Trace elements leaching from Pb-Zn mine waste (Plombières, Belgium) and environmental implications

Jillian Helser^{1,2,*} and Valérie Cappuyns^{1,2}

¹Department of Earth and Environmental Sciences, KU Leuven, 3001 Leuven, Belgium

²Research Centre for Economics and Corporate Sustainability (CEDON), KU Leuven,
1000 Brussels, Belgium

Received 26 May 2020; Accepted 23 September 2020; Available online 30 September 2020

Abstract

The geochemical and mineralogical characterization of mine waste provides essential information to understand the environmental and health impacts and to adequately manage present and historical mine waste sites. In the present study, mine waste samples from a former Zn-Pb mining site were subjected to different types of leaching tests, an in-vitro bioaccessibility test, and a mineralogical analysis. The samples were characterized by elevated pseudo-total Pb (up to 51,800 mg/kg), Zn (up to 60,100 mg/kg), Cd (up to 430 mg/kg), and As (up 3,170 mg/kg) concentrations, and contained, among other minerals, cerussite (PbCO_3) and galena (PbS). Lead is not only present in abundant concentrations, but also in highly bioaccessible forms, as determined from the in-vitro bioaccessibility test. This indicates the high risks

*Corresponding author at: KU Leuven, Department of Earth and Environmental Sciences, Celestijnenlaan 200E, Box 2411, 3001 Leuven, Belgium. E-mail addresses: jillian.helser@kuleuven.be (J. Helser), valerie.cappuyns@kuleuven.be (V. Cappuyns).

posed in the case of ingestion of fine dust particles. The partial dissolution of the Pb-bearing minerals as a function of pH was modeled using PHREEQC geochemical software and was compared with experimental data. The high Pb release is mainly controlled by the dissolution of cerussite, even at natural pH values. X-ray diffraction analyses revealed that the amount of cerussite decreased (by $\geq 50\%$) in all samples as a consequence of leaching with water. Other Pb and Zn minerals present in the samples also dissolved when extracted with water, but not to the magnitude of cerussite. Although the mining site has been inactive for over 100 years, the high concentrations of metal(loid)s within the samples are still evident. Not only are the metals present in high concentrations, but also as mobile forms, especially when pH changes. This study proved to be essential in understanding the different parameters controlling metal(loid)s and in identifying the potential threats the mine waste poses to human health and the environment. From this overall assessment, proper methods for an effective recovery or reprocessing of the mine waste can be further evaluated.

Keywords: Sulfidic mine waste, leaching, in-vitro bioaccessibility, metal(loid)s, environmental assessment, human health risks

1 Introduction

Historically, mining and mineral extraction have contributed considerably to the progression of human civilization (Jain et al., 2016); however, even centuries later, the associated waste produced can pose potential risks to both the environment and human health. One of the major environmental risks posed is the acidification and contamination of soil and water, especially in the case of sulfidic mine waste. Additionally, humans can be at risk to various contaminants, most commonly arsenic (As), chromium (Cr) and nickel (Ni), via inhalation, ingestion or direct contact (Environment Agency, 2009).

When a mining site is left uncovered or as erosion of the top layer occurs over time, the waste is left exposed, and potential contaminants can be dispersed and transported by wind and water, ending up in soils, surface water, and on/in various biota, disturbing environmental ecosystems (Ettler, 2016; Souissi et al., 2015). Soils can be a major sink for metal(loid)s and unlike organic contaminants, which can naturally attenuate (e.g., oxidized by microbial activity), most metal(loid)s do not undergo microbial or chemical degradation (Kirpichtchikova et al., 2006) and can

persist in the environment long after being introduced (Adriano, 2003); however, changes in their speciation and bioavailability are possible (Wuana and Okieimen, 2011).

The total content of metal(loid)s in a given environment is not sufficient for determining the environmental and health risks, it is only an indicator of the degree of contamination (Król et al., 2020). Because these risks are dependent on the toxicity, mobility, and bioavailability of metal(loid)s in the waste material; thus, an understanding of their solid phase speciation and associated leaching behavior is essential. The speciation of the metal(loid)s as well as influential parameters (e.g., pH, sorption/desorption reactions, redox potential, microbial activity, etc.) play a role in the mobility of these elements.

Numerous studies (Cappuyns et al., 2014; Hiller et al., 2013; van der Sloot and van Zomeren, 2012) have focused on the environmental risks that mine waste can pose by performing standardized leaching tests mimicking conditions found in nature (e.g., Toxicity Characteristic Leaching Procedure and EN 12457-2) or a worst-case scenario (e.g., pH-dependent leaching test and sequential extraction). These tests provide a combined approach of observing the potential short and long term effects and can aid in determining the best possible remediation methods.

Additionally, there are several recent studies on the associated human health risks which determine the bioaccessibility of elements in relation to the tolerance levels of humans (Bagherifam et al., 2019; Ettler et al., 2019; Kastury et al., 2017). At low concentrations, some metal(loid)s are essential for living organisms; however, above certain concentrations, all metal(loid)s can have adverse effects on human health (Poggio et al., 2009). Thereby, in vitro bioaccessibility tests can be effective in simulating the exposure to mining-related contaminants via human ingestion by mimicking conditions of the gastrointestinal system.

While the solid-phase speciation and associated chemical leaching of metal(loid)s from mine waste have been studied, there is still much to learn on the speciation of metal(loid)s in mine waste, and the associated environmental and human health risks. Moreover, historical mine waste sites often still contain some valuable metals which can be further extracted. Additionally, the processed waste can potentially be used as a secondary resource (e.g., in construction materials). By performing an initial characterization, the potential for metal recovery and valorization of the waste can be explored. As the assessment is site-specific, a complete characterization must be applied in the current study to then evaluate possible future methods for

recovering and reprocessing the waste.

Therefore, the objective of this paper is to investigate the solid-phase speciation of metal(loid)s in four different mine waste samples from a Pb-Zn mine waste deposit, linked to the chemical leaching under different conditions (pH, liquid/solid (L/S) ratio, temperature, and time). Additionally, the risk to humans upon ingestion of the mine waste particles is estimated by means of an in-vitro bioaccessibility test, and these data are evaluated relative to the chemical, mineralogical, and leaching characteristics. Modeling with PHREEQC is then used to simulate the release of metals as a function of pH based on the dissolution of minerals, to determine processes and phases controlling the release of metal(oid)s. With this detailed characterization, the valorization of this mine waste can be assessed and potential future perspectives can be proposed.

2 Study Area

Figure 1: Location of the mine waste heap where the samples were taken in Plombières, including the area (dashed rectangle) where 65 soil samples were taken, and the four samples chosen for this study specifically marked (boreholes marked with black circles).

The area studied in Plombières (Eastern Belgium) was a former Zn-Pb mining industry situated along the Guel river (Figure 1). The most dominant ore mineraliza-

tions present are the sulfide minerals sphalerite (ZnS) and galena (PbS) (Dejonghe, 1998). The mining practices in this area started as early as the Middle Ages and were most active from 1844, during the period of industrial mining, until 1882 (Dejonghe et al., 1993), after being drained of its easily accessible ores. The mining company then began to process imported ores until 1922, when all on-site activities came to an end. Today, there are approximately 11.4 megatons of mining waste present at this site. Currently, the site is host to a public nature reserve and is in close proximity to residential areas. Metal(loid)s are still present in the soil, however, the levels of metal(loid)s may have decreased over time due to natural attenuation and some vegetation has grown and provided coverage. As the area is frequented by visitors, it is important to understand the potential human health impacts that the present mine waste poses, in combination with the environmental risks.

3 Materials and Methods

3.1 Samples

In August 2018, 34 pits were dug with a spade and an auger within a rectangular area (50 x 70 m) in a mine waste deposit in Plombières. Sixty-five soil and mine waste samples were taken at different depths of the boreholes, depending on visual alterations in the profiles. All samples were oven-dried at 40°C, then, disaggregated in a porcelain mortar, ground to a powder and sieved (<180 µm) (Van Campen, 2019). An initial geochemical and mineralogical analysis was performed on all sixty-five samples, then based on this analysis, four samples were selected due to their elevated metal(loid) concentrations and variety of Pb/Zn-bearing minerals. The four samples were also selected to express the mineralogical heterogeneity of the mine waste site. The samples consist of mostly mine waste, encompassing slag material, and brick fragments remaining from the processing factory, etc. The description and characteristics of the samples are presented in Table 1.

3.2 Chemical and mineralogical sample characterization

Aqua regia (HCl/HNO₃, 3:1 solution) digestion (modified ISO 11466 method) was performed to determine the pseudo-total content of major and trace elements present

Table 1: Sample descriptions

Sample name	Description	Sample depth (cm)	Grain size	Color (Munsell soil color chart code)	pH
PL_1	Mine waste - very fine slag material	30 - 40	Fine sand	7.5 YR 4/1	7.4
PL_2	Mine waste - brick fragments, very fine slag material	70 - 100	Clay	2.5 YR 6/1	6.5
PL_3	Mine waste - rubble, very fine slag material	70 +	Clay	10 YR 4/3	6.8
PL_4	Mine waste - brick fragments	20 - 28	Coarse sand	10 YR 7/2	6

in the samples. 0.5 g of sample was mixed with 10 ml of aqua regia and left covered overnight. Then, the mixture was digested on a hotplate for 1 hr at 140°C and then the temperature was increased to 200°C until almost complete evaporation of the solution (approx. 1 hr). Additionally, 10 ml of 2.5 mol/l HCl was added to the dried mixture and heated for 10-15 minutes. After cooling, the solid residue was filtered through filter paper while rinsing with MilliQ H₂O (Millipore Q Gard 2) and the solution was diluted to 50 ml with MilliQ H₂O and homogenized. The remaining residue was oven-dried and weighed to determine the insoluble residue content. The test was performed in duplicates and two certified reference materials (i.e., BCR143R and QCM-31) were used for quality control. A comparison of the certified and the measured values of the reference materials can be found in Table S1. Solutions were stored in the refrigerator at 7-10°C until analysis and measured without dilutions with induced coupled plasma-optical emission spectroscopy (ICP-OES Varian 730 ES) within 1 week after digestion.

The quantitative mineralogical composition of the samples was determined using X-ray diffraction (XRD, Philips PW1830 Analytical x-ray BV) with CuK α radiation at 45 kV and 30 mA based on the Rietveld method. With the same operational settings, XRD was also used to determine the mineralogy of the residue that remained after the cascade leaching test for comparison. In all cases, ZnO was used as a standard for quantification.

The pH of the samples was measured in a water suspension (solid/ liquid ratio: 1/10) (18.30 field pH meter, Eijkelkamp, The Netherlands). Additionally, the grain size distribution was determined by Van Campen (2019) (Table 1; Figure S1).

3.3 Leaching and in-vitro bioaccessibility studies

Standardized leaching tests were performed under varying conditions (e.g., extraction fluid, pH, L/S ratio, duration, etc.) to chemically characterize the four mine waste samples and compare methods. Additionally, an in-vitro bioaccessibility test was also performed to determine the potential human health risks that the mine waste samples could pose. The summary of each of the leaching tests performed as well as the in-vitro bioaccessibility test are outlined in Table 2. All leaching tests were performed on dried samples. A particle size of $<180\text{ }\mu\text{m}$ was used for each sample because grains of $200\text{ }\mu\text{m}$ can be moved by an average wind speed of 12 km/h (Bell, 2016) and a particle size of $<250\text{ }\mu\text{m}$ is the upper bound fraction considered to adhere to the hands of the at-risk receptor (Duggan et al., 1985; Wragg et al., 2014). To more accurately compare results, the same particle size ($<180\text{ }\mu\text{m}$) was used for all leaching tests. The leaching tests were carried out at room temperature (approx. 20°C) in 30 ml Nalgene centrifuge tubes with screw caps. The sample and the extraction fluid were combined in the tubes and shaken laterally on a reciprocal shaker (Edmund Buhler GmbH) at 100 rpm for the listed duration (Table 2). After shaking, the tubes were centrifuged (GS-6 Centrifuge Beckman) for 10 min at 3200 rpm. As for the in-vitro bioaccessibility test, 50 ml tubes were used and were shaken upright at 250 rpm in a water bath (Grant GLS Aqua 18 plus) at 37°C for both phases for the listed duration (Table 2). All tests were performed in duplicates or triplicates and blanks were always used for quality control.

For both the leaching tests and the in-vitro bioaccessibility test, the pH and electrical conductivity (18.34 EC-meter, Eijkelkamp, The Netherlands) were measured, and the supernatant was filtered (using a syringe and a $0.45\text{-}\mu\text{m}$ Chromafil® filter) and analyzed using induced coupled plasma-optical emission spectroscopy (ICP-OES Varian 730 ES) for Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Sr, V, and Zn. For some samples, anions (i.e., Cl^- , F^- , SO_4^{2-} , and NO_3^-) were determined by ion chromatography (Dionex ICS-2000, Thermo Scientific). For most cases (except the alkaline leachates), the filtered supernatant for ICP-OES analysis was acidified to $\text{pH} < 2$ with HNO_3 and stored in the refrigerator (at $5\text{-}10^{\circ}\text{C}$) until analysis. The liquid aliquot for IC analysis was stored in the freezer (at approx. -17°C) until analysis (without acidifying).

- Toxicity characteristic leaching procedure (TCLP)

The U.S. Environmental Protection Agency (US EPA) Method 1311 Toxicity

Table 2: Description of parameters for different leaching tests and an in-vitro bioaccessibility test performed in this study.

Test	pH of extraction fluid	L/S ratio	Sample mass/ leachate volume	Temp.	Duration	Extraction fluid	Reference
Toxicity characteristic leaching procedure (US EPA Method 1311)	4.93 ± 0.05	20 l/kg	1 g/20 ml	20 – 25°C	18 h	Acetic acid and NaOH	(US EPA, 1992)
EN 12457-2 compliance test (BS EN 12457-2:2002)	neutral	10 l/kg	1g/10 ml	20 – 25°C	24 h	Ultrapure MilliQ H ₂ O	(EN 12457-2, 2002)
pH-dependent leaching test (Modified CEN/TS 14429:2005)	pH 0.5, 1, 2, 3, neutral, 9, 11, and 13	10 l/kg	1 g/10 ml	20 – 25°C	2 h	HNO ₃ and NaOH at varying concentrations and neutral solution (Ultrapure MilliQ H ₂ O)	(Gee et al., 2001)
Cascade leaching test (NEN 7349)	neutral	10 l/kg; Σ 100 l/kg	2 g/ 20 ml (Σ 200 ml)	20 – 25°C	2 weeks	Ultrapure MilliQ H ₂ O	(Cappuyns et al., 2006; NEN 7349, 1995)
In-vitro modified SBET bioaccessibility test	1 st phase (gastric): pH 1.5	50 l/kg	0.5 g/ 25 ml	37± 2°C	1 h	0.4 mol/l Glycine and HCl	(Poggio et al., 2009)
	2 nd phase (intestinal): pH 7	50 l/kg	0.5 g/ 25 ml	37± 2°C	3 h	Approx. 10 ml of fluid from the 1 st phase is replaced with NaHCO ₃	

Characteristic Leaching Procedure (TCLP) is designed to simulate the worst-case scenario of co-disposal in municipal landfills (Hageman et al., 2015) to determine the toxicity of the waste. Extraction fluid #1 (i.e., glacial acetic acid with 1 mol/l NaOH; pH 4.93 ± 0.05) was used, based on the preliminary test performed, as outlined in the standard procedure (US EPA, 1992). In addition to the ICP-OES analysis, the sulfate content was also determined using ion chromatography.

- EN 12457-2

The EN 12457-2 test was performed according to the guidelines of the European Committee for Standardization (CEN). It specifies a compliance test providing information on leaching of granular wastes and sludge under experimental conditions and is used for classifying waste materials in the EU (EN 12457-2, 2002).

- Cascade leaching test

The cascade leaching test (NEN 7349, 1995; Cappuyns et al., 2006) was performed on the four samples to study the longer-term mobility of metal(loid)s over two weeks. The leachate was separated for analysis and periodically renewed with fresh extraction fluid every 24 hrs for 17 days, except for days 5-6 and 12-13 (when, after extraction of the leachate, the tube was left sealed without renewing the fluid). After each extraction, the pH and electrical conductivity of the leachate were measured. Following the experiment, the residue was dried and saved for XRD analysis.

- pH-dependent leaching test

The samples were subjected to a pH-dependent leaching test (modified CEN/TS 14429 or modified US EPA method 1313 (Gee et al., 2001)). Seven different extraction fluids were used with varying concentrations of HNO₃ or NaOH, respectively: pH 0.5 (0.3 mol/l HNO₃), pH 1 (0.1 mol/l HNO₃), pH 2 (10^{-2} mol/l HNO₃), pH 3 (10^{-3} mol/l HNO₃), pH 9 (10^{-5} mol/l NaOH), pH 11 (10^{-3} mol/l NaOH), and pH 13 (0.1 mol/l NaOH). For each sample, an extraction at neutral pH with just ultrapure MilliQ water (Millipore Q Gard 2, $18.2 \text{ M}\Omega\cdot\text{cm}^{-1}$) was also included.

- In-vitro modified PBET bioaccessibility test

In addition to the leaching tests, a modified in-vitro bioaccessibility extraction test (Oomen et al., 2003; Poggio et al., 2009) was performed based on

the original physiologically based extraction test (PBET) described by Ruby et al. (1996). The test mimics the conditions (i.e., temperature, pH, agitation, enzyme/chemical conditions, and duration) in the worst-case scenario (the pH of the gastric acid ranges from 1.5 to 3.5 and in this case 1.5 was used) of the human gastric (1st phase) and intestinal (2nd phase) tract to determine the potential concentration of trace elements that are readily available for uptake in the case of ingestion of these particles.

3.4 PHREEQC simulation of leaching of metals from mine waste samples

PHREEQC (Parkhurst and Appelo, 1999), with the database minteq.v4.dat, was used to evaluate the concentrations of metals (with particular focus on Pb) leached at equilibrium in relation to the solubility of the present minerals at varying pH. The modeled concentrations were compared with the experimental values from the different leaching tests, especially the pH-dependent leaching test. Additional minerals not found in the database were added, using the thermodynamic data presented in Table S2. The mineralogical composition of each sample used as input was based on the mineralogical analysis performed and considering an L/S ratio of 10 l/kg.

4 Results

4.1 Sample characterization

The XRD analysis (Table 3, Figure S2) indicated that the studied samples are comprised mostly of quartz (21-43 wt %), amorphous phases (13-43 wt %) (except sample PL_4, < 0.5 wt %), and clay minerals (5-27 wt %) (Table 3). The amorphous phases in each of the samples are believed to be attributed to the presence of slag, as slag-like fragments were observed upon collection of the samples and during sample preparation. Sample PL_3 also contains a large amount of goethite (α -FeOOH) (25 wt %), which is a secondary Fe oxyhydroxide mineral, formed as a consequence of oxidation of iron-bearing minerals and commonly found in mine waste (Jamieson, 2011). Similarly, sample PL_3 also contains lepidocrocite (λ -FeOOH) (1 wt %), another iron oxyhydroxide mineral. Magnetite (Fe_3O_4) (samples PL_1 and PL_3),

and hematite (Fe_2O_3) (samples PL_1 and PL_4) are also present. Magnetite, which contains both Fe (II) and Fe (III) can contribute to acid generation (Moncur et al., 2009). Additionally, the majority of the samples contain primary Pb/Zn bearing sulfide minerals such as galena (< 0.5 -1 wt %) and sphalerite (2-9 wt %). Plumbojarosite and beudantite, both secondary sulfate Pb-bearing mineral, also represents a large fraction of sample PL_4 (4 and 12 wt %, respectively). Beudantite formation is usually associated with the oxidation of galena and arsenopyrite (FeAsS) with the release of As, Fe, and Pb (Roussel et al., 2000). Furthermore, the samples contain other Pb-bearing minerals such as anglesite (3 wt %) and cerussite (1-5 wt %). The presence of anglesite could be due to the oxidation of galena under acidic conditions, whereas in a pH-neutral environment cerussite is formed (Jamieson et al., 2015).

Table 3: Quantitative mineralogical composition obtained by the Rietveld method using Profex.

Mineralogy (wt %)	Formula	Sample name			
		PL_1	PL_2	PL_3	PL_4
<i>Amorphous</i>		43	13	31	42
<i>Quartz</i>	SiO_2	26	43	21	26
<i>Feldspar</i>	$\text{KAlSi}_3\text{O}_8 - \text{NaAlSi}_3\text{O}_8$	7		3	
<i>Cristobalite</i>	SiO_2	1			1
<i>Clay minerals</i>		3	2	12	
<i>Micas</i>		11	25	10	5
<i>Mullite</i>	$3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	2	1	2	
<i>Sphalerite</i>	ZnS		9		2
<i>Willemite</i>	Zn_2SiO_4	1			
<i>Cerussite</i>	PbCO_3	1	4	1	5
<i>Galena</i>	PbS	<0.5	1	1	<0.5
<i>Anglesite</i>	PbSO_4		3		
<i>Beudantite</i>	$\text{PbFe}_3(\text{AsO}_4)(\text{SO}_4)(\text{OH})_6$				12
<i>Plumbojarosite</i>	$\text{PbFe}_6^{3+}(\text{SO}_4)_4(\text{OH})_{12}$				4
<i>Goethite</i>	$\alpha\text{-FeOOH}$			25	
<i>Lepidocrocite</i>	$\lambda\text{-FeOOH}$			1	
<i>Magnetite</i>	Fe_3O_4	2		4	
<i>Hematite</i>	Fe_2O_3	1			2

The results from aqua regia digestion are presented in Table 4. Pseudo-total Pb concentrations are highest for PL_4 (51,800 mg/kg) and lowest for PL_3 (14,800 mg/kg). These elevated Pb concentrations could be expected based on the presence of Pb-bearing minerals in these samples (Table 3). High amounts of As are also found in each of the samples, especially in sample PL_4 (3,173 mg/kg), which contains the

As bearing mineral beudantite. The insoluble residue is presented in Table 4, based on the weight of the sample before and after aqua regia digestion. The residue (after digestion) was also analyzed using XRD (qualitative analyses were used instead of quantitative due to the shape of the patterns/undefined minerals) and the minerals measured consisted mostly of silicates and clay minerals. Some of the insoluble residues also contained feldspars (samples PL_1 and PL_3), anglesite (PbSO_4) (< 0.5 wt % in sample PL_2), and cotunnite (PbCl_2) (samples PL_2 and PL_4). As cotunnite is a highly soluble phase and is not present in the original samples, its presence in the residue can result from drying, in which Pb can react with Cl ions from the aqua regia solution (Šebek et al., 2014).

Table 4: Results (mean $\pm$ standard deviation (n=2)) from aqua regia digestion.

Element (mg/kg)	Sample name			
	PL_1	PL_2	PL_3	PL_4
Al	12300 $\pm$ 437	5410 $\pm$ 581	4810 $\pm$ 145	1590 $\pm$ 25
As	561 $\pm$ 34	221 $\pm$ 5	319 $\pm$ 2	3170 $\pm$ 75
Cd	70 $\pm$ 2	429 $\pm$ 5	39.9 $\pm$ 0.6	30.8 $\pm$ 0.2
Co	26.3 $\pm$ 0.5	14.3 $\pm$ 0.5	33.7 $\pm$ 0.2	7.3 $\pm$ 0.1
Cr	22.2 $\pm$ 0.7	11 $\pm$ 1	39.7 $\pm$ 0.5	6.8 $\pm$ 0.4
Cu	599 $\pm$ 24	301 $\pm$ 10	389 $\pm$ 3	369 $\pm$ 8
Fe	78100 $\pm$ 1220	13000 $\pm$ 246	154000 $\pm$ 847	98400 $\pm$ 1659
Mg	1850 $\pm$ 86	950 $\pm$ 45	781 $\pm$ 18	280 $\pm$ 11
Mn	1590 $\pm$ 25	225 $\pm$ 7	1370 $\pm$ 6	437 $\pm$ 21
Ni	57.2 $\pm$ 0.6	68.3 $\pm$ 0.7	89.1 $\pm$ 0.0	8.8 $\pm$ 0.1
Pb	42600 $\pm$ 2719	46800 $\pm$ 4464	14800 $\pm$ 802	51800 $\pm$ 2790
S	2260 $\pm$ 39	32400 $\pm$ 912	2000 $\pm$ 3	31000 $\pm$ 682
Sb	184.3 $\pm$ 0.0	186 $\pm$ 6	107 $\pm$ 2	413 $\pm$ 16
V	47 $\pm$ 1	14 $\pm$ 1	27.1 $\pm$ 0.1	14.8 $\pm$ 0.3
Zn	30200 $\pm$ 435	60100 $\pm$ 2827	11100 $\pm$ 20	7510 $\pm$ 346
% of insoluble residue	61 $\pm$ 2	72.0 $\pm$ 0.1	36 $\pm$ 1	57 $\pm$ 1

4.2 TCLP

The results of the TCLP in comparison with the US EPA regulatory threshold are presented in Table 5. In each sample, As is below the regulatory threshold, while the concentration of Cd leached from sample PL_2 is above the regulatory threshold. For each sample, the concentration of Pb is above the regulatory threshold and as

each sample has at least one element that is above the regulatory threshold, each sample is considered hazardous according to the US EPA TCLP (US EPA, 1992). There is no standard established for Zn, however, sample PL_1 has the highest amount of Zn leached (Table 5).

Table 5: Concentrations of metal(loid)s leached with the TCLP test. NSE, No standard established. The detection limit for As was 0.02 mg/l and for Cr 0.05 mg/l.

Concentration leached (mg/l)						
Element	As	Cd	Cr	Pb	Zn	
PL_1	< 0.02	0.80 ± 0.01	< 0.05	208 ± 5	171 ± 4	
PL_2	< 0.02	5.5 ± 0.2	0.08 ± 0.01	697 ± 11	79 ± 4	
PL_3	< 0.02	0.60 ± 0.01	< 0.05	55 ± 2	88.0 ± 0.6	
PL_4	< 0.02	0.10 ± 0.01	< 0.05	769 ± 23	13.0 ± 0.3	
(US EPA) Regulatory Threshold	5.0	1.0	5.0	5.0	NSE	

4.3 In-vitro modified bioaccessibility test

The results for the in-vitro modified bioaccessibility test are presented in Table 6. Lead, for all samples, was highly bioaccessible (76-98% of pseudo-total concentration), the majority (69-90% of pseudo-total concentration) being leached during the gastric phase. For each sample and all elements analyzed the percentage of the total concentrations of metal(loid)s leached in the first phase was always higher than in the second phase. This trend can be expected because the pH of the extraction fluid from the first phase (pH 1.5) is acidic and the second phase (pH 7) is neutral. However, when the extraction fluids were mixed with the samples, the pH changed slightly. The concentrations of metal(loid)s leached as a function of the final pH of the extraction fluid are plotted in Figure 4, together with the results of the other leaching tests.

Table 6: Concentrations of metal(loid)s leached (mg/kg) in the gastric and intestinal phase (in-vitro bioaccessibility SBET method). Results are presented as a percentage of the pseudo-total concentration (aqua regia digestion).

Sample name								
PL_1		PL_2		PL_3		PL_4		
conc. (mg/kg)	bioac. (%)	conc. (mg/kg)	bioac. (%)	conc. (mg/kg)	bioac. (%)	conc. (mg/kg)	bioac. (%)	
<i>1st Phase (Gastric)</i>								
As	45 ± 1	10	158 ± 1	71	9 ± 0.4	3	19 ± 1	1
Cd	42 ± 1	60	155 ± 13	36	22.28 ± 0.02	56	4.6 ± 0.4	15
Cu	314 ± 1	52	68 ± 0.3	23	169 ± 1	43	31 ± 1	8
Ni	18.4 ± 0.1	32	58 ± 1	85	13.9 ± 0.2	16	1.2 ± 0.2	14
Pb	29300 ± 700	69	40600 ± 400	87	11500 ± 80	77	46400 ± 100	90
Zn	22200 ± 10	74	6880 ± 300	11	8381.8 ± 0.1	76	590 ± 44	8
<i>2nd Phase (Intestinal)</i>								
As	< 4	0	7.7 ± 0.7	3	< 4	0	< 4	0
Cd	22 ± 2	31	86 ± 7	20	12.41 ± 0.03	31	1.7 ± 0.7	6
Cu	192 ± 6	32	33 ± 1	11	87 ± 1	22	20 ± 2	5
Ni	9.0 ± 0.2	16	26.0 ± 0.4	38	6.8 ± 0.1	8	0.6 ± 0.1	7
Pb	2890 ± 2400	7	3500 ± 1500	8	3020 ± 600	20	2700 ± 3700	5
Zn	14600 ± 700	48	3210 ± 120	5	3690 ± 60	33	225 ± 45	3

4.4 EN 12457-2 and pH-dependent leaching test

Anions (F^- , Cl^- , NO_3^- , and SO_4^{2-}) were also measured for the EN 12457-2 test and pH dependence leaching test at specific pH values. The expected sulfate content, assuming that all sulphur is present as sulfate (SO_4^{2-}), was first calculated and then compared with the measured sulfate concentrations (Table S3). Between 76 and 98% of the sulfur concentration was present as sulfate. A t-test was conducted and indicated that the expected sulfate concentrations (based on the measured S concentration with ICP-OES) are not significantly different from the actual sulfate concentrations measured with IC ($p > 0.05$).

Figure 2: Concentration of As, Cd, Cu, Zn, Fe, S leached (mg/kg) as a function of pH during the pH-dependent leaching test (average of 3 replicates). Note: shapes with white fill are below the detection limits. Error bars indicate standard deviation ($n=3$). When error bars are not visible, they are smaller than the markers.

In Table S4, the measured and expected sulfate concentrations are listed for the pH-dependent leaching test for each sample when mixed with extraction fluid of 10^{-2} mol/l HNO_3 (pH 2) and 10^{-3} mol/l HNO_3 (pH 3). Overall, higher sulfate concentrations are measured in less acidic environments (10^{-3} mol/l HNO_3), also in comparison with the sulfate concentrations leached in the EN 12457-2 test (Table S3). A t-test indicated that there is not a statistically significant difference ($p > 0.05$) between the expected versus the actual sulfate concentrations.

The metal(loid) concentrations leached as a function of pH during the pH-dependent leaching test are represented in Figure 2. While 23 different elements were measured, the mobility of specific elements (As, Cd, Cu, Pb, Zn) and major elements (Fe, S, P) affecting the mobility will primarily be focused on for this paper. For each of the samples, similar trends are observed for the release of major and trace elements as a function of pH. Typically, metals are most mobile at low pH and less soluble as pH increases. This is also true for the mine waste samples; however, as the pH increases from pH 6 onwards, a strong increase in the release of some metals (Cu, Pb) is also observed (Figure 2). This can be explained by the complexation of these metals with organic or inorganic ligands or forming hydroxyl complexes in solution (Cappuyns and Swennen, 2008; Halim et al., 2005). Additionally, arsenic occurs as an oxyanion and, therefore, is also more mobile at higher pH.

4.5 Cascade leaching test

The pH remained relatively stable (pH variation < 1.0) during the 2 weeks of the cascade leaching test for each of the samples (Figure 3). Despite this, relatively high levels of metals (i.e., Pb, Cd, and Zn) were still leached, especially for sample PL_2. The release of As varied between the samples, for PL_2, As release was below the detection limit; for sample PL_4 the leaching of As was not detected until the fifth measurement (L/S ratio: 50 l/kg); whereas, for samples PL_1 and PL_3 an earlier release of As was detected. Low leaching concentrations for As can be expected as the pH of the leachates ranges from 5.5 to 7.5. In the pH-dependent leaching tests (Figure 2) there is less leaching of As within this pH range compared to more alkaline and acidic conditions.

The quantitative mineralogical composition of the original samples was compared with that of the residue remaining from the cascade leaching experiment. Comparing the results (Table S5), it is evident that some cerussite ($\geq 50\%$ of original) has

Figure 3: The EC and pH as well as the cumulative concentration of As, Cd, Cu, Pb, Zn, and S released during the cascade leaching test. Note: Error bars indicate standard deviation (n=2), but are not visible because they are small in comparison with the markers.

dissolved in each of the samples. This can be expected as cerussite is a Pb-carbonate mineral and may partially dissolve when in contact with just deionized water, which can also be supported by the Pb concentration released into the leachate during the cascade leaching tests (Figure 3). There is also a difference in the abundance of other minerals between the original sample and the residue after the cascade leaching experiment; however, the differences are rather small, and could just be a result of the heterogeneity within the samples.

5 Discussion

5.1 Comparison of EN 12457-2 test, pH dependence leaching test, and in-vitro bioaccessibility test

The concentrations of Pb, Cd, Cu, and Zn leached as a function of pH during the pH-dependence leaching test are compared with the amounts leached in the EN 12457-2 test and both phases of the in-vitro bioaccessibility test (Figure 4). Despite different L/S ratios, temperature, and extraction fluid, there is a strong correlation between pH and the leaching of elements (except for the second phase of the in-vitro bioaccessibility test). Additionally, the L/S ratio plays a slight role in the bioaccessibility of metals (Hamel et al., 1998), this could explain some of the differences (i.e., the second phase of the bioaccessibility test) between the bioaccessibility test (L/S ratio of 50 l/kg) in comparison with the other tests presented in Figure 4, with L/S ratios of 10. While there are many studies (e.g., Hamel et al. (1998); Pelfrène et al. (2017)) which express the importance of the L/S ratio, further investigations would be necessary to determine how it affects the leaching of elements in these samples specifically.

5.2 Leaching tests in comparison with mineralogy and modeling

To determine which processes and which minerals are controlling the release of metal(loid)s, experimental results (the mineralogical composition of the samples and results of the pH-dependent leaching tests) were combined with geochemical modeling. In each of the samples, Pb minerals are present (Table 3). Therefore, by focusing on the Pb minerals (i.e., cerussite, galena, anglesite, beudantite, and plumbojarosite), the dissolution/precipitation of Pb-bearing minerals in the pH-dependent leaching experiments were calculated for each sample using PHREEQC. Values for the amount of dissolved or precipitated Pb were compared with the experimental values (Figure 5). Negative values indicate that the mineral precipitated and there was more of that mineral than originally present in the samples. Additionally, dissolution of Zn-bearing minerals (willemite and/or sphalerite) present in samples (PL_1, PL_2, and PL_3) were investigated in relation to the concentrations of Zn leached. The saturation indices (SI) were also calculated using PHREEQC based on the same in-

Figure 4: pH dependence leaching test in comparison with the first phase and second phase of the in-vitro bioaccessibility test as well as the EN 12457-2 for as a function of pH for Pb, Cd, Cu and Zn for samples PL_1, PL_2, PL_3, and PL_4. Note: shapes with white fill are below the detection limits. Error bars indicate standard deviation ($n = 2$ or 3).

puts as Figure 5 and the SI were used to select solubility-controlling phases for each of the mine waste samples at different pH values (Table S6).

Figure 5: Amount of the Pb-bearing minerals dissolved (positive values) or precipitated (negative values) (solid lines, presented on secondary y-axis) as a function of pH in comparison with the experimental values of Pb concentrations leached (dotted line, presented on primary y-axis) for samples PL_1, PL_2, PL_3 and PL_4.

Cerussite is present in all samples and follows a similar trend observed for the release of Pb as a function of pH (i.e., increased dissolution as pH decreases ($\text{pH} < 6$) and minimum dissolution at circumneutral pH) (Figure 5, Table S6). The dissolution of cerussite is also evident in the leaching tests with water, such as the cascade leaching test: XRD analysis of the residue remaining after the cascade leaching test showed that half of the cerussite originally present in the samples was dissolved (Table S5). Additionally, as seen in the model results (Figure 5), cerussite also has a maximum dissolution at high pH (≈ 13), which exceeds the amount of Pb released into the leachate as measured during the experiment. Cerussite seems to be the main phase contributing to the release of Pb, in comparison with the other Pb minerals present. This observation is also in agreement with other studies (e.g., Jamieson et al.

(2015)), in which is shown that Pb carbonates are more soluble than Pb sulfides (see reaction equation of the dissolution of cerussite in Equation 1).

Galena is also present in each sample but displays a different behavior amongst samples. The reaction equations of the dissolution of galena and anglesite can be found in Equation 2 and 3, respectively. In samples PL_1 and PL_3, galena is consistently dissolving (Figure 5). Whereas for samples PL_2 and PL_4, galena is only dissolving at $pH < 5$; and at $pH > 5$ galena is precipitating. In sample PL_2, this increase in the final concentration of galena at $pH > 5$ could be a result of anglesite reducing to galena (according to the model). At $pH < 5$ galena could be oxidizing to anglesite (Figure 5), which was also described by Jamieson et al. (2015). The SI of anglesite at $pH < 5$ is zero, which means that the mineral is saturated and maintains equilibrium. Anglesite is seen dissolving under alkaline conditions and displays a negative SI (i.e., undersaturation).

Beudantite and plumbojarosite are only present in sample PL_4. According to the model, both plumbojarosite and beudantite are dissolving completely at acidic, neutral, and alkaline pH. However, this does not match with experimental results. Also, the XRD results of the residue after cascade leaching demonstrate that concentrations of beudantite and plumbojarosite do not decrease when leaching at natural pH (Table S7), contrary to the PHREEQC model. The dissolution of beudantite in the model seems to be influenced by hematite, because the addition of the latter generates acidity at natural pH, promoting the release of metal ions (see the reaction equation of the beudantite in Table S2). Zn host phases, sphalerite (PL_2 and PL_4), and willemite (PL_1), both depict undersaturation under acidic conditions (Table S6). As the pH increases, the SI of both minerals approaches zero. In sample PL_4, sphalerite is always undersaturated.

There have been previous studies stating the strong affinity of Zn, Pb and As to Fe-minerals (Courtin-Nomade et al., 2016; Lottermoser, 2017). In particular, As has

been reported to have a strong affinity to stable minerals, such as goethite, jarosite, or hematite (Courtin-Nomade et al., 2002). Therefore, while As leaching has not been directly modeled in PHREEQC in this study, the dissolution of these stable Fe-bearing minerals, including beudantite, would mean an increased release of As to the leachate as well. Additionally, sample PL_2 does not contain any Fe oxy(hydr)oxides and this could be an explanation as to why this sample also contains the lowest As levels.

The Fe oxides (i.e., hematite and magnetite) and Fe oxyhydroxides (i.e., lepidocrocite and goethite) present in these samples are important phases controlling the mobility of metal(loid)s. The modeled values being above or below the experiment values could be, among other factors, a result of the sorption to or the release from Fe(hydr)oxides, respectively. Hiller et al. (2013) stated that Fe oxyhydroxides are the most important solid phases controlling the retention/release of metal(loid)s. The highest sorption of metal ions by Fe oxyhydroxides increases when pH increases, but at alkaline pH, especially for elements like Pb (see Eh-pH diagram in Figure S3), the increased leaching rate can be related to the elements amphoteric character, contributing to the formation of hydroxyl complexes (Król et al., 2020). Besides precipitation reactions, the sorption of Pb to Fe (hydr)oxides or other minerals most likely also explains the limited leaching of Pb (dotted line in Figure 5) at circumneutral pH, but also under alkaline conditions. Desorption from Fe (hydr)oxides, seems to occur mostly under acidic conditions. However, this sorption/desorption potential has a large range of variance according to the type of Fe (oxy)(hydr)oxides, displaying different reactivities, and the species of the metal(loid). Other factors, such as cation exchange capacity, redox potential, microbiological activity, and kinetics may play a role as well.

Kinetics are expected to hinder the dissolution of certain minerals especially depending on the other present minerals (Palumbo-Roe et al., 2013). Dissolution kinetics can be studied using PHREEQC to further understand this release over time to improve the understanding of the mine waste in the environment; however, this was not the focus of this paper.

5.3 Implications for health and environment

Under acidic conditions (Figure 5, Table S6), such as when 0.3 mol/l of HNO_3 is used as extractant during the pH dependence test, Pb bearing minerals (cerussite,

galena, plumbojarosite, beudantite), Zn-bearing minerals (willemite, sphalerite), and lepidocrocite and magnetite, present in each sample, dissolve ($SI < 0$). This is important in the consideration of bioaccessibility. If mine waste particles were to be ingested, for example, cerussite would dissolve in the gastric phase due to the acidic environment, releasing Pb. This agrees with previous studies (Casteel et al., 2006; Jamieson et al., 2015; Palumbo-Roe et al., 2013), which indicated that Pb is immediately available upon ingestion of mine waste containing cerussite, which greatly increases the bioaccessibility of the ingested material.

According to the in-vitro bioaccessibility experiments, Pb was highly bioaccessible in all samples (76-98% of pseudo-total concentration), with the majority (69-90% of pseudo-total concentration) being leached during the gastric phase. The samples have a large fraction of Pb that is easily released, even at ambient (circumneutral) pH conditions.

To further understand the bioaccessibility risk, the total concentrations of As, Cd, Cu, Pb, and Zn in the samples are compared with the tolerable daily intake (TDI). The approach is based on Karadaş and Kara (2011) and Ettler et al. (2012), in which the TDI is calculated using the human-toxicity maximum permissible levels of Baars et al. (2001), based on oral exposure for children and adults. The TDI is compared in a scenario of ingesting 100 mg/day of mine waste (e.g., as a result of hand-to-mouth behavior of children playing in the area, swallowing the particles after being cleared from the airways by the mucociliary escalator (Ettler et al., 2019; Kastury et al., 2018), consumption of contaminated plants or water, etc.) (Table 7).

Table 7: Amount of As, Cd, Cu, Pb, and Zn ingested (μg) assuming the daily ingestion rate of 100 mg, in comparison with the TDI calculated for an adult and child.

Sample name ($\mu\text{g/day}$)	As	Cd	Cu	Pb	Zn
PL_1	56	7	60	4263	3021
PL_2	22	43	30	4679	6013
PL_3	312	4	39	1479	1110
PL_4	317	3	37	5186	751
TDI ¹ for 20 kg child	20	10	2800	72	10000
TDI ¹ for 80 kg adult	80	40	11200	288	40000

¹TDI=Tolerable daily intake (calculated from Baars et al., 2001)

For each of the samples, Pb is above the calculated TDI for children and adults, the same also applies when comparing the overall toxicity of the samples using the

TCLP (Table 5) in comparison with the regulatory threshold. Additionally, As is above the TDI for children in all samples, and for adults, two samples (PL_3 and PL_4) are above the TDI.

While the bioaccessible fraction of Pb in these samples is quite high and the risk is significant if particles are ingested, it is important to consider that these samples are from a minimum of 20 cm below the surface. Therefore, these specific concentrations would only be ingested in certain instances, such as the upturning of the mine waste (e.g., gradual exposure through weathering or intentional digging/children playing in the area). However, it is important to consider the worst-case scenario to understand the potential risk. Additionally, as the particles decrease in size, the contaminants generally become more available for leaching, resulting in a higher yield of the bioaccessible fraction (Kumpiene et al., 2017).

The results from the different leaching tests and in-vitro bioaccessibility test allow for the assessment of the behavior of these mine waste samples in the environment under neutral, slightly alkaline, or slightly acidic pH conditions (e.g., considering contact with rain) and under more extreme conditions with acidic pH or high alkalinity (e.g., acid rain, the formation of acid mine drainage, gastrointestinal system, remediation methods such as co-disposal with lime to increase pH). Additionally, even though the samples studied are from the same site, considerable variability in the concentrations of metal(loid)s, as well as in the mineralogical composition, is seen: thus, heterogeneity within the site is evident.

6 Conclusions

Samples from a Pb-Zn mine waste heap were characterized, both mineralogically and chemically concerning the release of metal(loid)s.

The pseudo-total content revealed elevated Pb, Zn, Cd, and As concentrations. Mineralogical analysis of the samples revealed, among others, the presence of Pb minerals (e.g., cerussite and galena were found in each sample), Fe oxides (e.g., magnetite and hematite), Fe oxyhydroxides (e.g., lepidocrocite and goethite), beudantite, and plumbojarosite. Mineralogy was an important factor in determining the leaching of certain elements into the environment.

Besides mineralogy, the pH and L/S ratio were shown to be key parameters

influencing leaching and in-vitro bioaccessibility. Overall, there was an increase in concentrations of Zn, Pb, Cd, and Cu as pH decreased ($\text{pH} < 6$). It seems that the high leaching of As, Cu, Cd, Pb and Zn under acidic conditions is due to both the dissolution of minerals and desorption. Additionally, there was also an increased release of certain metal(loid)s (e.g., As, Pb, and Cu) at higher pH values ($\text{pH} > 8$).

XRD analysis of the residue after the leaching test, combined with modeling in PHREEQC, indicated that the dissolution of cerussite was a controlling factor in the release of Pb under acidic, neutral and alkaline conditions. At least half of the cerussite was shown to dissolve in each sample at natural pH according to the XRD analysis of the residue remaining after the cascade leaching test. The dissolution of other Pb minerals was also observed, but following a different trend than cerussite. The interactions of cerussite, anglesite, and galena at different pH revealed the tendencies to oxidize or reduce to form other Pb minerals (e.g., oxidation of galena in acidic environments to form anglesite). Zinc minerals (i.e., sphalerite and willemite) displayed a higher potential for dissolution under acidic pH conditions. It was also evident, when comparing the leaching tests with the model, that sorption/desorption to other minerals (e.g., Fe (oxyhydr)oxides) and precipitation of these metals were most likely to occur.

Additionally, the TCLP leaching test showed high Pb concentrations in comparison with the regulatory threshold, providing an indication that the waste is hazardous to the environment. The in-vitro bioaccessibility test indicated that Pb posed a high risk in the case of ingesting fine dust particles. The bioaccessible Pb in the investigated samples represented 76 to 98% of the pseudo-total Pb concentration. Also, by comparing the pseudo-total content of As, Cd, Cu, Pb, and Zn with the calculated TDI, it was shown that Pb exceeded the TDI for both children and adults for all cases. Additionally, As concentrations are also above the TDI for children in all cases and adults in half of the samples.

Based on the pH-dependent leaching behavior of these samples, the popular treatment method of co-disposal with lime would not be recommended, since As, Pb, and Cu were shown to leach under alkaline conditions. This shows the importance of a complete characterization paired with geochemical modeling, which assists in understanding the best treatment approaches and the magnitude of the environmental and health risks. Based on this overall assessment, further research will focus on proper methods for an effective recovery of metals and/or reprocessing of the mine waste.

Acknowledgments This project has received funding from the European Union's

EU Framework Program for Research and Innovation Horizon 2020 under Grant Agreement No 812580. Elvira Vassilieva and Nancy Weyns are acknowledged for their assistance with instrumental analyses. We thank Philippe Muchez, Axelle Van Campen, and Srećko Bevandić for the provision of the samples and initial analyses that allowed for the selection of samples. This manuscript benefited from the constructive reviews by Vojtěch Ettler and two anonymous reviewers.

References

- Adriano, D. (2003). *Trace elements in the terrestrial environments: Biogeochemistry, bioavailability and risks of metals*. Springer, New York, NY, USA, 2nd edition.
- Baars, A., Theelen, R., Janssen, P., Hesse, J., Apeldoorn, V., Meijerink, M., Verdam, L., and Zeilmaker, M. (2001). Re-evaluation of human-toxicological maximum permissible risk levels. Technical report, National Institute of Public Health and the Environment, Bilthoven, The Netherlands.
- Bagherifam, S., Brown, T. C., Fellows, C. M., and Naidu, R. (2019). Bioavailability of arsenic and antimony in terrestrial ecosystems: A review. *Pedosphere*, 29(6):681–720.
- Bell, F. G. (2016). *Fundamentals of Engineering Geology*. Elsevier Science.
- Cappuyns, V., Alian, V., Vassilieva, E., and Swennen, R. (2014). pH dependent leaching behavior of Zn, Cd, Pb, Cu and As from mining wastes and slags: Kinetics and mineralogical control. *Waste and Biomass Valorization*, 5(3):355–368.
- Cappuyns, V. and Swennen, R. (2008). The use of leaching tests to study the potential mobilization of heavy metals from soils and sediments: A comparison. *Water, Air, and Soil Pollution*, 191(1-4):95–111.
- Cappuyns, V., Swennen, R., and Devivier, A. (2006). Dredged river sediments: Potential chemical time bombs? A case study. *Water, Air, and Soil Pollution*, 171(1-4):49–66.
- Casteel, S. W., Weis, C. P., Henningsen, G. M., and Brattin, W. J. (2006). Estimation of relative bioavailability of lead in soil and soil-like materials using young swine. *Environmental Health Perspectives*, 114(8):1162–1171.

- Courtin-Nomade, A., Neel, C., Bril, H., and Davranche, M. (2002). Trapping and mobilisation of arsenic and lead in former mine tailings –Environmental conditions effects. *Bulletin de la Société Géologique de France*, 173(5):479–485.
- Courtin-Nomade, A., Waltzing, T., Evrard, C., Soubrand, M., Lenain, J.-F., Ducloux, E., Ghorbel, S., Grosbois, C., and Bril, H. (2016). Arsenic and lead mobility: From tailing materials to the aqueous compartment. *Applied Geochemistry*, 64:10–21.
- Dejonghe, L. (1998). Zinc-lead deposits of Belgium. *Ore Geology Reviews*, 12:329–354.
- Dejonghe, L., Ladeuze, F., and Jans, D. (1993). *Atlas des gisements plombo-zincifères du synclinorium de Verviers: est de la Belgique*. Number no. 33 in Mémoires pour servir à l’Explication des Cartes Géologiques et Minières de la Belgique. Ministère des Affaires Économiques, Service géologique de Belgique.
- Duggan, M. J., Inskip, M. J., Rundle, S. A., and Moorcroft, J. S. (1985). Lead in playground dust and on the hands of schoolchildren. *Science of The Total Environment*, 44(1):65–79.
- EN 12457-2 (2002). Characterisation of waste leaching compliance test for leaching of granular waste materials and sludges—part 2. Technical report, The European Committee for Standardization (CEN), The European Committee for Standardization (CEN), Brussels.
- Environment Agency (2009). Human Health Toxicological Assessment of contaminants in Soil. Technical report, Environment Agency, (England and Wales), Bristol, UK, 2009.
- Ettler, V. (2016). Soil contamination near non-ferrous metal smelters: A review. *Applied Geochemistry*, 64:56–74.
- Ettler, V., Cihlová, M., Jarošíková, A., Mihaljevič, M., Drahota, P., Kříbek, B., Vaněk, A., Penížek, V., Sracek, O., Klementová, M., Engel, Z., Kamona, F., and Mapani, B. (2019). Oral bioaccessibility of metal(loid)s in dust materials from mining areas of northern Namibia. *Environment International*, 124:205–215.
- Ettler, V., Kříbek, B., Majer, V., Knésl, I., and Mihaljevič, M. (2012). Differences in the bioaccessibility of metals/metalloids in soils from mining and smelting areas (Copperbelt, Zambia). *Journal of Geochemical Exploration*, 113:68–75.

- Gee, C., Ramsey, M. H., and Thornton, I. (2001). Buffering from secondary minerals as a migration limiting factor in lead polluted soils at historical smelting sites. *Applied Geochemistry*, 16(9-10):1193–1199.
- Hageman, P. L., Seal, R. R., Diehl, S. F., Piatak, N. M., and Lowers, H. A. (2015). Evaluation of selected static methods used to estimate element mobility, acid-generating and acid-neutralizing potentials associated with geologically diverse mining wastes. *Applied Geochemistry*, 57:125–139.
- Halim, C. E., Short, S. A., Scott, J. A., Amal, R., and Low, G. (2005). Modelling the leaching of Pb, Cd, As, and Cr from cementitious waste using PHREEQC. *Journal of Hazardous Materials*, A125(1-3):45–61.
- Hamel, S. C., Buckley, B., and Liou, P. J. (1998). Bioaccessibility of Metals in Soils for Different Liquid to Solid Ratios in Synthetic Gastric Fluid. 32(3):358–362.
- Hiller, E., Petrák, M., Tóth, R., Lalinská-Voleková, B., Jurkovič, , Kučerová, G., Radková, A., Šottník, P., and Vozár, J. (2013). Geochemical and mineralogical characterization of a neutral, low-sulfide/high-carbonate tailings impoundment, Markušovce, eastern Slovakia. *Environmental Science and Pollution Research*, 20(11):7627–7642.
- Jain, R. K., Cui, Z. C., and Domen, J. K. (2016). Chapter 1 - Introduction. In *Environmental Impact of Mining and Mineral Processing*, pages 1–15. Butterworth-Heinemann, Boston.
- Jamieson, H. E. (2011). Geochemistry and mineralogy of solid mine waste: Essential knowledge for predicting environmental impact. *Elements*, 7(6):381–386.
- Jamieson, H. E., Walker, S. R., and Parsons, M. B. (2015). Mineralogical characterization of mine waste. *Applied Geochemistry*, 57:85–105.
- Karadaş, C. and Kara, D. (2011). In vitro gastro-intestinal method for the assessment of heavy metal bioavailability in contaminated soils. *Environmental Science and Pollution Research*, 18(4):620–628.
- Kastury, F., Smith, E., and Juhasz, A. L. (2017). A critical review of approaches and limitations of inhalation bioavailability and bioaccessibility of metal(loid)s from ambient particulate matter or dust. *Science of the Total Environment*, 574:1054–1074.

- Kastury, F., Smith, E., Karna, R. R., Scheckel, K. G., and Juhasz, A. (2018). An inhalation-ingestion bioaccessibility assay (IIBA) for the assessment of exposure to metal(loid)s in PM10. *Science of The Total Environment*, 631-632:92–104.
- Kirpichtchikova, T. A., Manceau, A., Spadini, L., Panfili, F., Marcus, M. A., and Jacquet, T. (2006). Speciation and solubility of heavy metals in contaminated soil using X-ray microfluorescence, EXAFS spectroscopy, chemical extraction, and thermodynamic modeling. *Geochimica et Cosmochimica Acta*, 70(9):2163–2190.
- Król, A., Mizerna, K., and Bożym, M. (2020). An assessment of pH-dependent release and mobility of heavy metals from metallurgical slag. *Journal of Hazardous Materials*, 384(October 2019).
- Kumpiene, J., Giagnoni, L., Marschner, B., Denys, S., Mench, M., Adriaensen, K., Vangronsveld, J., Puschenreiter, M., and Renella, G. (2017). Assessment of Methods for Determining Bioavailability of Trace Elements in Soils: A Review. *Pedosphere*, 27(3):389–406.
- Lottermoser, B. (2017). *Environmental Indicators in Metal Mining*. Springer International Publishing, Aachen, Germany.
- Moncur, M. C., Jambor, J. L., Ptacek, C. J., and Blowes, D. W. (2009). Mine drainage from the weathering of sulfide minerals and magnetite. *Applied Geochemistry*, 24(12):2362–2373.
- NEN 7349 (1995). Leaching characteristics of earthy and stony building and waste materials - Leaching tests. Determination of the leaching of inorganic components from building and monolithic waste materials with the cascade test. Technical report.
- Oomen, A. G., Rompelberg, C. J., Bruil, M. A., Dobbe, C. J., Pereboom, D. P., and Sips, A. J. (2003). Development of an in vitro digestion model for estimating the bioaccessibility of soil contaminants. *Archives of Environmental Contamination and Toxicology*, 44(3):281–287.
- Palumbo-Roe, B., Wragg, J., Cave, M. R., and Wagner, D. (2013). Effect of weathering product assemblages on Pb bioaccessibility in mine waste: Implications for risk management. *Environmental Science and Pollution Research*, 20(11):7699–7710.
- Parkhurst, D. L. and Appelo, C. (1999). User’s guide to PHREEQC (version 3) – a computer program for speciation, batch-reaction, one-dimensional transport and inverse geochemical calculations.

- Pelfrêne, A., Cave, M. R., Wragg, J., and Douay, F. (2017). In vitro investigations of human bioaccessibility from reference materials using simulated lung fluids. *International Journal of Environmental Research and Public Health*, 14(2):1–15.
- Poggio, L., Vrščaj, B., Schulin, R., Hepperle, E., and Ajmone Marsan, F. (2009). Metals pollution and human bioaccessibility of topsoils in Grugliasco (Italy). *Environmental Pollution*, 157(2):680–689.
- Roussel, C., Néel, C., and Bril, H. (2000). Minerals controlling arsenic and lead solubility in an abandoned gold mine tailings. *Science of the Total Environment*, 263(1-3):209–219.
- Ruby, M. V., Davis, A., Schoof, R., Eberle, S., and Sellstone, C. M. (1996). Estimation of lead and arsenic bioavailability using a physiologically based extraction test. *Environmental Science and Technology*, 30(2):422–430.
- Šebek, O., Ettler, V., Strnad, L., Vonásková, V., Drahota, P., and Mihaljevič, M. (2014). Evaluation of 7 digestion methods for multielement analysis of industrial materials with anomalous composition: example of Pb smelter flue gas residues.
- Souissi, R., Souissi, F., Ghorbel, M., Munoz, M., and Courjault-Radé, P. (2015). Mobility of Pb, Zn and Cd in a soil developed on a carbonated bedrock in a semi-arid climate and contaminated by Pb–Zn tailing, Jebel Ressas (NE Tunisia). *Environmental Earth Sciences*, 73(7):3501–3512.
- US EPA (1992). Method 1311 Toxicity Characteristic Leaching Procedure (Report). Technical Report July 1992, U.S. Environmental Protection Agency (EPA), Washington, DC.
- Van Campen, A. (2019). *Mineralogical and chemical characterisation of a mine waste site at Plombières [Unpublished Master’s Thesis]*. PhD thesis, KU Leuven.
- van der Sloot, H. A. and van Zomeren, A. (2012). Characterisation leaching tests and associated geochemical speciation modelling to assess long term release behaviour from extractive wastes. *Mine Water and the Environment*, 31(2):92–103.
- Wragg, J., Cave, M., and Gregory, S. (2014). The solid phase distribution and bioaccessibility of arsenic, chromium, and nickel in natural ironstone soils in the UK. *Applied and Environmental Soil Science*, 2014:1–12.
- Wuana, R. A. and Okieimen, F. E. (2011). Heavy Metals in Contaminated Soils: A Review of Sources, Chemistry, Risks and Best Available Strategies for Remediation. *ISRN Ecology*, 2011:1–20.