

Article

Metals Leaching in Permeable Asphalt Pavement with Municipal Solid Waste Ash Aggregate

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Abstract: The leaching behaviors of four heavy metals (Zn, Pb, Cu and Cr) from unbounded municipal solid waste incineration-bottom ash aggregate (MSWI-BAA) and permeable asphalt (PA) mixture containing MSWI-BAA were investigated in the laboratory. The horizontal vibration extraction procedure (HVEP) test and a simulated leaching experiment were conducted on MSWI-BAA with three particle sizes, but only the simulated leaching experiment was carried out on a type of PA specimen (PAC-13) with and without these MSWI-BAAs. Leaching data were analyzed to investigate the leaching characteristics, identify the factors affecting leaching and assess the impact on the surrounding environment. Results indicated that the leaching process was comprehensively influenced by contact time, leaching metal species and MSWI-BAA particle size, regardless of MSWI-BAA alone or used in PAC-13 mixture. The leaching concentrations of Cr, Zn and Pb from MSWI-BAA in HVEP testing was strongly related to MSWI-BAA particle size. The use of MSWI-BAA in PAC-13 mixture did not change the basic tendency of heavy metal leaching, but it led to an increase of Cr and Zn in leachate overall. The leachate from the MSWI-BAA and PAC-13 mixture with MSWI-BAA was shown to be safe for irrigation and would have very little negative impact on surrounding surface and underground water quality.

Keywords: permeable asphalt; heavy metal; leaching behavior; MSWI-BAA; stormwater

1. Introduction

Incineration with energy recovery is recommended as a preferred option for dealing with municipal solid waste (MSW) to effectively reduce the original waste volume and mass by approximately 90% and 70%, respectively, and generate electricity and heat [1–3]. However, a considerable amount of residual material is still generated after the incineration process: typically MSW incineration fly ash (MSWI-FA) and MSW incineration bottom ash (MSWI-BA) [4,5]. MSWI-BA accounts for nearly 80% of the total residual by mass and is complex, consisting of combustion residue and non-combustible constituents of the waste feed [6–8]. In Europe and Asia, MSWI-BA is often classified as non-hazardous waste [9]. For this reason, MSWI-BA is commonly discarded in landfills.

In 2017, 84.63 million tons of MSW were treated by incineration in China, accounting for nearly 39% of the total mass [10], which produced approximately 20.31 million tons of MSWI-BA. It is reported that the amount of MSWI-BA generated is expected to exceed 28 million tons by 2020 according to the National Thirteenth Five-Year Plan of China [11,12]. If all these MSWI-BAs are to be disposed of in landfill sites; around 12.73 million m³ of landfill space (calculated by the density of 2.20 g/cm³ [13,14]) will be needed. Therefore, MSWI-BA treatment has been a tremendous challenge to most Chinese cities with high population densities and limited land resources.

Traditionally, landfilling is regarded as the most convenient and inexpensive approach for disposal of MSWI-BA. However, it results in significant environmental problems. Studies indicate that MSWI-BA

contains various heavy metals such as zinc (Zn), lead (Pb), copper (Cu) and chromium (Cr), which are present in high concentrations [3,15,16]. The leaching of these metals from MSWI-BA when exposed to rainwater can seriously contaminate the surrounding sensitive recipients, including soil, surface and sub-surface water bodies [5,17,18]. Environmental safety, thus, has become a great concern for MSWI-BA management.

The recycling of MSWI-BA as road construction material, especially considering the reduction of natural aggregate usage, is recommended as an important management option and has gained worldwide attention. Numerous studies were conducted on the physicochemical and engineering properties of MSWI-BA. It is concluded that MSWI-BAA made by fresh MSWI-BA after being pretreated, has a good particle size distribution and similar properties to natural aggregate and is suitable to be used in asphalt mixtures and cement concrete [4,5,9,13,14,19,20]. Some studies have consequently used MSWI-BAA to partially replace natural aggregate in asphalt mixtures. It is reported that the substitution of MSWI-BAA with coarse and fine natural aggregates in traditional, dense hot-mix asphalt (HMA) can meet the technical requirements, but the characteristics of being lightweight, and having a smaller specific weight, compared to natural aggregate, must be seriously considered [14,21,22]. It is, therefore, suggested that MSWI-BAA is more suitable for use in low-traffic-volume roads [23].

Rapid urbanization coupled with climate change is placing increasing pressures on urban stormwater management [24]. The increase in impervious surfaces with asphalted roads and rooftops significantly increases stormwater volumes and peak flowrate, while also decreasing stormwater quality and impeding groundwater recharge [25–27]. Permeable asphalt (PA) pavement is a popular and practical, low-impact development (LID) technology that serves as an ideal alternative to conventional low-traffic-volume pavement because it can help to address the issues stated above by providing in situ restoration of the urban hydrological cycle and reducing the need for traditional stormwater facilities [28]. PA pavement consists of various layers with porous materials, which not only allow stormwater to infiltrate into the ground, unlike conventional asphalt pavement, but can also simultaneously remove pollutants (e.g., total suspended solids (TSS) and heavy metals) from stormwater runoff on site, thus raising their value as a LID option in current urban development [25,29–31]. As the PA mixture (the surface material of the PA pavement) requires relatively low strength compared to conventional dense asphalt mixtures, researchers have explored the feasibility of recycling MSWI-BA aggregate (MSWI-BAA) in PA mix designs. The results are encouraging, indicating that PA mixtures containing MSWI-BAA have better performance than those without, and the replacement ratio can be up to 80% [23].

On the other hand, the potential environmental impacts associated with the use of MSWI-BAA in asphalt mixtures are of great concern [21,32–34]. Results indicate that the leaching concentrations of heavy metals (e.g., Pb, Zn, Cu, Cr and Cd) from HMAs containing MSWI-BAA are significantly reduced compared to unbound MSWI-BAA. It has been concluded that there is very little environmental risk for substituting MSWI-BAA for natural aggregate in dense asphalt mixtures. Previous investigations have provided valuable information for the leaching characteristics of heavy metals from dense asphalt mixtures containing MSWI-BAA; however, there are few studies focusing on PA mixtures containing MSWI-BAA. High voids in PA mixtures provide benefits for stormwater management in urban areas, but it can also lead to an increase in contact between the PA material and the infiltrated stormwater during wet weather.

To encourage the utilization of MSWI-BAA in PA mixtures, investigating the leaching behavior of unbound MSWI-BAA and within PA mixtures to identify environmental consequences is warranted. The objectives of this study are to investigate and compare the heavy metal leaching of unbound MSWI-BAA and PA mixtures containing both the coarse and fine MSWI-BAA at optimal replacement ratios. In this study, heavy metals present in MSWI-BAA with three particle sizes (0.075–2.36 mm, 2.36–4.75 mm and 4.75–9.5 mm) were identified based on X-ray Fluorescence (XRF) tests. The leaching behaviors of heavy metals in MSWI-BAA with three particle sizes were investigated with HVEP tests and simulation experiments. The leaching behaviors of PA mixtures containing these MSWI-BAA

were examined by simulation experiments. The difference in leaching behavior between unbounded MSWI-BAA and PA with MSWI-BAA were compared and analyzed. The leaching data were also compared to limit values in Chinese standards for surface water, subsurface water and irrigation water, to assess the environmental risk for the utilization of MSWI-BAA in PA mixtures.

2. Materials and Methods

2.1. Materials

2.1.1. MSWI-BAA

The MSWI-BAA used in this study was made by the MSWI-BA collected from a waste-to-energy facility located in Nanjing City, China. After the incineration process, fresh MSWI-BA was water-quenched immediately and air-dried for 7 days, and then delivered to the lab. The received MSWI-BA was naturally weathered in the lab for another 90 days for potential hydration and stabilization prior to pretreatment. The processes used for MSWI-BA pretreatment included impurity removal, magnetic separation, crushing and sieving. Three MSWI-BAA sizes were prepared: 0.075–2.36 mm, 2.36–4.75 mm and 4.75–9.5 mm. It should be noted that both sampling and preparation were carried out in accordance with Chinese standards of HJ/T 20-1998, HJ/T 298-2007 and JTG E42-2005 [35–37].

To identify the main species and contents of heavy metals in MSWI-BAA of different sizes, XRF was utilized. Three groups of MSWI-BAA samples were oven dried at 105 °C until a constant mass was obtained, and then the samples were milled into powder (<0.075 mm). After that, these powder samples were separately packed in sealable polypropylene bags prior to further testing. The weight percentages of all the elements above detection limit are shown in Table 1. It can be noted that Zn, Cu, Cr and Pb are present in relatively high levels in these three MSWI-BAA samples, accounting for approximately 0.7–2.2% of the total mass. Thus, these four metals were selected as the tracer metals for the leaching tests in this study.

Table 1. XRF analysis results of MSWI-BAA samples.

Element	MSWI-BAA (% by Weight)		
	0.075–2.36 mm	2.36–4.75 mm	4.75–9.5 mm
Ca	51.55	44.56	43.97
Si	12.85	17.27	19.60
Al	6.94	8.65	8.82
Cl	4.78	4.88	5.67
Fe	5.92	5.65	4.77
S	4.49	3.49	3.61
Mg	2.26	2.44	2.61
P	2.66	3.90	2.23
Ti	1.98	1.65	1.63
K	2.16	2.46	2.53
Na	1.59	2.14	3.22
Zn	1.32	1.92	0.48
Cu	0.22	0.12	0.10
Cr	0.17	0.13	0.10
Pb	0.19	0.03	0.03
Sr	0.12	0.08	0.04
Ba	0.60	0.41	0.44
Total	99.80	99.78	99.85

2.1.2. PAC-13 Mixture Containing MSWI-BAA

A type of PA mixture with a maximum aggregate size of 13.2 mm, PAC-13 mixture, was designed in accordance with the Technical Specification for Permeable Asphalt Pavement (CJJ/T 190-2012) [38]. To focus on the realistic leaching behavior of PAC-13 containing MSWI-BAA on site, PAC-13 mixtures used in this study were designed with the same aggregate gradation and air void content (20%), as shown in Figure 1. Three sizes of MSWI-BAA (0.075–2.36 mm, 2.36–4.75 mm and 4.75–9.5 mm) were separately used as partial replacements of the same aggregate size in the PAC-13 mixture with optimal replacement ratios of 30%, 20% and 30% (by aggregate weight). Thus, four types of PAC-13 specimens, including three PAC-13 specimens containing MSWI-BA and one specimen without (control), were used in this study. The optimal replacement ratio of MSWI-BAA for each mixture was determined to satisfy the technical requirements for PAC-13 mixtures.

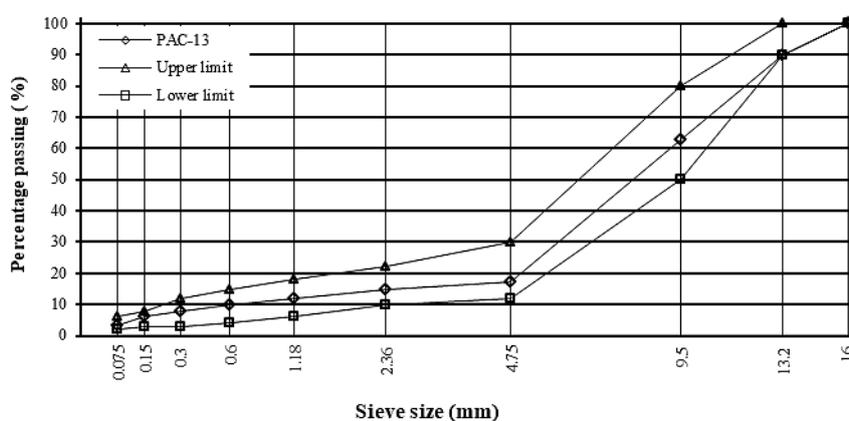


Figure 1. Aggregate gradation of PAC-13 mixture.

All the PAC-13 specimens were compacted by a Marshall hammer with 50 blows per side at 170 °C, according to Method T0702 [39]. Each specimen was prepared in a 101.6 mm diameter mold with height 63.5 ± 1.3 mm. The optimum asphalt contents of 5.4%, 5.1%, 5.7% and 4.9% were separately used for three PAC-13 specimens containing MSWI-BAA with particle sizes of 0.075–2.36 mm, 2.36–4.75 mm and 4.75–9.5 mm, and one specimen without MSWI-BAA. It should be noted that all the materials utilized for preparing these specimens satisfied the technical requirements of CJJ/T 190-2012 [38].

2.2. Methods

2.2.1. Leaching Test of MSWI-BAA

To assess the environmental risk resulting from the possible release of heavy metals (Zn, Pb, Cu and Cr) from MSWI-BAA in unbounded form, the standard test and a simulated leaching experiment were conducted in the lab.

The HVEP test (as shown in Figure 2) was conducted in accordance with the Chinese standard (HJ 557-2009) [40] to evaluate the potential maximum leaching toxicity of heavy metals from unbounded MSWI-BAA when exposed to stormwater. For preparing the liquid waste sample, 100 g of MSWI-BAA sample was set with 1 L distilled water in a flask after passing through a 3 mm sieve. The mixture sample was vibrated with frequency of 110 times/min and amplitude of 40 mm for 8 h, and then rested at room temperature (20 °C) for 16 h. The liquid extracted was then separated from the solid phase by filtration through a 0.45 μ m glass fiber filter and then stored in the refrigerator at 4 °C before digestion. A total of three MSWI-BAA samples and one blank were tested.



Figure 2. HVEP test in this study: (a) Liquid waste samples; (b) the horizontal-vibration machine.

The simulated leaching experiment was designed to assess the realistic leaching of heavy metals from unbounded MSWI-BAA exposed to stormwater over a long period of time. The simulated experiment was continued for 28 days. Although the pH level is suggested as one of the main factors influencing MSWI-BA's leaching behavior [17], distilled water with an initial pH value of 6.8 was used here to simulate the stormwater. The liquid/solid (L/S) ratio of 10:1 was chosen based on results from [41] and the HVEP test method. For each experimental sample, 100 g of MSWI-BAA was mixed with 1 L of synthetic stormwater in a capped flask. Timing commenced immediately after application of the synthetic stormwater. At each sampling event, 10 mL of leachate was collected from a flask using a pipette, dispensed into a polypropylene sample bottle, and then 3 mL of nitric acid was added to the sample to keep it stable. Samples were stored in the refrigerator at 4 °C until further analyses. It should be noted that the first leachate sample was collected immediately after the application of synthetic stormwater to the MSWI-BAA sample. Herein, a total of three MSWI-BAA samples with different sizes were used and 14 sampling events were conducted during the experiment for each sample.

2.2.2. Simulated Leaching Experiment of PAC-13 Mixture Containing MSWI-BAA

The experimental procedure for the PAC-13 mixtures containing MSWI-BAA was the same as that for the unbounded MSWI-BAA. Four PA specimens were used, as shown in Figure 3: (1) PAC-13 with 30% MSWI-BAA of 0.075–2.36 mm; (2) PAC-13 with 20% MSWI-BAA of 2.36–4.75 mm; (3) PAC-13 with 30% MSWI-BAA of 4.75–9.5 mm; and (4) PAC-13 without MSWI-BAA. For each PA specimen, a total of 14 sampling events were conducted during the experiment.



Figure 3. PAC-13 specimens with and without a municipal solid waste incineration-bottom ash aggregate (MSWI-BAA) used in the simulated leaching experiment.

2.2.3. Sample Determination and Data Analysis

After the leaching tests, all of the leachate samples were first digested by a microwave digestion procedure. The total concentrations of Zn, Cu, Cr and Pb in leachates were then determined by inductively coupled plasma-mass spectrometry (ICP-MS).

For data analysis, Microsoft Excel[®] and SPSS[®] were used to conduct a variety of tests on the data to identify the difference of leaching characteristics and determine the factors affecting heavy metal leaching. The two-factor analysis of variance (ANOVA) was conducted on the data from the HVEP test while the one-factor ANOVA was conducted on the data from simulated experiments. Linear regression was also used to determine if linear relationships were likely.

3. Results

3.1. HVEP Results

Table 2 presents the leaching concentrations of heavy metals Zn, Cu, Cr and Pb from unbounded MSWI-BAA samples with three particle sizes obtained through the HVEP test. For all MSWI-BAA samples, the leaching concentration of Cr was the highest, followed by Cu, Zn and Pb. The leaching concentration of Cr from MSWI-BAA with particle size of 4.75–9.5 mm was the highest, while Pb leaching from MSWI-BAA of the same particle size was the lowest. For each heavy metal, the leaching concentration seemed to be related to MSWI-BAA particle size. Moreover, an MSWI-BAA with a larger particle size was likely to release more Cr and Zn, and an MSWI-BAA with smaller particles was likely to release more Pb. These results suggest that the heavy metal leaching from unbounded MSWI-BAA in the HVEP test is a result of the combined effect of both the leaching metal species and MSWI-BAA particle size.

Table 2. Leaching concentrations of heavy metals from MSWI-BAA by the HVEP test.

Heavy Metal ¹	Leaching Concentration (µg/L)			Limit Value (µg/L)		
	0.075–2.36 mm	2.36–4.75 mm	4.75–9.5 mm	GB/T 14848 (Class III)	GB 3838 (Class II)	GB 5084
Cr	45.64	50.73	106.08	50 (VI) ²	50 (VI) ²	100 (VI) ²
Cu	28.93	20.49	26.88	1000	1000	1000
Zn	4.77	7.04	6.79	1000	1000	2000
Pb	5.35	0.32	0.24	10	10	100

¹ Heavy metal concentration in leachate sample is the total concentration; ² these limit values are intended for Cr(VI).

3.2. Simulated Leaching Experiment Results

3.2.1. Leaching Process of MSWI-BAA

Figures 4 and 5 present the results of the simulated leaching experiment using unbounded MSWI-BAA with three different particles. As demonstrated in Figure 4, overall, the leaching concentrations of heavy metals changed over contact time with varying tendencies. Cr and Cu leaching values showed a fluctuating, increasing trend with contact time, while the others, surprisingly, did not. During the first 10 days, Zn and Pb showed a fluctuating, decreasing trend, and then remained at a relatively low level. In addition, Cr concentration in leachate increased faster than Cu throughout the experiment, and it remained the highest level in the second half of the period. This result indicates that the leaching trend of heavy metal from unbounded MSWI-BAA is mainly dependent on the type of leaching metal rather than the MSWI-BAA particle size.

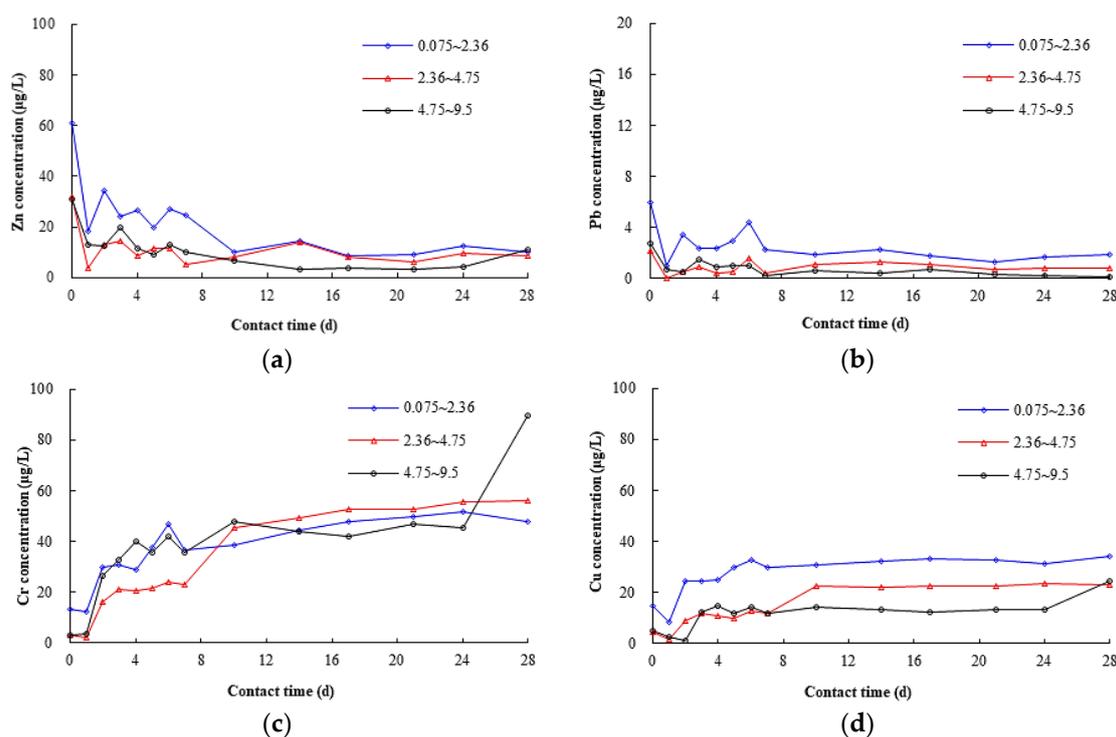


Figure 4. Variation of leaching concentrations of each heavy metal with contact time for MSWI-BAA: (a) Zn; (b) Pb; (c) Cr; and (d) Cu.

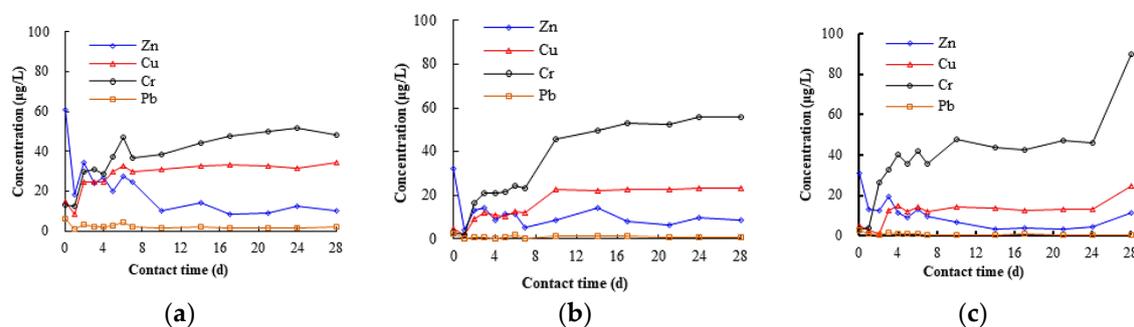


Figure 5. Variation of leaching concentrations of heavy metals with contact time for different MSWI-BAA particle sizes: (a) 0.075–2.36 mm; (b) 2.36–4.75 mm; (c) 4.75–9.5 mm.

Regarding the leaching level of each heavy metal (as shown in Figure 4), the leaching concentration of Pb and Cu from MSWI-BAA with the smallest particle size (0.075–2.36 mm) generally remained at the highest level, followed by the particle size of 2.36–4.75 mm and 4.75–9.5 mm. But Cr showed a different pattern. Cr concentration in leachate from MSWI-BAA with 2.36–4.75 mm remained at the lowest level in the first 10 days, but remained at the highest level during the following 17 days. Moreover, in the experimental period, the highest leaching concentration (90.06 µg/L) was found for Cr from MSWI-BAA with a particle size of 4.75–9.5 mm at the last sampling event, while the lowest leaching concentration (0.17 µg/L) was found for Pb from MSWI-BAA of the same particle size at the last sampling event, which is consistent with the observation in the HVEP test. These results suggest that the overall level of each heavy metal in leachate seems to be affected by MSWI-BAA particle size, with the MSWI-BAs with smaller particles leading to higher levels of leaching of Zn, Pb and Cu.

As shown in Figure 5, for each MSWI-BAA sample, the changes in Zn, Pb, Cr and Cu concentration in leachate over contact time are similar, but the levels are different. In general, the highest level measured in this experiment was Cr, followed by Cu, Zn and Pb. For the MSWI-BAA of 4.75–9.5 mm,

a remarkable increase in leaching concentration was observed for Cr, Cu and Zn at the last sampling event, which means their solid and liquid phase equilibriums may not be attained even after 28 days in the leaching period. The results from the simulated leaching experiment validate the suggestion that the leaching of heavy metals from MSWI-BAA is a very slow process, which is comprehensively influenced by contact time, the type of heavy metal leaching and MSWI-BAA particle size, under experimental conditions. With the increasing contact time, the leaching trend is mainly dependent on the type of leaching metal, while the leaching level is greatly affected by the MSWI-BAA particle size.

3.2.2. Leaching Process of PAC-13 with MSWI-BAA

Figure 6 presents the leaching data of each heavy metal varying with contact time, while Figure 7 shows the leaching data of each PA specimen varying with contact time. Figure 6 shows that the leaching concentrations of Zn, Pb, Cu and Cr change in a similar manner with contact time regardless of whether MSWI-BAA is present. Leaching concentrations of Zn, Pb and Cu were stable within a narrow range between 19.14 and 29.15 $\mu\text{g/L}$. By contrast, the leaching concentration of Cr increased with contact time, and increased faster in the last 7 days. With the exception of some sampling points, Cr and Zn from the control specimen resulted in lower leaching concentrations compared with those specimens containing MSWI-BAA. This might mean that the use of MSWI-BAA in PAC-13 mixtures may lead to increased leaching of Cr and Zn, but these results did not seem to suggest that the use of MSWI-BAA to partially replace a natural aggregate in PAC-13 mixtures can change the basic leaching trend of heavy metals during the experimental period.

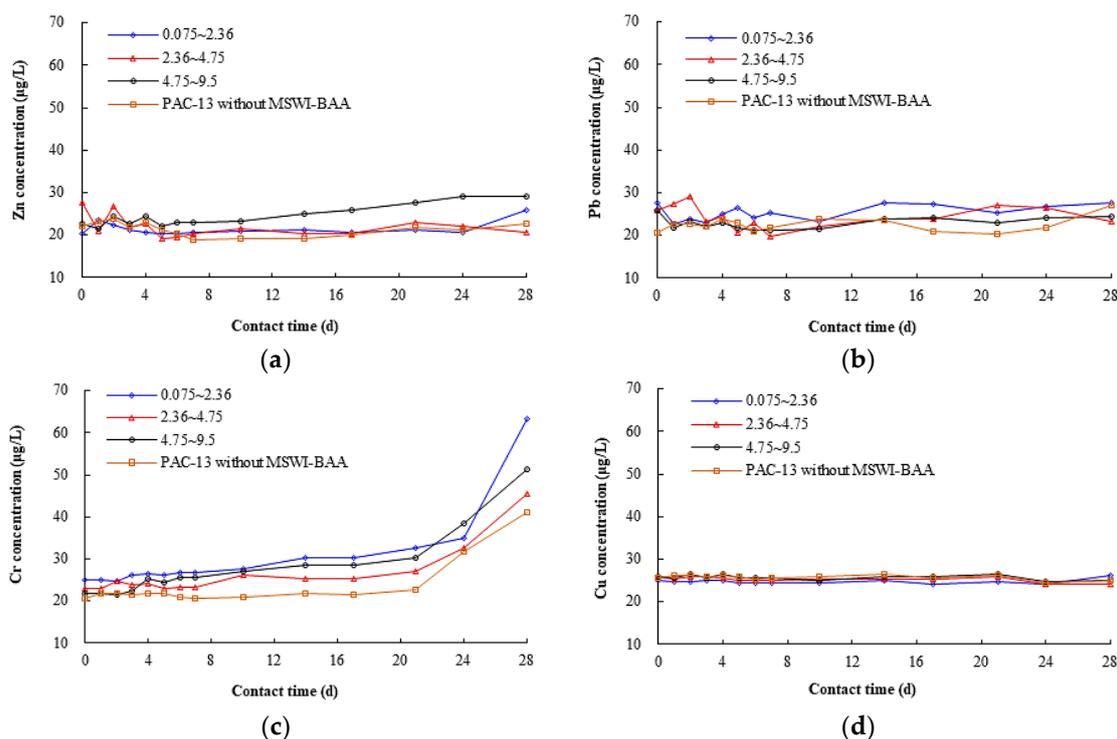


Figure 6. Variation of leaching concentrations of each heavy metal with contact time for PAC-13 specimens with and without MSWI-BAA: (a) Zn; (b) Pb; (c) Cr; and (d) Cu.

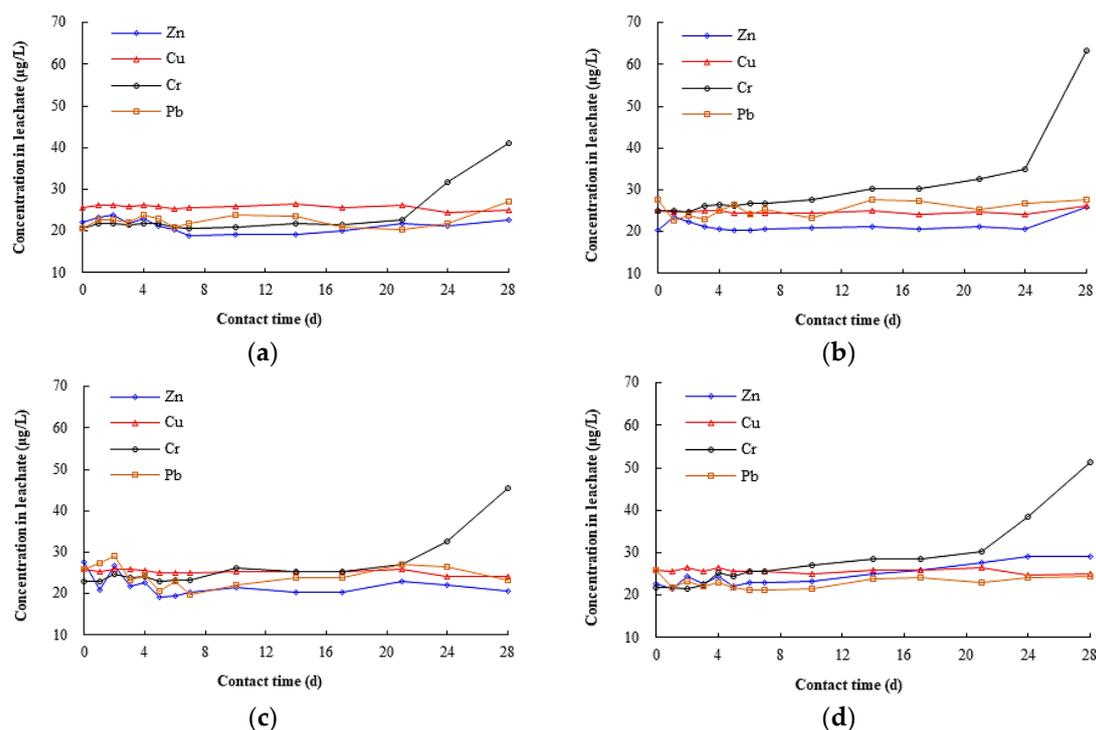


Figure 7. Variation of leaching concentrations of four heavy metals with contact time for PAC-13 specimens with and without MSWI-BAA: (a) PAC-13 without MSWI-BAA; (b) PAC-13 with MSWI-BAA of 0.075–2.36 mm; (c) PAC-13 with MSWI-BAA of 2.36–4.75 mm; and (d) PAC-13 with MSWI-BAA of 4.75–9.5 mm.

For the three PAC-13 specimens containing MSWI-BAA, the leaching trend of each heavy metal was similar, regardless of the MSWI-BAA particle size. In general, the leaching of Cu was the most stable throughout the experiment and the concentration fluctuated in a narrow range between 24.09 and 26.39 $\mu\text{g/L}$. The leaching concentrations of Pb and Zn showed a fluctuation in a relatively wider range. However, the leaching concentration of Cr showed an increasing trend with contact time. These observations indicate that different types of heavy metals produce different leaching trends and leaching levels because some heavy metals are affected by particle size.

Figure 7 shows that for all PAC-13 specimens, the leaching trends of Zn, Cu, Cr and Pb are similar. For the control specimen, Zn, Pb and Cu showed a relatively stable leaching process; however, Cr showed an increase during the last 7 days. Regarding the mean leaching level, Cu was the highest (25.77 $\mu\text{g/L}$), followed by Cr (23.67 $\mu\text{g/L}$), Pb (22.52 $\mu\text{g/L}$) and Zn (21.35 $\mu\text{g/L}$). For PAC-13 containing MSWI-BAA, the order of mean leaching concentrations of these four heavy metals varied with particle size used, but the mean leaching level of Cr was the highest in all cases. These results suggest that the type of heavy metal is an important factor affecting the leaching trends and levels with or without MSWI-BAA. In addition, the particle size of MSWI-BAA used in the PAC mixture seems to have an effect on the leaching level of only some heavy metals.

4. Discussion

4.1. Leaching of Heavy Metals from MSWI-BAA by HVEP Test

Results showed that Pb and Zn leaching values were much lower than those of Cu and Cr in the HVEP test, which indicates that Cr and Cu are easier to extract compared to Pb and Zn. However, Seniunaite et al. [3] reported relatively higher leaching concentrations for Zn and Pb from MSWI-BA by the standard method of EN 12457-2. Thus, although the experimental conditions (e.g., temperature, L/S ratio, leaching time and leachant) were the same in both standard tests, opposite

results were found. This was possibly due to the different heavy metal contents and chemical compositions of the two MSWI-BA samples used.

The HVEP data also showed that the leaching concentration of each heavy metal varied with various MSWI-BAA particle sizes (as shown in Table 2). Two-factor ANOVA was conducted on the leaching data, and the results show a significant difference in leaching concentration among the four heavy metals ($p = 0.011$) and no significant difference in leaching concentration among three MSWI-BAA samples ($p = 0.43$). This result provides evidence for the suggestion that the type of heavy metal is the main factor affecting the heavy metal leaching from MSWI-BAA.

Linear regressions were attempted using the leaching data for each heavy metal. The correlation coefficients between MSWI-BAA particle size and leaching concentrations of Cr, Zn, Pb and Cu are 0.81, 0.66, -0.76 and 0.054, respectively. This means that the leaching of Cr, Zn and Pb are strongly related to MSWI-BAA particle size. For Cr and Zn, the smaller the MSWI-BAA particle size, the higher the leaching concentration will be, while the opposite is true for Pb.

4.2. Leaching of Heavy Metals from MSWI-BAA by Simulated Experiment

As different leaching behaviors were found for heavy metals from unbounded MSWI-BAA in the simulated leaching experiment, the one-factor ANOVA was conducted on the leaching data. Significant differences in leaching concentration were found among MSWI-BAA samples ($p < 0.01$, for the three groups). Combining the results from the HVEP test, it was demonstrated that the leaching trend and leaching level of heavy metals from unbounded MSWI-BAA was affected by the leaching metal species, especially in the long term. This is consistent with Saikia et al. [42] who also pointed out the nature of the host phase is important for heavy metal leachability.

Regarding the leaching process, Zn, Cu and Pb leaching values remained relatively stable in the second half of the experiment; however, Cr kept increasing with contact time, which is really a slow process. Although contact time affects the leaching of heavy metals, the time for attaining the solid and liquid phase equilibrium is related to the metal species leaching. Specifically, the leaching data of Cr showed that equilibrium may not be attained even with 28 days of leaching, given the increasing trend. Haykiri-Acma et al. [43] also reported a similar finding—that the increase in leaching time led to enhanced Cr leaching, but the natural rain water they used had an initial pH value of around 5.5, which is lower than the one used in this study.

The leaching process of these heavy metals is probably due to the dissolution of chemical constituents in MSWI-BA and the microstructure of MSWI-BA in addition to the type of heavy metal. It is reported [42–45] that MSWI-BA has various secondary minerals, such as calcium silicate hydrate gel and ettringite, and can form various surface complexes of hydrous oxides and silicates when it contacts water. These secondary minerals and surface complexes can be easily dissolved in water and incorporate metallic ions through chemical and physical processes, including ion exchange, physical adsorption and chemical adsorption. These physical and chemical processes can be promoted by MSWI-BA particles due to their porous microstructure and irregular shape with rough surface texture [44,45]. However, the heavy metals adsorbed on an MSWI-BA surface can release again when conditions change (e.g., pH value, temperature or contact time). Therefore, the leaching of heavy metals from MSWI-BAA is a slow and complicated process, showing a fluctuation in leaching concentration throughout the experiment. Unfortunately, the influence of the porous microstructure of MSWI-BA on the leaching could not be fully explained here, due to the lack of scanning electron microscopy (SEM) analysis on the MSWI-BAA samples before and after the leaching tests.

Not surprisingly, an obvious difference was found in leaching levels between the HVEP test and simulated leaching experiments for each heavy metal, as shown in Figure 8. For all MSWI-BAA samples, most of the Zn concentrations in the simulated experiment were higher than those in the HVEP test, which is opposite to what was shown for Cr and Cu. However, most of the Pb concentrations in the simulated leaching experiment were between the highest and lowest leaching levels in the HVEP test. Although both tests were conducted under the same experimental conditions (e.g., temperature, L/S

ratio, leachant and initial pH), the objectives were different. The HVEP test was actually an accelerated process to evaluate the maximum toxicity of MSWI-BAA, and the simulated leaching experiment was used for investigating the leaching under realistic conditions. It is said that different types of leaching tests give different results but reflect different aspects of leaching behavior [42]. Thus, both standard and simulated methods are important and necessary for better understanding of leaching behavior of heavy metals from MSWI-BAA.

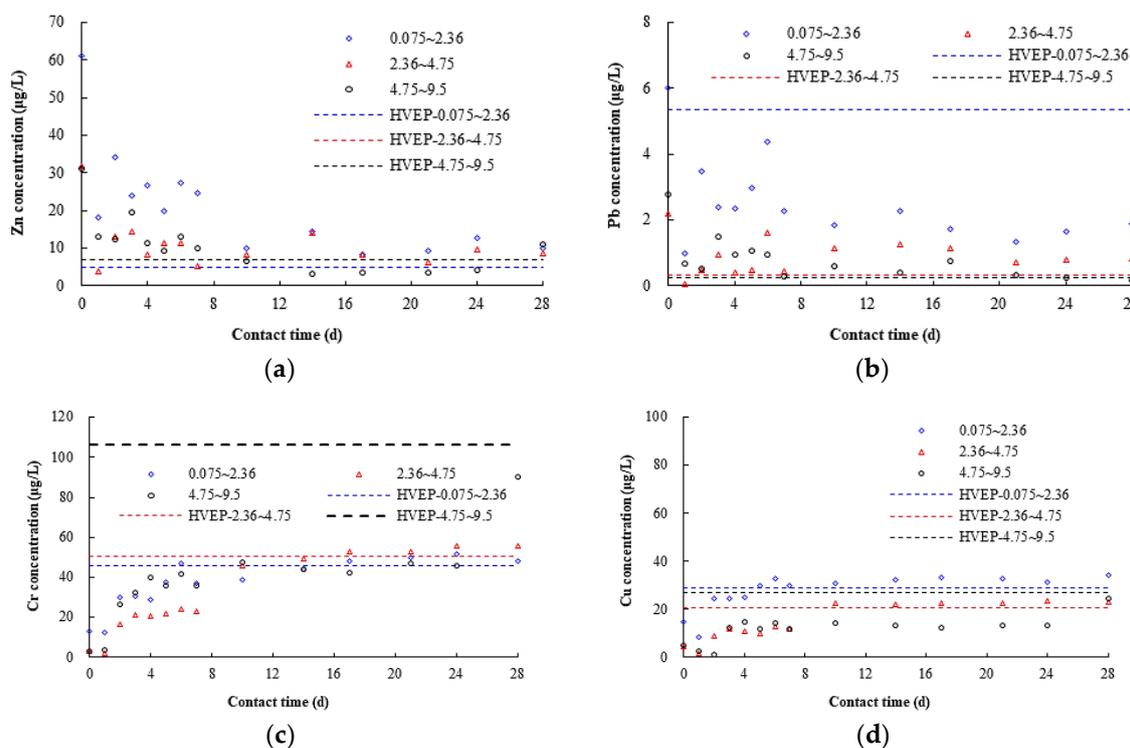


Figure 8. Leaching concentrations of heavy metals from MSWI-BAA by both the HVEP test and simulated leaching experiment: (a) Zn; (b) Pb; (c) Cr and (d) Cu.

4.3. Leaching of Heavy Metals from PAC-13 containing MSWI-BAA

The interesting part of the experiment conducted on the PAC-13 specimens is that the leaching concentrations changed with contact time in some cases, for specimens containing MSWI-BAA. The outcomes were similar to those data from the control specimen (as shown in Figures 6 and 7). This might suggest that the leaching of each heavy metal might be governed by the same process, regardless of whether PAC-13 contains MSWI-BAA or not. Huang et al. [32] reported a similar result but the specimen they used was a conventional, dense asphalt mixture with different percentages of MSWI-BAA (0, 25, 50, 75 and 100%).

For three PAC-13 specimens containing MSWI-BAA, the leaching concentrations of heavy metals were affected by their species because significant differences were identified in leaching concentrations among three PAC-13 specimens with MSWI-BAs of 0.075–2.36 mm ($p = 0.00033$), 2.36–4.75 mm ($p = 0.011$) and 4.75–9.5 mm ($p = 0.022$) in the one-factor ANOVA analysis. Significant differences were also found in leaching concentrations among Zn ($p = 0.0013$), Cu ($p = 0.00016$) and Pb ($p = 0.010$) in terms of their leaching behaviors, indicating that MSWI-BAA particle size plays a role in heavy metal leaching when used as substitute material for a natural aggregate in PA mixtures. Tasneem et al. [34] explained that when MSWI-BAA is combined with a natural aggregate in PA mixtures, the leaching of heavy metals is not only affected by the type of leaching metal and MSWI-BAA particle size, but also affected by the combined effect of the PA mixture and MSWI-BAA.

To further analyze the influence of an asphalt binder on heavy metal leaching, leaching data from both the unbounded MSWI-BAA and PAC-13 mixture containing MSWI-BAA were used to create Figure 9. The leaching values of metals from PAC-13 specimens containing MSWI-BAA showed different patterns from the unbounded MSWI-BAA. Specifically, the leaching concentrations of Zn and Pb from PAC-13 with MSWI-BAA were generally higher than those from unbounded MSWI-BAA, and the leaching process was more stable throughout the experiment. However, the leaching concentrations of Cr from PAC-13 with MSWI-BAA were generally lower than those from unbounded MSWI-BAA, and it showed a more slowly increasing process. Moreover, unlike Zn, Pb and Cr, the leaching of Cu from PAC-13 with MSWI-BAA was stable over time. A similar leaching pattern for Cu and Zn was reported by Tasneem et al. [34] using HMA, but with different contents of MSWI-BAA and for unbounded MSWI-BAA. Huang et al. [32] also reported a similar finding for Cr and Cu, but the leaching time was 10 days, which is shorter. One of the potential reasons for these results is asphalt encapsulation. The asphalt binder in a mixture forms an immobilizing film on the rough surface of MSWI-BAA particles as a surface cover, which can effectively isolate an MSWI-BAA's contact with water, thereby decreasing element mobility [21,42]. The compaction for preparing specimens is also considered an important factor affecting metal leaching [32]. In addition, the leaching might be chemically varied due to pyrolysis and the varied polarity of asphalt [34], which needs further study.

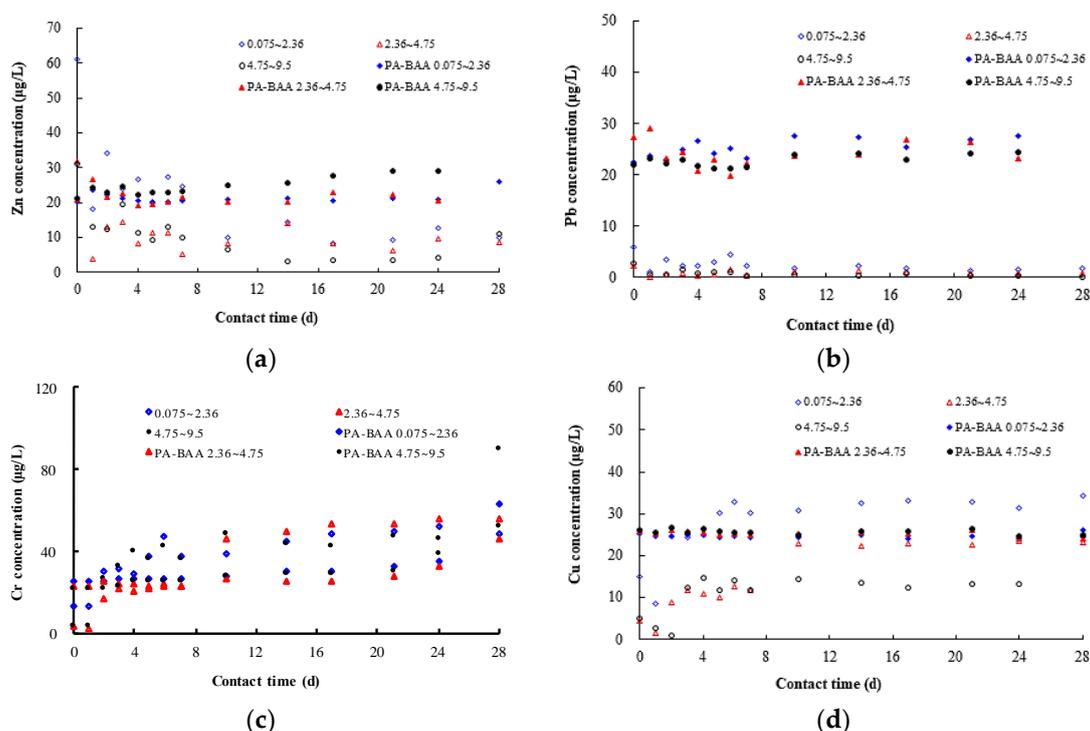


Figure 9. Leaching concentrations of heavy metals from unbounded MSWI-BAs and PAC-13 specimens containing MSWI-BAs: (a) Zn; (b) Pb; (c) Cr and (d) Cu.

4.4. Environmental Risk Evaluation

To assess the direct environmental impact of using MSWI-BAA in a PA mixture on surrounding water and to explore the feasibility of recycling effluent discharging from PA with MSWI-BAA for irrigation purposes, all leaching data were compared to the regulatory limit values in the Chinese standards for surface water (GB 3838-2002) [46], subsurface water (GB/T 14848-2017) [47] and irrigation water (GB 5084-2005) [48].

Table 2 shows the comparison of leaching concentrations from the HVEP test to limit values in the standards. As shown in this table, all the leaching concentrations of Cr, Cu, Zn and Pb match the limit values recommended for Class III subsurface water, Class II surface water and irrigation

water, which means that these leachates can be water sources for drinking, industrial and agricultural purposes, without considering other requirements. In this sense, these four heavy metals in MSWI-BAA do not pose a short-term risk of toxicity to surrounding waters when MSWI-BAA is directly exposed to stormwater for several hours.

Similarly, the leaching concentrations of Cu, Zn and Pb in the simulated experiment were far below the corresponding limit values listed in Table 2. However, Cr concentrations exceeded the limit of 50 µg/L for Class III subsurface water and Class II surface water after 17 days of leaching, which means that these leachates are not suitable for drinking and industrial purposes, but safe for irrigation. Specially, the highest Cr concentration measured at the last sampling event was almost 1.8 times the limit value, and it would be worse over time due to its increasing tendency. These results indicate that, although the leaching of Zn, Pb and Cu from MSWI-BAA over a long period of time has little direct effect on surrounding water quality, the leaching of Cr should be of great concern.

For PAC-13 containing MSWI-BAA, all Zn and Cu concentrations were below the limit values listed in Table 2. All Pb concentrations exceeded the limit of 10 µg/L for Class III subsurface water and Class II surface water, but were below the limit for irrigation water. Cr concentrations were below the limit values for Class III, Class II and irrigation water, except for the last sampling point. These results indicate that these leachates cannot be the water source for drinking and industrial purposes, but they are safe for irrigation. However, similarly to unbounded MSWI-BAA, the leaching of Cr from PAC-13 containing MSWI-BAA should be of great concern. In addition, the leaching of Pb should be given substantial attention due to the extremely high Pb concentration in leachate from PAC-13 with MSWI-BAA.

5. Conclusions

This study investigated and compared leaching behaviors for four heavy metals (Zn, Pb, Cu and Cr) from unbounded MSWI-BAA and PAC-13 mixtures containing MSWI-BAA. The HVEP test and simulated leaching experiments were conducted on MSWI-BAA of three particle sizes (0.075–2.36 mm, 2.36–4.75 mm and 4.75–9.5 mm), but only the simulated leaching experiment was conducted on PAC-13 mixtures with and without MSWI-BAA. Leaching data were also compared to the regulatory limit values to evaluate the toxicity of leachate.

The HVEP data from unbounded MSWI-BAA showed that the type of leaching heavy metal directly affected the leaching. MSWI-BAA particle size was proven to have very good linear relationships with the leaching concentrations of Cr, Zn and Pb, which indicates that the leaching levels of Cr, Zn and Pb are strongly correlated to MSWI-BAA particle size.

Regarding the simulated leaching experiment for unbounded MSWI-BAA, the leaching concentrations of four heavy metals showed different trends over contact time. Increase in leaching time led to regular increases in Cr and Cu and regular decreases in Pb and Zn, indicating that contact time is another factor affecting heavy metal leaching.

For the PAC-13 mixture with MSWI-BAA, in general, the leaching concentration of Cu remained stable over time, Pb and Zn concentrations showed a small fluctuation and Cr showed a continuously increasing trend throughout the experiment. Similar tendencies in leaching concentrations over the contact time were also observed for the control mixture. This indicates that the presence of MSWI-BAA in a PAC-13 mixture does not necessarily change the basic tendency of heavy metal leaching over time, but it is able to lead to an increase in Cr and Zn in leachate overall.

The Cr and Cu concentrations in leachate from PAC-13 containing MSWI-BAA showed an overall decrease compared with unbounded MSWI-BAA, which suggests that the encapsulation of MSWI-BAA particles by asphalt binder is effective for reducing Cr and Cu concentrations in leachates.

All leaching data indicate that the leaching process of heavy metals was comprehensively influenced by contact time, the metal species leaching and MSWI-BAA particle size whether MSWI-BAA is used alone or mixed with a natural aggregate in PAC-13 mixtures. According to the results of environmental risk assessment, both unbounded MSWI-BAA and PAC-13 mixtures containing

MSWI-BAA have very little negative impact on surrounding surface and subsurface water quality, and the leachate is safe for irrigation. But the leaching of Cr and Pb should be monitored and mitigated.

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References

1. Ji, Z.; Pei, Y. Geopolymers produced from drinking water treatment residue and bottom ash for the immobilization of heavy metals. *Chemosphere* **2019**, *225*, 579–587. [CrossRef] [PubMed]
2. Hjelmar, O. Disposal strategies for municipal solid waste incineration residues. *J. Hazard. Mater.* **1996**, *47*, 345–368. [CrossRef]
3. Seniunaite, J.; Vasarevicius, S. Leaching of copper, lead and zinc from municipal solid waste incineration bottom ash. *Energy Procedia* **2017**, *113*, 442–449. [CrossRef]
4. Gao, X.; Yuan, B.; Yu, Q.L.; Brouwers, H.J.H. Characterization and application of municipal solid waste incineration (MSWI) bottom ash and waste granite powder in alkali activated slag. *J. Clean. Prod.* **2017**, *164*, 410–419. [CrossRef]
5. Tang, P.; Florea, M.V.A.; Spiesz, P.; Brouwers, H.J.H. Characteristics and application potential of municipal solid waste incineration (MSWI) bottom ashes from two waste-to-energy plants. *Constr. Build. Mater.* **2015**, *83*, 77–94. [CrossRef]
6. Department for Environment Food and Rural Affairs of UK. Incineration of Municipal Solid Waste. 2013. Available online: https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/221036/pb13889-incineration-municipal-waste.pdf (accessed on 17 July 2019).
7. Brück, F.; Fröhlich, C.; Mansfeldt, T.; Weigand, H. A fast and simple method to monitor carbonation of MSWI bottom ash under static and dynamic conditions. *Waste Manag.* **2018**, *78*, 588–594. [CrossRef]
8. Zekkos, D.; Kabalan, M.; Syal, S.M.; Hambright, M.; Sahadewa, A. Geotechnical characterization of a municipal solid waste incineration ash from a Michigan monofill. *Waste Manag.* **2013**, *33*, 1442–1450. [CrossRef]
9. Margallo, M.; Taddei, M.B.M.; Hernández-Pellón, A.; Aldaco, R.; Irabien, A. Environmental sustainability assessment of the management of municipal solid waste incineration residues: A review of the current situation. *Clean Technol. Environ. Policy* **2015**, *17*, 1333–1353. [CrossRef]
10. National Statistical Bureau of the People's Republic of China. *Chinese Statistical Yearbook-2018*; China Statistics Press: Beijing, China, 2018.
11. National Bureau of Statistics and Ministry of Ecology and Environment of the People's Republic of China. *China's Environmental Statistic Yearbook-2018*; China Statistics Press: Beijing, China, 2019.
12. National Development and Reform Commission and Ministry of Housing and Urban-Rural Development of the People's Republic of China. National Thirteenth Five-Year Plan for the Municipal Solid Waste Harmless Treatment Facilities Development. Available online: <http://www.ndrc.gov.cn/zcfb/zcfbtz/201701/W020170122611891359020.pdf> (accessed on 14 February 2018).
13. An, J.; Golestani, B.; Nam, B.H.; Lee, J.L. Sustainable utilization of MSWI bottom ash as road construction materials, part I: Physical and mechanical evaluation. *Airfield Highw. Pavements* **2015**, *9*, 225–235. [CrossRef]
14. Kim, J.; Tasneem, K.; Nam, B.H. Material characterization of municipal solid waste incinerator (MSWI) ash as road construction material. *Pavement Perform. Monit. Model. Manag.* **2014**, 100–108. [CrossRef]
15. Sorlini, S.; Collivignarelli, M.C.; Abba, A. Leaching behaviour of municipal solid waste incineration bottom ash: From granular material to monolithic concrete. *Waste Manag. Res.* **2017**, *35*, 978–990. [CrossRef]

16. Del Valle-Zermeño, R.; Chimenos, J.M.; Giró-Paloma, J.; Formosa, J. Use of weathered and fresh bottom ash mix layers as a subbase in road construction: Environmental behavior enhancement by means of a retaining barrier. *Chemosphere* **2014**, *117*, 402–409. [[CrossRef](#)] [[PubMed](#)]
17. Silva, R.V.; De Brito, J.; Lynn, C.J.; Dhir, R.K. Environmental impacts of the use of bottom ashes from municipal solid waste incineration: A review. *Resour. Conserv. Recycl.* **2019**, *140*, 23–35. [[CrossRef](#)]
18. Wielgosiński, G.; Wasiak, D.; Zawadzka, A. The use of sequential extraction for assessing environmental risks of waste incineration bottom ash. *Ecol. Chem. Eng. S* **2014**, *21*, 413–423. [[CrossRef](#)]
19. Loginova, E.; Volkov, D.S.; Van De Wouw, P.M.F.; Florea, M.V.A.; Brouwers, H.J.H. Detailed characterization of particle size fraction of municipal solid waste incineration bottom ash. *Clean. Prod.* **2019**, *207*, 866–874. [[CrossRef](#)]
20. Yong, J.Y.; Lee, J.Y.; Kim, J.H. Use of raw-state bottom ash for aggregates in construction materials. *J. Mater. Cycles Waste Manag.* **2019**, *21*, 838. [[CrossRef](#)]
21. Chen, J.; Chu, P.; Chang, J.; Lu, H.; Wu, Z.; Lin, K. Engineering and environmental characterization of municipal solid waste bottom ash as an aggregate substitute utilized for asphalt concrete. *J. Mater. Civ. Eng.* **2008**, *20*, 432–439. [[CrossRef](#)]
22. Hassan, H.F. Recycling of municipal solid waste incinerator ash in hot-mix asphalt concrete. *Constr. Build. Mater.* **2005**, *19*, 91–98. [[CrossRef](#)]
23. Luo, H.; Chen, S.; Lin, D.; Cai, X. Use of incinerator bottom ash in open-graded asphalt concrete. *Constr. Build. Mater.* **2017**, *149*, 497–506. [[CrossRef](#)]
24. He, J.; Valeo, C.; Bouchart, F.J.C. Enhancing urban infrastructure investment planning practice for a changing climate. *Water Sci. Technol.* **2006**, *53*, 13–20. [[CrossRef](#)]
25. Huang, J.; Valeo, C.; He, J. The influence of design parameters on stormwater pollutant removal in permeable pavements. *Water Air Soil Pollut.* **2016**, *227*, 311. [[CrossRef](#)]
26. Valeo, C.; Gupta, R. Determining surface infiltration rate of permeable pavements with digital imaging. *Water* **2018**, *10*, 133. [[CrossRef](#)]
27. Xue, H.; Yang, T.; Liu, X.; Wu, S. Analysis of heavy metal contamination in urban road-deposited sediments in Nanjing, China. *Fresenius Environ. Bull.* **2018**, *27*, 6661–6667.
28. Huang, J.; He, J.; Valeo, C.; Chu, A. Temporal evolution modeling of hydraulic and water quality performance of permeable pavements. *J. Hydrol.* **2016**, *533*, 15–27. [[CrossRef](#)]
29. Zhao, Y.; Zhou, S.Y.; Zhao, C.; Valeo, C. The influence of geotextile type and position in a porous asphalt pavement system on Pb(II) removal from stormwater. *Water* **2018**, *10*, 1205. [[CrossRef](#)]
30. Zhao, Y.; Tong, L.; Zhu, Y. Investigation on the properties and distribution of air voids in porous asphalt within relevant to the Pb(II) removal performance. *Adv. Mater. Sci. Eng.* **2019**, *2019*, 1–13. [[CrossRef](#)]
31. Ma, X.; Li, Q.; Cui, Y.C.; Ni, A.Q. Performance of porous asphalt mixture with various additives. *Int. J. Pavement Eng.* **2018**, *19*, 355–361. [[CrossRef](#)]
32. Huang, C.M.; Chiu, C.T.; Li, K.C.; Yang, W.F. Physical and environmental properties of asphalt mixtures containing incinerator bottom ash. *J. Hazard. Mater.* **2006**, *137*, 1742–1749. [[CrossRef](#)]
33. Toraldo, E.; Saponaro, S. A road pavement full-scale test track containing stabilized bottom ash. *Environ. Technol.* **2015**, *36*, 1114–1122. [[CrossRef](#)]
34. Tasneem, K.M.; Eun, J.; Nam, B.H. Leaching behaviour of municipal solid waste incineration bottom ash mixed with hot-mix asphalt and Portland cement concrete used as road construction materials. *Road Mater. Pavement Des.* **2016**, *6*. [[CrossRef](#)]
35. National Environmental Protection Administration of the People's Republic of China. *Technical Specifications on Sampling and Sample Preparation from Industry Solid Waste HJ/T 20-1998*; China Environmental Science Press: Beijing, China, 1998.
36. National Environmental Protection Administration of the People's Republic of China. *Technical Specification on Identification for Hazardous Waste HJ/T 298-2007*; China Environmental Science Press: Beijing, China, 2007.
37. Ministry of Communications of the People's Republic of China. *Test Methods of Aggregate for Highway Engineering JTG E42-2005*; China Communications Press: Beijing, China, 2005.
38. Ministry of Housing and Urban-Rural Development of the People's Republic of China. *Technical Specification for Permeable Asphalt Pavement CJ/JT 190-2012*; China Architecture and Building Press: Beijing, China, 2012.

39. Ministry of Transport of the People's Republic of China. *Standard Test Method for Bitumen and Bituminous Mixtures for Highway Engineering JTG E20-2011*; China Communication Press: Beijing, China, 2011; China Environmental Science Press: Beijing, China, 2010.
40. Ministry of Environmental Protection of the People's Republic of China. *Solid Waste-Extraction Procedure for Leaching Toxicity-Horizontal Vibration Method NJ 557-2009*; Ministry of Environmental Protection of the People's Republic of China: Beijing, China, 2009.
41. Bendz, D.; Suer, P.; Sloot, H.; Kosson, D.; Flyhammar, P. *Modelling of Leaching and Geochemical Processes in an Aged MSWIBA Subbase Layer*; Värmeforsk Service AB: Stockholm, Sweden, 2009.
42. Saikia, N.; Kato, S.; Kojima, T. Composition and leaching behaviours of combustion residues. *Fuel* **2006**, *85*, 264–272. [[CrossRef](#)]
43. Haykiri-Acma, H.; Yama, S.; Ozbek, N.; Kucukbayrak, S. Mobilization of some trace elements from ashes of Turkish lignites in rain water. *Fuel* **2011**, *90*, 3447–3455. [[CrossRef](#)]
44. Bayuseno, A.P.; Schmahl, W.W. Understanding the chemical and mineralogical properties of the inorganic portion of MSWI bottom ash. *Waste Manag.* **2010**, *30*, 1509–1520. [[CrossRef](#)] [[PubMed](#)]
45. Zhu, Y.; Zhao, Y.; Zhao, C. Experimental study on environmental safety of cement stabilized MSWI-BA macadam base. *Bull. Chin. Ceram. Soc.* **2018**, *37*, 3296–3302.
46. National Environmental Protection Administration, General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China. *Environmental Quality Standards for Surface Water GB 3838-2002*; China Environmental Science Press: Beijing, China, 2002.
47. General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China, Standardization Administration of the People's Republic of China. *Standard for Groundwater Quality GB/T 14848-2017*; China Standard Press: Beijing, China, 2017.
48. General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China, Standardization Administration of the People's Republic of China. *Standards for Irrigation Water Quality GB 5084-2005*; China Standard Press: Beijing, China, 2005.



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