic contents in pre-mixed solids and fractions leached from each solid.

Fig. 3. Fractions of arsenic leached from mixtures of soils and amendments.

very important parameters determining the speciation and solubility of As in soil [41,44]. Pentavalent arsenic As(V) and trivalent arsenic As(III) are considered the most important As species in the soil environment. While both species can be present in dissolved forms in the environment, As(V) is the predominant soluble species under oxidizing conditions, whereas As(III) is primarily the soluble species under reducing conditions [41].

In an oxidizing environment (high redox potential), As(V) is dominant but the overall As solubility is low. Under acidic conditions, the species is mainly retained in the soil, while under neutral or alkaline conditions, the As(V) species become soluble to a certain extent. Masscheleyn et al. [44] reported that at redox potential of 200 mV (oxidizing) As(V) was the soluble species and the concentration was less than 10 mg/kg at pH 5, but was more than 30 mg/kg at pH 6.7. In the present study, As in the weak acid Soil B was not soluble, while in the near neutral Soil A, a small portion of As was leached. Considering the soils were both top soil from the surface of an aerobic environment, it was possible that As in the two soils was present mainly as As(V).

On the other hand, in a reducing environment (low redox potential), As(V) is transformed to As(III), which is generally more soluble than As(V) species, resulting in a higher mobility of As overall. Under acidic conditions, the reduction of As(V) to As(III) is more significant [44]. In this study the very high leached fractions of As in the two near neutral amendments suggest that the two solids likely provided a reducing environment, where As could be present as both As(V) and As(III) with As(III) as the main soluble species.

When the soils were mixed with the amendments, the leached fraction of As increased with increasing fraction of the amendments in the mixture and the degree of the increase was higher than that for the predicted results, which implies that a higher portion of As in the amendments contributed to the leached fraction after being mixed with the soils. For both soils, the mixing with the amendments created a more reductive environment, in which more insoluble As(V) species could be reduced to the soluble As(III) species. Consequently, higher proportions of As could be leached than calculated based on the leaching results for each solid. In the mixtures with Soil B, the amendment provided the sole source of As. When the mixing reduced the pH from near neutral to weak acidic (Fig. 1), the reduction of As(V) to soluble As(III) was more significant than in the near neutral mixtures of Soil A. Therefore, the differences between the leached fractions measured and that predicted in the mixtures with Soil B was bigger than that for Soil A. From another point of view, this could also be explained by the adsorption of As at different pH. Research has found that, in general, higher pH favours the adsorption of As(III) [45,46]. Smith et al. [46] observed a significant decline of As(III) adsorption when the

soil pH was below 6. Leaching is a result of equilibrium between adsorption and desorption. In this study, upon mixing the amendments with the weak acidic Soil B, the adsorption of the soluble As(III) species by the soil could be very low, while, under neutral conditions the soluble As(III) species in the mixtures with Soil A could be adsorbed to a certain extent.

Another possible reason contributed to the higher leached fractions of As than that predicted may be the dilution effect that the mixing with the soils of lower As concentrations promoted the extent of leaching of As from the amendments to the water. Since As was present in the soils at much lower levels than in the amendments, the mixing of small fractions of the amendments with the soils resulted in lower levels of As in the mixtures than in the amendments. Keeping the solids and water at a fixed ratio, the leaching process in this study reached equilibrium. The leached fraction of an element was, therefore, related to not only the forms of the element present in the solids, but also the concentration of the element in the solids. In the case of Soil A, the concentrations of As in the soil, SL 1 and SL 2 were 2.7, 4 and 5 mg/kg, db, respectively, whereas in the mixtures, the levels were between 2.7 and 2.8 mg/kg, db, much lower than in the amendments alone. Although the leaching of As in the soil may not vary significantly, the lower concentrations in the mixtures than in the amendments mean that, at equilibrium, larger fractions of As could be leached from the amendments in the mixtures than from the amendments alone. Based on the calculation, 6–8% of As in the mixtures would be leached, while the measured results showed that 7–10% was leached.

In the case of Soil B, where there was very low level of As and the As present remained unleached, the dilution effect of the soil could be even greater. The contents of As in the mixtures were between 0.41 and 0.59 mg/kg, db compared to 4–5 mg/kg, db in the amendments, which may explain the bigger difference between the measured and the predicted leached fractions from the mixtures with Soil B than from the Soil A mixtures.

It should be noted that the concentrations of As in the leachates from the mixtures with Soil B were very low and close to the detection limit of 5 μg/L. In the two samples with the lowest mass fractions of the amendments (0.5% C SL 2 and 0.5% C SL 1) where As was not detected, the concentration of As could be from 1 to slightly below 5 μg/L, corresponding to a leached fraction ranging from 2.4% to 10%.

The removal of As has been associated with the presence of soil minerals, such as oxidation and adsorption of As(III) by hydroxides of Fe and Mn and other minerals [43,45], adsorption and coprecipitation of As(III) on ferric sulphide [41] as well as soil organic matters (e.g. humic acid) [43,47]. However, since the mass fractions of the amendments in the mixtures were very low (1–5%), the contents of Fe and Mn in the mixtures were similar to that in the soils (Table 3); and the effect of the increase in organic carbon in the soil–amendment mixtures on the removal of As was also insignificant.

3.3.2. Leaching behaviour of cadmium

Leaching tests showed that Cd was not detected in any of the leachates from the pre-mixed solids and the mixtures of soils and amendments. The mobility of Cd in soil has often been found to be low [22,25]. The adsorption of Cd by lignite was also found to vary very little at pH between 5 and 7 [16], which was the pH range of this study.

As discussed in Section 3.1, when the soils were mixed with the amendments, all mixtures with Soil B fell into Grade C_2 category as a result of the high Cd level in Soil B. The result of leaching tests suggests that the presence of Cd in Soil B may not be an issue for land application due to its very low leachability.
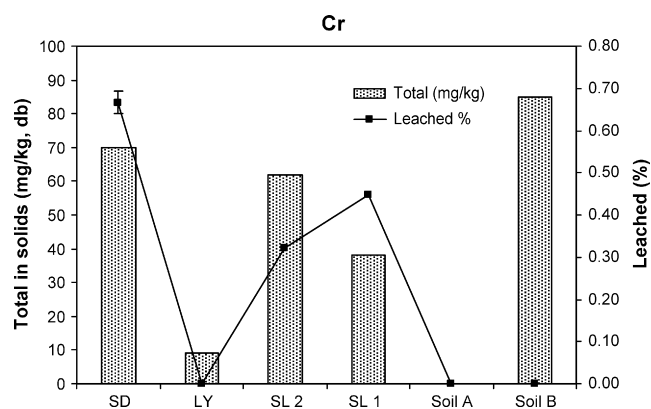
Fig. 4. Chromium contents in pre-mixed solids and fractions leached from each solid.

3.3.3. Leaching behaviour of chromium

The concentrations of Cr in the six pre-mixed solids and the fractions that can be leached from each solid are shown in Fig. 4. Fig. 5 compares the measured and calculated results of the fractions of Cr leached from Soil A and Soil B after being mixed with the amendments SL 1 and SL 2.

The concentrations of Cr in the pre-mixed solids, particularly in the sludge and Soil B were relatively high compared to As and Cd. However, the element was present predominantly in un-leachable forms in the sludge with less than 0.7% leached; and fully remained in the soil during leaching tests.

The mixing of Soil B with both sludge–lignite amendments did not result in further release of Cr. It seemed that Cr in leachable forms at low levels in the amendments was somehow fixed when the solids were mixed with Soil B. For Soil A, when the sludge-containing amendments were mixed with the soil, in which Cr was not present, the leached portion of Cr increased to more than 7% by adding 0.5% C from SL 2, more than 10 times that of the sludge and SL 2. A comparison with the calculated values showed that there might have been transformation of a portion of Cr to the leachable form during the mixing of Soil A with the amendments. But as the fraction of the amendments in the soil increased, the leaching of Cr seemed to be hindered significantly. This decrease was in proportion to increasing mass fraction of the amendments. Similar to the case of As, this change of leaching behaviour of Cr in soil after being mixed with biosolids amendments may be associated with the speciation and solubility of Cr at different pH and redox conditions.
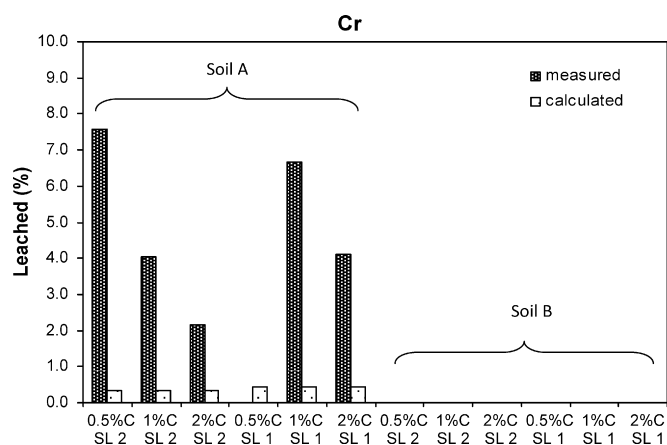
The behaviour of Cr in the environment is complex. The mobility of Cr is dependent on the speciation of Cr, which is considerably affected by the conditions of the environment. Trivalent Cr(III) and hexavalent Cr(VI) are the two stable species in the environment. Under natural conditions, Cr(III) is readily adsorbed on solid phase, while most Cr(VI) solids are relatively soluble and, therefore, Cr(VI) is generally considered to be more mobile and consequently more bioavailable than Cr(III) in soil–water systems [48,49]. The pH and redox conditions are the essential parameters that affect the speciation of Cr. Cr(III) is primarily present in a reducing environment, whereas an oxidizing condition favours Cr(VI) species. Under acidic to slightly alkaline conditions, the solubility of Cr(VI) is controlled by adsorption–desorption on mineral oxides [49]. Cr(VI) can be adsorbed on mineral oxides with exposed inorganic hydroxyl groups on the surface and the adsorption increases with decreasing pH [49].

In this study, Cr was absent in Soil A. When the amendments were mixed with Soil A, the environment of the mixtures became more oxidizing than that of the amendments, from which Cr originated. The less soluble species of Cr were likely to be oxidized to soluble Cr(VI) species resulting in the dramatic increase of Cr in the mixtures. As the mass fraction of the amendments increased, the pH of the mixtures decreased (Fig. 1), a condition that accommodated the adsorption of Cr(VI) and its subsequent removal from the solutions. Although the levels of minerals in the mixtures may not be significantly different than that in the soils, their adsorption for the soluble Cr species was affected by the change of the pH. Consequently, the leached fraction decreased with increasing mass fraction of the amendments and decreasing pH.

In the weak acidic environment of Soil B, although the content of Cr was high, it was present predominantly in insoluble forms. After the mixing with the amendments, the pH remained weakly acidic, which favoured the adsorption of Cr. The small portion of the soluble Cr species from the amendments seemed to have been adsorbed under this condition and remained unleached in the mixtures. The change of the environment to more oxidising seemed to not lead to transformation of Cr to the soluble Cr(VI) or the resulting Cr(VI) was adsorbed by the soil.

On the other hand, Loy Yang lignite from Victoria has been reported to be able to adsorb dissolved Cr(III) to up to 100% at weak acidic pH [13]. Hsu et al. [50] reported the adsorption of Cr(VI) on black carbon at pH 3–7. They identified that the adsorption of Cr(VI) onto black carbon was followed by the subsequent reduction to Cr(III). In this study, the lignite may also have contributed to the decrease of the leached fraction of Cr in the mixtures with Soil A with increasing mass fraction of the amendments, i.e. the increasing fraction of the lignite, and the absence of leached Cr in the mixtures with Soil B.

The reason for the undetected leached Cr from the mixture of Soil A with 0.5% C SL 1 was unclear. It could be an experimental error considering the rest of the results followed an explicit trend.

3.3.4. Leaching behaviour of copper

Fig. 6 shows the concentrations of Cu in the six pre-mixed solids and the fractions that can be leached from each solid. Fig. 7 presents the percentage of Cu leached from Soil A and Soil B after being mixed with the amendments SL 1 and SL 2.

The concentrations of Cu in the sludge and the sludge-containing amendments were very high. Although the fractions of Cu leached were very low, the absolute amount of leached Cu was high. The leached fractions of Cu in the soils were very low. For the mixtures of Soil A with the amendments, the results from the leaching tests were much higher than the calculated results. The dilution effect may also be one of the reasons, as the concentrations of Cu in the mixtures with both Soil A and Soil B were between 40 and 60 mg/kg, while the concentrations in the amend-
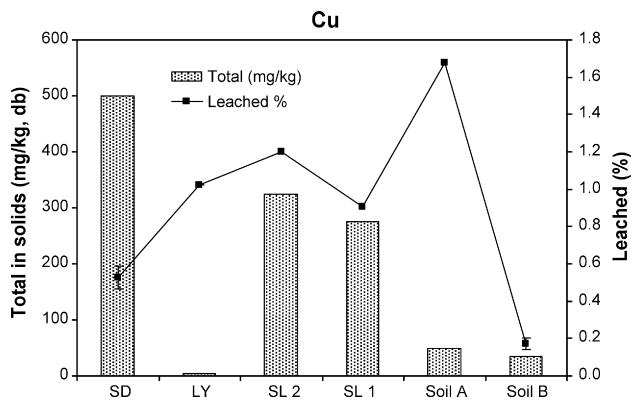

Fig. 5. Fractions of chromium leached from mixtures of soils and amendments.

Fig. 6. Copper contents in pre-mixed solids and fractions leached from each solid.

Fig. 8. Lead contents in pre-mixed solids and fractions leached from each solid.

ments were 275 and 325 mg/kg, respectively. The concentration of Cu in the leachate of the soil was 84 μg/L, but in the leachates of the mixtures the concentrations were 100–140 μg/L. Obviously the small fraction of the amendments leached high levels of Cu to the leachates. On the other hand, the leached fraction of Cu in the mixtures of Soil B and the amendments increased with increasing fraction of the amendments. The difference between the measured results and the predicted was small. This may not be explained with only the dilution effect, as the difference between the contents of Cu in the amendments and Soil B were greater than that for Soil A.

The change of pH on the adsorption/desorption of Cu in the solids upon mixing may have played an important role. Adsorption of heavy metals as cations in soil is a process of binding with exposed inorganic hydroxyl groups on the surface of soil minerals [51]. At high pH, the equilibrium favours the adsorption of the metal cations and the coprecipitation with the soil minerals. With decreasing pH, the adsorption process competes with protons for the available exchanging sites on the mineral surface, while the minerals may also dissolve releasing metal ions. When Soil A was mixed with the amendments, the pH slightly decreased. As Cu in Soil A was highly mobile, the solubility of Cu increased with decreasing pH leading to the higher leached fractions from the soil than predicted. In the case of Soil B, the mixing of Soil B with the amendments increased the pH of the mixtures. Although the soluble fraction of Cu in Soil B was very low, the increased pH may have improved the adsorption of Cu and reduced the total solubility of Cu in the mixtures.

Therefore, while the dilution effect led to a higher solubility of Cu from the amendments in the mixtures than predicted, the change of the pH in the mixtures resulted in a higher solubility of Cu from
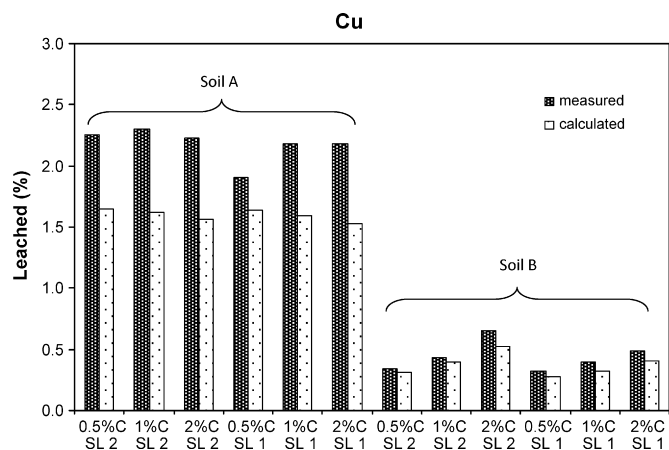
Soil A but an immobilization of Cu from Soil B. The leached fractions of Cu in the mixtures could be a combination of both effects.

3.3.5. Leaching behaviour of lead

Fig. 8 shows the concentrations of Pb in the six pre-mixed solids and the fractions that can be leached from each solid. The concentration of Pb in Soil B was the highest among all pre-mixed solids, but the metal was present mainly in un-leachable forms. In the other solids, Pb was also present in un-leachable forms except for the case of the sludge, which released a low fraction of Pb. However, Pb present in the sludge–lignite mixtures was not detected in the leachates indicating a possible fixation of the metal by the lignite. Studies of the leachability of Pb in soils or adsorption by lignite have often found that, compared with many other heavy metals the mobility Pb is the lowest [22,25] and the adsorption by lignite [13] and chars [27] is the highest.

3.3.6. Leaching behaviour of mercury

Hg was present in all solids at very low levels and the leaching tests showed that Hg was not detected in any of the leachates.

3.3.7. Leaching behaviour of nickel

Fig. 9 shows the concentrations of Ni in the six pre-mixed solids and the fractions that can be leached from each solid. Fig. 10 presents the percentage of Ni leached from Soil A and Soil B after being mixed with the amendments SL 1 and SL 2.

According to the results in Fig. 9, the total content and the leached fraction of Ni in the sludge were both high. In Soil B, although very low fractions of Ni were leached (0.6%), the content of Ni was high, whereas Soil A contained a very low level of Ni, but a portion (15%) of this was leached. Like Cu, Ni is one of the

Fig. 7. Fractions of copper leached from mixtures of soils and amendments.
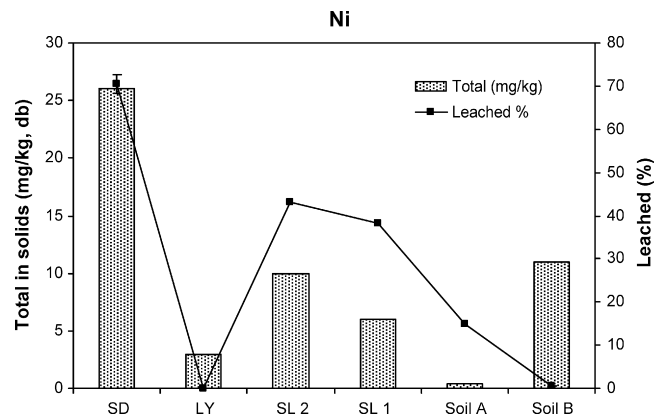

Fig. 9. Nickel contents in pre-mixed solids and fractions leached from each solid.

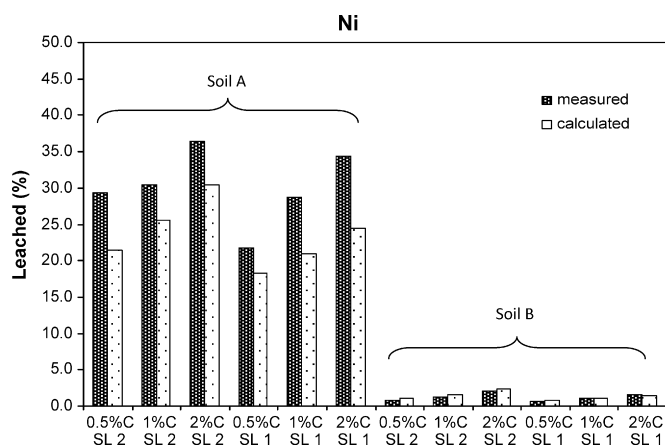Fig. 10. Fractions of nickel leached from mixtures of soils and amendments.

Fig. 12. Fractions of zinc leached from mixtures of soils and amendments.

heavy metals that usually have high mobility in the soil environmental [52] and low adsorption by carbonaceous materials [27]. When Soil A was mixed with the amendments, the leached fraction of Ni increased with increasing fraction of the amendments. Like the case of Cu, the dilution effect (with Ni contents in Soil A, SL 1 and SL 2 at 0.4, 6 and 10 mg/kg, db, respectively) and the pH effect may also present, both contributed to improving the leaching of Ni, since the measured values of the leached fractions were significantly higher than the calculated results. In the case of Soil B the measured results were very close to the calculated values and the leached fractions of Ni in all the mixtures were very low. As the concentration of Ni in SL 1, SL 2, Soil B and the mixtures were at a similar level (6, 10, 11 and 11 mg/kg, db, respectively), there was no dilution upon mixing the solids. Therefore, the leaching behaviour of Ni was not affected by the mixing. Since Ni in the mixtures came mainly from the soil, the effect of the pH seemed to be insignificant on the leaching of Ni.

3.3.8. Leaching behaviour of zinc

Fig. 11 shows the concentrations of Zn in the six pre-mixed solids and the fractions that can be leached from each solid. Fig. 12 presents the percentage of Zn leached from Soil A and Soil B after being mixed with the amendments SL 1 and SL 2.

As mentioned in Section 3.1, Zn was present at very high levels in the sludge–lignite dewatered products compared to that in the dewatered product of pure sludge, because during the dewatering process it may have been captured by the lignite and was not removed. Results in Fig. 11 demonstrated that the leached proportion of Zn in these lignite-containing dewatered products was
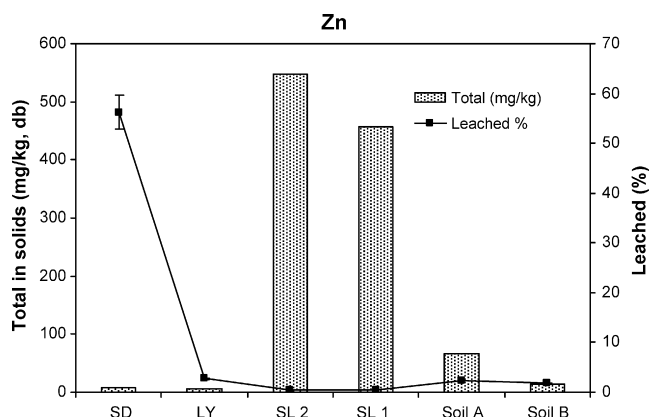

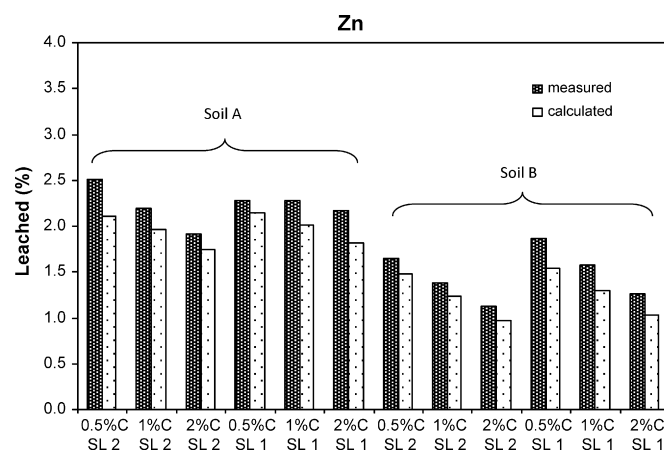Fig. 11. Zinc contents in pre-mixed solids and fractions leached from each solid.

very low. It was in contrast to the leaching behaviour of Zn in the sludge only dewatered product, which was present at a low level but was leached to a significant extent. The leached fraction of Zn in the sludge was 56%, whereas only 0.37% and 0.44% of Zn in SL 1 and SL 2 were leached, respectively. In this case, the lignite acted as an adsorbent for Zn and inhibited the leaching of Zn in the mixtures. The leaching behaviour of Zn in the soil and amendment mixtures (Fig. 12) further demonstrated that although the concentrations of Zn in the amendments were very high, the leached fractions in the mixtures were very low. As the fraction of the lignite increased, the leached fraction of Zn decreased. This is applicable for both Soil A and Soil B cases.

The dilution effect or pH effect were not significant for the leaching of Zn in the soil–amendment mixtures. The measured results were only slightly higher than that calculated. This could be because that the strong adsorption of Zn by the lignite reduced the mobility of Zn and/or that the adsorption of Zn by the soils was not affected by the pH as much as for the other elements.

3.3.9. Mobility of heavy metals and effect of solids properties

Comparison of the leached fractions of the heavy metals in the mixtures of soils and amendments shows that Ni and As in Soil A mixtures were the most mobile followed by Cr, Zn and Cu. As had the highest mobility in Soil B mixtures followed by Ni and Zn. In all the mixtures, Pb, Cd and Hg remained rather immobile. The mobility order of these heavy metals in these mixtures is similar to those reported previously. Zhao et al. [25] observed in soil column leaching tests that the retention of the metals followed the order of Pb > Cd > Cr > As, while Dong et al. [22] reported an order of adsorption as Pb > Cd > Cr by soil.

The adsorption of these metals on lignite and some carbonaceous materials has been found to follow a similar order. Havelcova et al. [16] found that the adsorption capacity of Cd by a lignite from Czech Republic was higher than that of Pb, which in turn was higher than that of Cu and then Zn. In a study by Pentari et al. [15] of the same four metals, the adsorption capacity of Pb by a Greek lignite was the highest, but for the other three metals the same order of adsorption capacity was reported. Uchimiya et al. [27] investigated the adsorption of Ni, Pb, Cu and Cd by a biochar and observed that the trend of the removal extent was Ni < Cd < Cu < Pb.

When studying the leaching behaviour of heavy metals, such as Cu, Ni and Zn, in soils and lignite, pH is a critical factor that affects the mobility and fate of the metals. This is related to the mechanisms of the retention of heavy metals in the soil and the lignite. Immobilization of heavy metals in soil is mainly by adsorption and subsequent coprecipitation on the soil minerals, while for materials such as lignite which contain oxygen-containing func-

tional groups, the mechanism of heavy metal removal is mainly by ion exchange. The adsorption and immobilization of the metals are generally favoured at higher pH.

For As and Cr, since the two elements are present in the environment in various oxidation and reduction species and their solubility is greatly associated with the speciation of the elements, the redox conditions of the environment as well as pH plays a critical part in the determination of the mobility of the elements.

4. Conclusions

The potential of using biosolids from sludge–lignite dewatering processes as soil amendments was investigated. The study demonstrated that using the dewatered products as soil amendments had the potential to improve nutrient contents such as C, N, P and K in soils. The eight heavy metals in all the mixtures of soil and amendment were below the guideline levels for biosolids application which requires no specific management controls on end use, except for Cd in the mixtures with one of the soils.

Results of leaching tests showed that, although some metals such as Cu and Zn were present in the sludge solids at high levels, the leachability of the eight heavy metals was generally low. Cd and Hg were present in all the solids predominantly in unleachable forms.

The retention of the metals in the mixtures with near neutral Soil A was in the order of Cu, Zn > Cr > As > Ni. In the weak acidic Soil B mixtures, Cr remained unleachable and the order of metal retention was Cr > Cu > Zn, Ni > As.

Mixing of the soils with the sludge–lignite amendments altered the leaching behaviours of some of the heavy metals. The variation of the pH and redox conditions in the soil and amendment mixtures may have altered the species of As and Cr and, hence, their solubility in the mixtures. The solids pH also played a very important role in the leaching behaviour of Cu and Ni, possibly combined with the dilution effect due to mixing with the soils containing much lower levels of the metals.

On the other hand, the lignite in the amendments acted as an adsorbent that fixed heavy metals, such as Pb and Zn and possibly Cr, reducing their leachability. Further work should focus on the study using simple systems (e.g. single element) of the adsorption/desorption mechanisms of each element in the mixtures and the effect of the properties of each solid and quantification of the adsorption capacity of the lignite to bind these heavy metals.

Acknowledgements

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