



# Article The Sequential Extraction of Municipal Solid Waste Incineration Bottom Ash: Heavy Metals Mobility and Sustainable Application of Ashes

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Abstract: This manuscript focuses on the sustainable utilization of municipal waste incineration ashes in construction, taking into account their substantial concentration of beneficial elements and the potential environmental pollution caused by the leaching of toxic elements due to naturally occurring processes. To assess heavy metal mobility in ashes, a sequential extraction method based on the European Community Bureau of Reference (BCR) was applied. It enables the determination of heavy metal fractions and provides valuable insights into their potential environmental impact and bioavailability. More than 80% of Cd, and Zn, and over 75% of Cu, exhibited strong associations with the most mobile exchangeable fraction, while over 60% of Al and Fe were predominantly bound to reducible. The distribution of As and Cr was relatively balanced between exchangeable and oxidizable fractions, whereas 100% of Pb was exclusively associated with oxidizable fractions, indicating immobilization of this element in the ash. The calculated Risk Assessment Codes and Individual Contamination Factors indicated a quite high to very high risk level for the element's mobility and environmental contamination. For elements like Pb, Cd, Cu, and Zn, higher concentrations in the samples are associated with higher overall environmental risk. For elements like As and Cr, higher concentrations in the samples are associated with lower overall environmental risk. Studied ash exhibits potential as a resource, but equally it demands rigorous environmental management to ensure responsible utilization. The observed metal mobilization underscores the necessity for stringent containment and treatment measures to mitigate the risk of environmental contamination.

Keywords: BCR sequential extraction; heavy metals mobility; construction materials; MSWI ashes

### 1. Introduction

The generation of waste worldwide is rising due to population growth and economic development. In 2020, 2.24 billion metric tons of solid waste were generated, with 0.79 kg per person per day, and these numbers are expected to increase by 73% in 2050 [1]. Building sustainable and livable cities relies on the proper management of waste. In the European Union countries (EU), the amount of waste generated in 2018 exceeded 2.3 million metric tons, encompassing waste produced by economic activities and households [2]. Waste incineration is one of the increasing waste management options in the EU countries. From 1995 to 2018, there was a substantial increase of 117% in waste incineration, with the volume rising from 32 million tons (67 kg per capita) in 1995 to 70 million tons (136 kg per capita) in 2018 [3]. The primary factor behind this increase has been a reduction in landfill usage, as the European Union no longer recommends landfilling. Additionally, there has been a rise in waste-to-energy (WtE) incineration, a process that involves the combustion of municipal solid waste to generate electricity and/or heat that contributes to European climate mitigation and supports a circular economy. This entails moving away from a disposable mindset towards a sustainable economy that operates on a circular model, involving recycling, reusing, remaking, and sharing resources instead of the traditional



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). linear approach of extraction, production, and disposal. Essentially, the circular economy seeks to transform waste management in Europe by considering it a valuable resource rather than mere waste to dispose of. Within the context of a circular economy, the emphasis of waste management lies in safeguarding the value and characteristics of waste materials through the provision of premium-grade secondary raw materials to the economy.

Nevertheless, the utilization of various forms of waste-based resources resulting from incineration can potentially pose environmental risks. This is due to the reduction in waste volume and mass during the incineration process [4], which can lead to a relative concentration increase of heavy metals and toxic elements such as Arsenic (As), Cadmium (Cd), Cobalt (Co), Copper (Cu), Chromium (Cr), Mercury (Hg), Nickel (Ni), Lead (Pb), and Zinc (Zn). Understanding the concentration of heavy metals in incineration residues, specifically bottom ash (BA), fly ash (FA), and air pollution control (APC) residues, is of utmost importance. For this study, the focus will be solely on BA, which constitutes 90 wt% of the solid residues generated during the municipal waste incineration process. Hence, in this study, BA will be referred to as municipal solid waste incineration (MSWI) ashes. Considering the environmental implications and the objective of retaining MSWI ashes within the production cycle for an extended period, this study aimed to evaluate the mobility of heavy metals using the Community Bureau of Reference (BCR) standardized 3-step sequential extraction method [5].

The primary purpose behind the development of sequential extraction procedures was to provide valuable insights into the mobility and accessibility of elements in sediments [6]. Nevertheless, these procedures have found application in various other materials, including contaminated soils, incinerated sludge ash, municipal solid waste, and ash from municipal solid wastes [7].

The European Community Bureau of Reference (BCR) method aims to minimize errors in sample treatment and analysis, identify the most suitable analytical procedure, and provide reference materials for inter-laboratory result comparisons and demonstrated greater operational effectiveness compared to previously proposed methods as suggested by Fernández et al. [8]. Utilizing uncomplicated substrates effectively mitigated the issue of metal redistribution within the substrate components [9].

By calculating and comparing the Risk Assessment Code (RAC) and Individual Contamination Factor (ICF), this study aimed to assess the environmental risks associated with various heavy metals present in MSWI ashes. Additionally, by comparing the results obtained using the BCR procedure with established permissible concentration limits in water and soils, the feasibility of utilizing MSWI ashes as road construction material under globally accepted norms (such as WHO and EU standards) was assessed. This assessment plays a crucial role in determining the potential environmental implications of utilizing MSWI ashes in road construction while striving to achieve economic circularity and sustainable resource utilization. Due to the substantial demand for construction materials, with global aggregate demand estimated to surpass 50 billion metric tons annually by 2019 [10], coupled with the finite availability of natural resources and challenges associated with landfilling [11], there is a growing need, both from a practical and legal standpoint, to ensure the comprehensive utilization of secondary materials in a sustainable manner.

#### 2. Materials and Methods

#### 2.1. Characterization of the Incineration Facility and Samples

In this study, samples of Municipal Solid Waste Incineration Bottom Ash (MSWI BA) were obtained from a municipal waste incineration facility situated in southern Poland that operates in a city with approximately 1 million inhabitants. The incineration process is conducted within a grate furnace. This process unfolds in several distinct zones. The initial heating zone is where the waste undergoes heating through radiation or convection until it reaches a temperature just above 100 °C. This initial stage prompts the evaporation of moisture present in the waste. The temperature is further increased to surpass 250 °C, causing volatile components such as moisture and gases to be released from the waste in

the volatile release zone. In the third zone of the grate, complete waste incineration takes place. The loss on ignition in this zone is minimal, accounting for less than 0.5% of the total mass. Volatile products generated earlier are subjected to oxidation by molecular oxygen. This oxidation primarily occurs in the upper section of the incineration chamber, with temperatures reaching 1000 °C. To minimize the presence of unburned CO in the exhaust gas, a secondary air supply is introduced in the post-combustion zone, facilitating complete combustion. The flue gas remains within this zone for approximately 2 s, with a minimum temperature of 850 °C. This controlled process ensures the effective thermal treatment of municipal waste, optimizing energy recovery and minimizing environmental impacts. The facility is able to incinerate 220 thousand metric tons annually. The residues formed during the thermal waste transformation process make up approximately 25% in relation to the input stream [12].

For the purpose of this study, an averaged 100 kg of the MSWI BA was collected from the bottom ash pile. Before the collection of MSWI ashes, they were subjected to valorization which refers to the process of extracting valuable or useful materials from the ash generated during the incineration process including ferrous and non-ferrous metals recovery. MSWI ashes were grayish in color, porous with medium density, and relatively light (Figure 1). Before sequential extraction, the ash was ground and milled to a fine fraction.



Figure 1. The MSWI BA sample.

#### 2.2. Description of the Methods

To analyze the chemical composition of the raw bottom ash (BA), Bureau Veritas Minerals in Vancouver, Canada conducted inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES). Specifically, LF2000 and AQ200 analyses were utilized, facilitating the determination of major and trace element concentrations in the raw MSWI ash.

Prior to analysis, samples were prepared by averaging, followed by the separation of unburned materials such as large particles of glass, porcelain, metal, and fibers. Subsequently, 20 g of BA was ground into a powder fraction using an agate mill and transferred to the laboratory.

The ICP process employed in this study utilizes fusion techniques to achieve complete decomposition of even the most refractory matrices, ensuring the determination of total element concentrations. The analytical procedure consists of two main steps:

 Sample fusion: In this step, samples are subjected to fusion using a mixture of lithium borate/tetraborate. This fusion process effectively breaks down the sample matrix, allowing for the release of all elements of interest; (b) Digestion with nitric acid: Following the fusion step, the resulting material is digested with nitric acid. This acid digestion further ensures the solubilization of elements, making them amenable to analysis.

The loss on ignition (LOI) was determined by measuring the difference in sample weight before and after ignition at a high temperature of 1000 °C. This process quantifies the loss of volatile components and provides information about the sample's composition and properties.

Furthermore, the concentrations of selected elements (Al, As, Cd, Cr, Cu, Fe, Pb, and Zn) in the leachates obtained after the BCR sequential extraction procedure were measured at the Faculty of Chemistry, Jagiellonian University, using the ICP-MS method. Each leachate (100 mL) was analyzed immediately after extraction without further acidification, as the samples were promptly transported to the laboratory following the extraction procedure. The volume of leachates used for analysis exceeded the required amount to ensure the repeatability of the analyses. Multiple aliquots of the original sample (leachate) were independently subjected to ICP-MS analysis, resulting in multiple replicate measurements for each analyzed element. These replicate measurements were subsequently subjected to statistical analysis to assess both precision and accuracy. The statistical analysis included calculating the average concentration for each analyzed element, along with the corresponding standard deviation, thereby providing a comprehensive evaluation of measurement quality and reliability. The composition of the chemicals used in each extraction step was also analyzed. This information was crucial for background correction, interference assessment, method validation, accounting for matrix effects, and ensuring traceability. All of these factors contribute to the accuracy and reliability of the results obtained through ICP analysis. The selected elements are considered toxic and additionally are known to be strategic for the EU economy, therefore the information on the potential chemical bonds of these elements and the information on their mobility is important from the environmental but also economic point of view.

#### 2.3. The BCR Sequential Extraction

The BCR sequential extraction scheme, originally designed for soils and sediments, is commonly applied to assess the environmental implications of bottom ash from municipal solid waste incineration (MSWI).

In this study three fractions (F) were separated by different chemical reagents in the following stages (as shown in Figure 2):



Figure 2. The Overview of the sequential extraction based on the BCR procedure.

F1: a 16 h extraction with 0.11 M acetic acid (HAc) to remove soluble species, cation exchange sites, and carbonates—acid soluble fraction.

A mixture of 80 mL of acetic acid (0.11 mol/L) and 2 g of ash was prepared before being shaken in an orbital shaker for 16 h. The mixture was further filtered to separate the extract and residue using a pressure filtration kit (Glassco) and a vacuum pump (2.5 atm) through a polycarbonate membrane filter (Whatman) with a mesh size of 0.45  $\mu$ m. In the next stage, the residue was washed in 20 mL of deionized water. The extract was stored in a polypropylene container at 4 °C for further analysis.

F2: a 16 h extraction with 0.1 M hydroxylamine hydrochloride acidified using nitric acid to pH = 2 (NH<sub>2</sub>OH-HCl) to remove elements bound with Fe–Mn oxides fraction.

The residue of the first extraction step was added to 80 mL of 0.1 mol/L acidified hydroxylamine hydrochloride using nitric acid to pH = 2. After being shaken in the orbital shaker for 16 h, the separation of the residue from the second step and the extract was similar to the first extraction using a polycarbonate membrane filter and a filtration apparatus. The residue was washed in 20 mL of deionized water and the extract was stored in a polypropylene container at 4 °C for further analysis.

F3: an extraction with 30% H<sub>2</sub>O<sub>2</sub> and HNO<sub>3</sub> to extract elements from compounds soluble in organic matter and sulfides fraction.

20 mL of 30% hydrogen peroxide was added to the residue of the second extraction in a beaker covered with a watch glass. After 1 h of digestion at room temperature, the residue was further digested for 1 h in a water bath without cover, resulting in a reduction in the volume of the solution as a result of evaporation. Next, 20 mL of hydrogen peroxide was added again to the solution and digested for 1 h in a steam bath. To cool the moist residue, 50 mL of 1 mol/L ammonium acetate was added to the solution before mixing it in the orbital shaker for 16 h. In the final step, the extract and the solution were separated as in the previous two steps, using the above mentioned procedure.

It is important to mention that one of its key objectives is to dissolve "elements bound with the carbonate fraction," requiring the pH to be around 4 after the F1 extraction step. In the case of soil, the prescribed recipe, as outlined in reference [5], entails using 1 g of the sample with 40 milliliters of acetic acid (HAc). This recipe is suitable due to the generally lower alkalinity of soil samples. In such circumstances, a smaller amount of acid is sufficient to attain the desired pH level. Therefore, based on a 40 mL solution of 0.11 mol/L HAc, the calculated amount of Ca is  $4.4 \times 10^{-3}$  moles. However, when dealing with incineration bottom ash, we must consider the substantial differences in alkalinity compared to soil samples. In our calculations, based on the data presented in Figure 3 of our study, we observed that BA contains approximately 10% calcium (Ca). Assuming all of this calcium is in the form of CaO, it amounts to roughly  $2.5 \times 10^{-3}$  moles of CaO per 1 g of IBA, which translates to  $5 \times 10^{-3}$  moles of alkalinity (equivalent to  $2 \times$  OH- ions per Ca atom). This inherent alkalinity significantly influences the pH conditions experienced during the extraction process. As evident from our results, extraction F1 indeed resulted in an acidic pH for the BA sample. This observation aligns with known behavior where heavy metal mobility is influenced by variations in pH. Typically, research studies focus on pH ranges from 12.5 down to 9 or 10, with notable emphasis on the increased mobility of metals under acidic conditions.



Figure 3. The main chemical composition of the MSWI raw sample.

## 3. Results and Discussion

MSWI BA predominantly comprises particles with sizes ranging from 2 to 25 mm and is notable for retaining a substantial portion of waste components in nearly unaltered states. On average, the samples contained 60% of typical BA material by weight, with the remaining portion primarily composed of fragments from glass products, ceramics, and a small percentage of metal products, i.e., nails, can lids, and wires. The raw MSWI ash was Si-dominated material with high concentrations of Ca and lower content of Al, Fe, Mg, and K (Figure 3). Over 69% of the sum of SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, and Al<sub>2</sub>O<sub>3</sub> may indicate pozzolan properties of this material which can make it considered as a substitute for cement in construction and therefore fulfill the requirements for a circular economy. Additionally, SO<sub>3</sub> content  $\leq$  4.0%, and LOI content  $\leq$  10% are the indicators of pozzolan materials as suggested by [13]. In the studied sample the S<sub>tot</sub> was 0.52% and LOI 3.9%.

Earlier investigations, e.g., ref. [14] hinted at the potential of bottom ash to display pozzolanic characteristics in cement-based systems, thereby proposing potential applications of municipal solid waste incineration (MSWI) bottom ash in blended cement formulations. However, the pozzolanic properties of bottom ash itself proved to be significantly limited resulting in lower mechanical strength compared to Portland cement [15]. On the other hand, the utilization of calcium chloride during 40 °C-curing demonstrated the enhancement of pozzolanic characteristics in bottom ash [16].

The optimal approach entails maximizing the utilization of MSWI ash by incorporating it as a cement additive, thereby promoting sustainable waste management practices and safeguarding the availability of natural building resources. This strategy aligns with the principles of sustainable development and contributes to achieving the set goals. Nevertheless, we must keep in mind that MSWI ashes also contain heavy metals and potentially toxic elements that can be released into the environment if not treated properly by, for example, leaching from the constructions as a result of naturally occurring processes such as natural weathering or precipitation which can lead to partial dissolution of these materials. A total of six potentially toxic metals: As, Cd, Cr, Cu, Pb, and Zn, and common metals: Al and Fe, that might indicate the dissolution of MSWI ashes, were analyzed. The concentration of these elements in the raw sample is shown in Figure 4. The concentration of As and Cd hardly exceeded a few mg kg<sup>-1</sup> (3.0 and 2.2 respectively) whereas the concentration of Cr was 266.76 mg kg<sup>-1</sup> and Pb was 893.3 mg kg<sup>-1</sup>. The content of Cu was 1967.9 mg kg<sup>-1</sup> and the content of Zn was 2373 mg kg<sup>-1</sup>.



Figure 4. The concentration of the potentially toxic elements in the raw material.

Figure 5 illustrates the distribution of select elements within different fractions obtained through the sequential extraction procedure. Each bar represents the percentage of a selected element (e.g., Al, As, Cd, Cr, Cu, Fe, Zn, and Pb) associated with a particular fraction (e.g., F1—green, F2—blue, F3—yellow) based on the sequential extraction results. Additionally, Table 1 shows the concentration of selected elements in specific fractions The fractions are defined as follows:



Figure 5. Cont.



**Figure 5.** Distribution of elements in fractionations (F1—exchangeable fraction; F2—reducible fraction; F3—oxidizable fraction); Relative%—the proportion of each fraction to the total concentration.

**Table 1.** The concentration of selected elements in specific fractions; >DL—below detection limits of the methods applied for this study.

	Al	As	Cd	Cr	Cu	Fe	Pb	Zn
	$[\mu g \ L^{-1}]$	$[\mu g \ L^{-1}]$	$[\mu g L^{-1}]$	$[\mu g L^{-1}]$	$[\mu g L^{-1}]$	$[\mu g L^{-1}]$	$[\mu g L^{-1}]$	$[\mu g L^{-1}]$
F1	23,576.5	5.9	52.3	165.9	17,957.0	25,102.7	<dl< td=""><td>75,913.0</td></dl<>	75,913.0
F2	37,492.7	<dl< td=""><td>5.7</td><td>32.8</td><td>2751.9</td><td>43,891.1</td><td><dl< td=""><td>3803.8</td></dl<></td></dl<>	5.7	32.8	2751.9	43,891.1	<dl< td=""><td>3803.8</td></dl<>	3803.8
F3	425.5	4.8	0.8	165.2	2427.3	193.6	54.4	271.6

F1 (Exchangeable fraction): Represents the most mobile and bioavailable form of elements bound-to-easily-soluble under acidic conditions;

F2 (Reducible fraction): Shows elements associated with Fe–Mn oxides, which are less mobile but can be released under reducing conditions;

F3 (Oxidizable): Signifies elements associated with organic matter and sulfides, potentially released under oxidizing conditions. Represents the least mobile and least bioavailable form of elements, tightly bound within mineral matrices.

Understanding the distribution of elements in these fractions is critical for assessing their mobility and potential environmental impact. The data presented here informs discussions regarding the suitability of MSWI BA for various applications and its environmental implications.

Investigations into MSWI ash composition indeed revealed a Si-dominated material with the potential for pozzolanic properties, suggesting its suitability as a cement substitute in construction, in alignment with circular economy principles. These inherent properties are valuable for considering sustainable resource utilization. However, our research also sheds light on a crucial aspect that requires careful consideration. The detection of elevated levels of hazardous metals, including As, Cd, Cr, Cu, Pb, and Zn, in the ash residues raises significant environmental concerns. It is imperative to emphasize that these hazardous elements have the potential to mobilize, posing environmental risks if not appropriately managed.

Of particular concern is the post-extraction metal mobilization. Our procedure results indicated that over 70% of the pseudo-total concentrations of Cd, Cu, and Zn were associated with fraction F1, recognized as the most mobile and bioavailable fraction (Figure 5). This mobility is of concern, as these elements can potentially contribute to water and soil contamination.

The presence of zinc (Zn) primarily in F1 in the sequential extraction procedure can be attributed to the characteristics of this fraction and the chemical speciation of Zn in the sample. Zn is known to form relatively soluble compounds under mildly acidic conditions. In F1, the extraction solution typically contains acetic acid (pH 2.5), which is capable of dissolving Zn compounds that are not strongly bound to the solid matrix. In many environmental samples, Zn can be present in forms that are weakly adsorbed or bound to the surface of particles. These weak associations can make Zn more susceptible to extraction in the F1. Zn may also exist in the sample in mobile forms, such as Zn ions or soluble Zn compounds. These forms are easily extracted by the acidic solution used in F1. The fact that Zn is found in F1 suggests that it is present in a labile form that could potentially be released into the environment if the sample were subjected to conditions similar to those of the extraction procedure. The other fractions in the procedure represent progressively more tightly bound forms of metals, with F3 (oxidizable fraction) representing the most stable, immobile forms [17–19].

Cadmium, in particular, is well-known for its high toxicity in the environment [20], attributed to its ability to substitute calcium in mineral structures, facilitated by its similar ionic radius, chemical behavior, and charge [21].

Furthermore, the mobility of metals is closely linked to their chemical forms within the ash matrix. Copper (Cu) and zinc (Zn) ions found in soluble minerals or adsorbed onto particle surfaces are more susceptible to leaching compared to Cu and Zn which are tightly bound within poorly soluble mineral matrices or metallic forms. Additionally, the immobilization or release of metal ions is influenced by various ash characteristics, with pH playing a significant role. Typically, higher pH levels correlate with lower metal concentrations in leachates [22].

In light of these findings, the results underscore the multifaceted nature of MSWI ash, highlighting the critical need for a balanced approach. While it exhibits potential as a resource, it equally demands rigorous environmental management to ensure responsible utilization. The observed metal mobilization, especially for Cd, Cu, and Zn, underscores the necessity for stringent containment and treatment measures to mitigate the risk of environmental contamination.

The pH-dependent mobility of heavy metals in MSWI bottom ash has significant implications for its use and environmental impact. Under acidic conditions, heavy metals in the ash become more mobile [23], posing a risk of leaching into the environment and causing soil and water contamination [24]. This highlights the importance of proper management of MSWI bottom ash to prevent environmental harm. Conversely, understanding this pH-dependent behavior can guide strategies for its use. For applications where heavy metal leaching is a concern, maintaining an alkaline pH environment may be necessary to minimize metal mobilization. Therefore, the development of treatment or stabilization methods to control pH becomes crucial. Recognizing the pH-dependent mobility of heavy metals in MSWI bottom ash is essential for both safe utilization and environmental protection. Although copper and zinc have lower concentrations in MSWI bottom ashes compared to aluminum and iron, their considerable economic value justifies their possible recovery.

The As and Cr were almost equally distributed between F1 and F3 (Figure 5). According to Huang et al. [25], there were high proportions of As observed in F1 (40%) and F3 (around 20%). The study suggested that As is unlikely to occur as carbonate but is more likely present as soluble arsenates at a pH of 7.5, such as Zn, Cr, or Cu arsenates.

The results indicated that only Pb was bonded to the least mobile fraction F3 (Figure 5). For the F1 and F2 fractions, the obtained results were below the detection limits of the method used. Under oxidizing conditions, some metals appear to be predominantly extracted [7]. Previous studies have indicated that organic matter can undergo degradation in such conditions, leading to the binding of Pb to organic ligands through complexation. This phenomenon may occur as a result of incomplete waste combustion or subsequent biodegradation processes [21]. In our case, we may assume that due to low LOI, Pb is not

immobilized in the fraction bond with organic matter. Rather, it can be associated with sulfides that can oxidize under certain conditions, releasing metal ions, including Pb, into solution. However, this association might result in Pb being found in both the oxidizable and reducible fractions. We can assume also that in the F3 fraction, Pb may be associated with highly refractory minerals, such as aluminosilicates or refractory oxides. These minerals are extremely stable and do not readily release Pb under typical environmental conditions. Pb may be chemically bound within the mineral matrix of the waste material itself or within a glassy phase and thus will not easily be leached out even if MSWI BA will be used in construction bends.

To evaluate metal pollution from the studied MSWI BA a risk assessment code (RAC) [26,27] was applied. RAC is a classification system that assesses the potential risk associated with the concentrations of specific elements (in this case, Pb, Cd, Cu, and Zn) in a given environmental context. The RAC utilizes the percentage of metal found in a fraction bound to the most mobile fraction (F1) as a basis for assessing risk.

The RAC is expressed as the percentage of acid-soluble fraction metal (F1) in total metal content (HM) [28]:

### $RAC = F1/HM \times 100\%$

It categorizes the risk into different levels, typically ranging from low to high. Higher RAC values indicate a greater potential risk to both the environment and human health. The classification of RAC includes:

- 1. Safe level (less than 1%);
- Low-risk level (1–10%);
- 3. Medium-risk level (10–30%);
- 4. High-risk level (30–50%);
- 5. Very high-risk level (over 50%) [28].

A higher RAC value suggests that the concentrations of these elements exceed certain thresholds or regulatory limits, which could potentially lead to environmental contamination and adverse effects on human health. It signifies a need for closer scrutiny and potential remediation measures to mitigate the risks. Thus, the RAC serves as a valuable tool in environmental risk assessment, allowing researchers and decision-makers to prioritize and evaluate the risks linked to diverse environmental hazards and their potential impacts on ecosystems and human health. This enables them to assess the significance of potential environmental issues and allocate resources effectively for implementing risk management and mitigation strategies.

Table 2 shows the RAC results which indicate the relative risk of each element's acidsoluble fraction (F1) in comparison to the total concentration of that element in the sample. Lower RAC values suggest lower potential environmental risks, while higher RAC values may indicate greater potential risks. In most cases, the RAC values are relatively low, indicating a low to very low environmental risk associated with these elements in their acid-soluble fractions.

Element	RAC 1 Safe Level (Less Than 1%)	RAC 2 Low-Risk Level (1–10%)	RAC 3 Medium-Risk Level (10–30%)	RAC 4 High-Risk Level (30–50%)	RAC 5 Very High-Risk Level (Over 50%)
As	0.197				
Cd		2.377			
Cr	0.062				
Cu	0.913				
Pb	0				
Zn		3.201			

Table 2. The RAC in the MSWI BA leachates.

In addition, an Individual Contamination Factor (ICF) was calculated. The ICF assesses the extent of metal contamination in environmental samples (e.g., soils or sediments) by comparing the measured metal concentrations with a reference or background value. It categorizes the contamination level into classes, ranging from uncontaminated to extremely contaminated. Higher ICF values indicate a greater degree of contamination.

A higher ICF value signifies a greater proportion of elements in the stable fraction (F3) relative to the easy mobilization fraction (F1 + F2), indicating a lower contamination status. The ICF is calculated using the following equation [29]:

$$ICF = F3/(F1 + F2),$$

where the sum of the F1 and F2 fractions was divided by the concentration of the F3 fraction. The ICF is used to assess the degree of contamination of a particular element in a specific sample, therefore helping to assess the risk for the environment. If the ICF  $\leq$  1 it shows low contamination. If the ICF is between 1 and 3, the contamination level is moderate. Considerable contamination is when the ICF is between 3 and 6 and very high contamination occurs when the ICF is higher than 6 [30].

As shown in Table 3, the ICF shows a very high contamination probability for Cd, Cu, and Zn. Moderate contamination risk was calculated for As and Cr and only Pb exhibited a low contamination probability.

Table 3. The ICF in the MSWI BA leachates.

Element	$ICF \leq 1$ Low Contamination	$1 \ge ICF \le 3$ Moderate Contamination	$\label{eq:ICF} 3 \geq ICF \leq 6$ Considerable Contamination	$\label{eq:ICF} \begin{split} ICF \geq 6 \\ Very \ High \ Contamination \end{split}$
As		2.2		
Cd				72.6
Cr		2.2		
Cu				9.5
Pb	1			
Zn				>200

The relationship between the RAC and the ICF for specific elements (Pb, Cd, Cu, and Zn) shows a positive correlation, indicating that higher contamination levels of these elements in the samples lead to increased overall risk. In simple terms, when the concentrations of Pb, Cd, Cu, and Zn are higher (resulting in higher ICF values), they pose a greater potential risk to both the environment and human health, resulting in higher RAC values. The ICF and RAC values for these elements highlights the need for careful monitoring and effective risk management strategies to mitigate their impact on the environment. Elevated concentrations of these heavy metals may lead to ecological disruptions, soil and water contamination, and adverse health effects.

Conversely, there is a negative correlation observed for As and Cr. When the concentrations of As and Cr are higher, leading to higher ICF values, they do not necessarily pose a significant risk or have a reduced potential for adverse impacts on the environment and health, resulting in lower RAC values. Nevertheless, it is important to note that the statement is addressing the relative risk levels based on the ICF and RAC values. It suggests that even though As and Cr are toxic elements, their elevated concentrations in the samples, when assessed in the context of ICF and RAC values, do not proportionally increase the perceived risk. This is because ICF and RAC values are relative indices and not absolute measures of risk. They take into account the background or reference values and the sample concentrations, leading to an assessment of the degree of contamination and potential risk. However, while their concentrations may not present an immediate high risk, continuous monitoring and further research are essential to ensure that long-term exposure to these elements does not lead to subtle or cumulative impacts on the environment and human health over time.

Furthermore, there is potential for the utilization of MSWI BA in various applications such as cement production, road construction, and brick manufacturing [31]. However, the use of MSWI BA in these applications may be constrained due to the presence of minor components that have negative environmental impacts or affect the properties of the final products. Therefore, it is important to control the concentrations of elements that may negatively influence the environment. To do this, the results of the chemical composition of the raw samples as well as the results of the extraction procedure were compared with the existing norms for permissible limits of heavy metals in soil [32] and water [33] as shown in Tables 4 and 5, respectively. The concentrations of Cr, Cu, Pb, and Zn significantly exceeds the EU standard for soil, whereas only Cd is below this threshold [32].

**Table 4.** Comparison of the heavy metal content in the raw samples with permissible limits of heavy metals and toxic elements in soil [32].

Element	EU Standard for Soil [mg kg <sup>-1</sup> ]	Concentration in the Raw Samples $[mg kg^{-1}]$
Cd	3	2.2
Cr	150	266.76
Cu	140	1967.9
Pb	300	893.3
Zn	300	2373

**Table 5.** Comparison of the heavy metal content in the leaches with permissible limits of heavy metals and toxic elements in water [33]; F1, F2, F3—concentration of each element in specific fractions obtained using sequential extraction procedure.

Element	EU Standard for Water $[mg L^{-1}]$	Concentration in the Leachate $[mg L^{-1}]$		
		F1	F2	F3
Cd	0.01	0.0523	0.0057	0.0008
Cr	0.05	0.1659	0.0328	0.1652
Cu	0.05	17.957	2.7519	2.4273
Fe	0.03	25.1027	43.8911	0.1936
Pb	0.1	0	0	0.0544
Zn	5	75.913	3.8038	0.2716
As	0.05	0.0059	0	0.0048
Mn	0.1	-	-	-
- No data.				

The concentrations of cadmium (Cd) in F2 (0.0057 mg L<sup>-1</sup>) and F3 (0.0008 mg L<sup>-1</sup>) are below the EU standard for water (0.01 mg L<sup>-1</sup>), indicating that they meet the permissible limit for cadmium in water. However, the concentration of cadmium in F1 (mg L<sup>-1</sup>) is slightly higher than the EU standard [33]. The concentrations of chromium (Cr) in F2 (0.0328 mg L<sup>-1</sup>) are below the EU standard for water (0.05 mg L<sup>-1</sup>), indicating that it meets the permissible limit for chromium in water. However, the concentrations of chromium in F1 (0.1659 mg L<sup>-1</sup>) and F3 (0.1652 mg L<sup>-1</sup>) are slightly above the EU standard [33]. The concentrations of copper (Cu) in all three leachates (F1, F2, and F3) are significantly above the EU standard for water [33]. The concentration of iron in all three leachates is significantly above the EU standard for water, indicating that the leachates exceed the permissible limit for Fe in water. The concentration of Pb in F1 and F2 is below the detection limit of the used method and thus meets the permissible limit for lead in water. F3 has a concentration of Pb exceeding the EU standard for water. The concentration of Zn in F1 (75.913 mg  $L^{-1}$ ) is significantly above the EU standard for water (5 mg  $L^{-1}$ ), indicating that it greatly exceeds the permissible limit for zinc in water. F2 has a concentration (3.8038 mg  $L^{-1}$ ) above the standard but is considerably lower than F1. F3 has the lowest concentration  $(0.2716 \text{ mg L}^{-1})$  and is well below the EU standard for water. The concentration of As in all three leachates is below the EU standard for water, indicating that the leachates meet the permissible limit for arsenic in water. The data for Mn in the leachates (F1, F2, and F3) are not available, and thus, a comparison with the EU standard for water cannot be made. The use of the stabilization/solidification methods for treating MSWI BA provides an alternative approach where the toxic components can be incorporated into cementitious materials through physical and chemical immobilization. An example of this is the pozzolanic solidification of MSWI-FA using a saturated Ca(OH)<sub>2</sub> solution, which can potentially induce pozzolanic properties in the ash [34]. This process results in the formation of calcium-silicate-hydrate and ettringite, which help stabilize heavy metals like Cd, Pb, and Zn [35,36].

## 4. Conclusions

- Municipal Solid Waste Incineration Bottom Ash (MSWI BA) shows promise for construction use due to its high Si, Al, and Fe content. However, concerning levels of As, Cd, Cr, Cu, Pb, and Zn raise environmental leaching concerns;
- 2. Risk assessment (RAC and ICF) calculations indicate the need for measures to mitigate environmental and health impacts;
- 3. The sequential extraction method reveals that Cd, Cu, and Zn are highly mobile in MSWI BA, while Al and Fe are less mobile. Pb is completely immobilized;
- Concentrations of potentially toxic elements in MSWI BA exceed EU standards, highlighting the importance of proper management and adherence to regulatory guidelines;
- 5. By understanding metal mobility, effective waste management strategies can be developed to minimize environmental risks associated with trace elements, promoting safer utilization of MSWI BA;
- 6. Our research underscores the multifaceted nature of MSWI ash, highlighting the critical need for a balanced approach. While it exhibits potential as a resource, it equally demands rigorous environmental management to ensure responsible utilization. The observed metal mobilization, especially for Cd, Cu, and Zn, underscores the necessity for stringent containment and treatment measures to mitigate the risk of environmental contamination.

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