

Česká zemědělská univerzita v Praze

Czech University of Life Sciences,
Prague, Czech Republic

Faculty of Agrobiological Sciences, Food and Natural Resources

Department of Soil Science and Soil Protection



Universität für Bodenkultur Wien

University of Natural Resources and Applied Life Sciences,
Vienna, Austria

Department of Forest- and Soil Sciences

Institute of Soil Research



Universität für Bodenkultur Wien

Environmental stability of the processing waste from a sulfide mining district of Namibia, Africa – A model rhizosphere solution approach

Master's thesis

Natural Resources and Environment, CULS

&

Natural Resources Management and Ecological Engineering, BOKU

Bc. Jaroslav Novotný

Supervisors:

doc. RNDr. Aleš Vaněk, Ph.D., CULS Prague, Czech Republic

Priv.-Doz. Dr. Markus Puschenreiter, BOKU Vienna, Austria

Statement

I declare that I wrote my diploma thesis “Environmental stability of the processing waste from sulfide mining district of Namibia, Africa – A model rhizosphere solution approach” by myself and I have used only the sources mentioned at the end of the thesis.

In Prague 11th March 2015

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2015

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Year of Soils

“The soil is the great connector of lives, the source and destination of all. It is the healer and restorer and resurrector, by which disease passes into health, age into youth, death into life. Without proper care for it we can have no community, because without proper care for it we can have no life.”

Wendell Berry

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Zusammenfassung

Das im Norden Namibias gelegene Berg Aukas ist ein historisches Bergbaugebiet in dem bis zu 1978 Zn, Pb und V Erze abgebaut sowie abgerüstet wurden, bevor es ohne jegliche Sanierungsmaßnahmen stillgelegt wurde. Der durchgeführte Prozess der kinetische Batch-Auslaugung, des durch Aufschwemmung entstandenen Mülls (Abfallerz) in 500µM Zitronen-, Oxal sowie Essigsäure Lösungen, zielte darauf ab, die Freisetzung von Spurenmetallen in dem Rhizosphären ähnlichen Milieus zu simulieren. Es wurde angenommen, dass durch das Vorkommen von niedermolekularen organischen Säuren, welche durch das Wurzelsystem der Bodenvegetation in der verlassenen Bergbauregion (>30 Jahre) entstehen, die Solubilisierung von Spurenmetallen angeregt wird und dadurch Endprodukte der Metalauslaugung in den Unterboden oder in das Grundwasser gelangen.

Die Ergebnisse des Experimentes lassen vermuten, dass nur Zitronensäure einen signifikanten Einfluss auf die Alteration der Metalle und die daraus entstehende Mobilisierung der Schadstoffe hat. Die maximalen Auflösungsraten lagen bei 2% Cd, 0,8 Pb und 0,3% Zn. Der Einfluss von Oxal- sowie Essigsäure hingegen war vernachlässigbar und vergleichbar mit dem Einfluss von Wasser. Die Ausfällung von neugeformten Eisenhydroxiden sowie Eisenoxiden, gefolgt von der Resorption von Pb, Cd und letztendlich Zn, weist auf den prinzipiellen Mechanismus der Metallstabilisierung hin, welcher von dem Modell prognostiziert wurde.

Mit Rücksicht auf die Anwesenheit von niedermolekularen organischen Säuren, kann man daraus schlussfolgern, dass nur eine relativ geringe Konzentration von Metallen aus dem Abfallerze entwichen ist. Unter Einbeziehung neutraler bis hin zu leicht alkalischen Bedingungen (geringfügig organisch), stellt die Auslaugung von Zn, Pb und Cd, verglichen mit der luft- und wasserübertragenen Verschmutzung, nur eine geringe Umweltbelastung für angrenzende Ökosysteme und Gemeinschaften dar.

Stichworte

Metall; Rhizosphäre; Niedermolekulare organische Säuren; Lösung; Auslaugung; Abfallerz

Summary

Berg Aukas located in northern Namibia is a historic mining area, where Zn, Pb and V ores were mined and roasted on site until 1978, when the mine was closed without any remediation. Kinetic batch leaching of the flotation wastes (tailings) in 500 μM solutions of citric, oxalic and acetic acids was performed to simulate the release of trace metals in the rhizosphere-like environment. There was an assumption that low-molecular-weight organic acids (LMWOAs), originating from roots of cover vegetation on the abandoned mine tailings dams (>30 years), may induce trace element solubilisation and thus cause metal leaching to subsoil layers or groundwater.

The experiment demonstrated that only citric acid may significantly contribute to mineral waste alteration accompanied by contaminant mobilization; the maximum dissolution rates corresponded to 2% (Cd), 0.8% (Pb) and 0.3% (Zn) of their total amounts. While in contrast, the role of oxalic and acetic acids in the complex process of contaminant leaching was mainly negligible and/or comparable with water. The precipitation of newly formed Fe (hydr)oxides followed by the re-adsorption of Pb, Cd and eventually Zn from the model solutions seems to be the principal mechanism which leads to the metals stabilization, as predicted by speciation modelling.

Conclusion is that the relatively low concentrations of metals were released from the flotation waste in the presence of model LMWOA solutions in Berg Aukas tailings dams. Considering the neutral and slightly alkaline (and lowly organic) conditions in tailings, leaching of Zn, Pb and Cd, being the main contaminants in the flotation waste, to subsoil layers or groundwater promoted by LMWOAs poses a relatively low environmental risk for the area compared to wind and water-borne dispersion of contaminated tailings with potential negative consequences for adjacent ecosystems and residential communities.

Keywords

Metal; Rhizosphere; Low-Molecular-Weight Organic Acids; Solution; Leaching; Flotation Waste

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1 Introduction

Metals/metalloids represent a significant natural integral part of all soils where their presence in the mineral fraction comprises a store of potentially-mobile metal species as important components of clays, minerals and iron/manganese oxides that, in turn, have a dramatic influence on soil geochemistry (Violante et al., 2008). A root-soil interface, called rhizosphere or rhizospheric soil, receiving much organic compounds exudated by roots and the associated microbial community including low-molecular-weight organic acids (LMWOAs), which are prevalent on the Earth surface (Xiao and Wu, 2014), is given great concern in speciation analysis of these trace metals/metalloids (Ahumada et al., 2001).

However, metals/metalloids origin in soil can be both pedogenic and anthropogenic (Bolan et al., 2008). Therefore, metals/metalloids loading in soil is a function of the parent material and associated weathering processes plus subsequent atmospheric and water-borne deposition caused by human activities such as mining and smelting of metalliferous ores, electroplating, gas exhaust, energy and fuel production, fertilizer and pesticide application, and others (Robinson et al., 2005). High concentrations of trace metals/metalloids and the potential for acid mine drainage (AMD) generation from sulfide oxidation contribute to the severe impairment of most metal mine tailings left behind mineral processing operations (Lottermoser, 2010).

The main role of LMWOAs is in their complexing abilities through metal chelation and, what is crucial, for the mobilization of these trace elements with all related consequences for the attached ecosystem compartments (Magdziak and Drzewiecka, 2011). In soil-like environments as old and unmanaged tailings are, chemical complexation with organic ligands, both biotic and abiotic, are one of a great importance in controlling metals/metalloids bioavailability, leaching behavior and toxicity (Violante et al., 2008).

Therefore, mine tailings (flotation waste) deposits may represent a serious threat to the ecosystems and human health. The main aim of conducted laboratory study is to determine whether the concentrations of trace metals/metalloids in leachates from mine tailings could be affected by the presence of LMWOAs associated to ongoing vegetation succession on the abandoned mine tailings in Berg Aukas (>30 years).

2 Objectives

Present study aims to test the environmental stability of the flotation waste (tailings), derived by sulfide ore separation, from the former Zn–Pb–V mining district, situated in northern Namibia, Africa – Berg Aukas. The goal is to determine how LMWOAs influence the dissolution/weathering of tailings and how they affect the release/mobility of metal/metalloids contaminants in the soil. Following two main hypotheses are subject for evaluation:

- i) LMWOAs, potentially released by plants growing on mine tailings, may induce trace element solubilisation and thus cause metal leaching to subsoil layers or groundwater;
- ii) there are different mobilization mechanisms responsible for trace element solubilization upon the presence of specific LMWOA compounds.

To assess the hypotheses, the role of LMWOAs in the soil-like system, characterizations and environmental impacts of tailings are reviewed and further studied for the given locality. The experimental part consists of batch leaching experiments with LMWOAs solutions (citric, oxalic and acetic acid) at concentrations relevant to rhizospheric soil solutions (500 μM). The leaching experiments with duration of up to 168 h were supplemented by thermodynamic speciation-solubility modeling. Obtained data together with given mineralogical investigations are base to clarify the speciation and possible solubility controls on metal/metalloids release in these solutions simulating rhizosphere environment.

3 Literature Review

3.1 Low-Molecular-Weight Organic Acids in Soil Environment

Plant roots, being in the intimate contact with and constantly extracting nutrients and water from and exuding materials into the soil, substantially modify the physical, chemical, and physicochemical properties of boundary between the outermost root tissues and the particles of soil, which are closest to them (Conklin, 2008). The turnover of fine roots, leakage or diffusion of molecules across the cell membranes (i.e., exudation), and sloughing off of cells and tissue fragments during the root growth are pathways for release of plant assimilates from the roots (Frey, 2007).

The composition of these compounds, known as the root exudates or the rhizodeposits, varies with respect to the signals of biotic or abiotic origins (Reuben et al., 2008). Rhizodeposits comprise about 200 organic substances (Fisher, 2010). For most of them our understanding of their real significance in the soil is very limited, but currently this issue is enormously studied and the number of new publications corresponds to it. These substances can be discharged into the rhizosphere actively as secretions or passively as diffusates from the intact root cells (Fisher, 2010).

It has been examined on the range of different plant species that anywhere 1 g of produced root can release from 10 to 250 mg of carbon or about from 10 to 40% of photosynthetically fixed carbon (McNear, 2013). Group of organic carbon forms is very diverse and can have the most influence on rhizosphere processes and phenomena (Jones et al., 2009). On the opposite such example of inorganic carbon form is HCO_3^- .

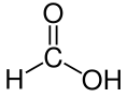
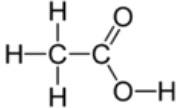
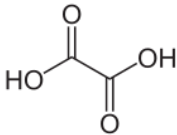
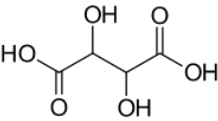
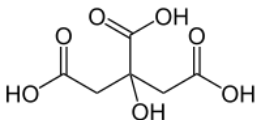
Among the root exudates, expressly released to breakdown both organic and inorganic components in soils, so that they may be assimilated, the low molecular weight organic substances are one of the major portion, with a molecular weight of about 200 g mol^{-1} or less such as carboxylic acids, carbohydrates, amino acids, lipids and phenols (Farrar et al., 2003). Their chemical compositions differ according to the configuration of functional groups. Simple carboxylic acids are one of the most important and belong to the subgroup of the low-molecular-

weight organic acids (LMWOAs) (White, 2013). The functional group determines the acidity and solubility of LMWOAs.

In the present broad spectrum of organic compounds occurring in the rhizosphere, particular attention is focused on LMWOAs (Drzewiecka et al., 2012). Importance of LMWOAs is based on their metal chelating/complexing properties for mobilization of mineral nutrients and other elements (Wu et al., 2003). Furthermore, they are weak substances with a wide range of food, industrial and pharmaceutical applications for home or industrial use.

The five aliphatic organic acids that are found commonly associated with the microbial activity or the rhizosphere chemistry including the pH values, at which the most acidic carboxyl group has a 50% probability to be dissociated in aqueous solution, are listed in Table 1. They have different numbers of functional groups, pH_{dis} and ligand forms.

Tab. 1: Common aliphatic organic acids in soils (Sposito, 2008).

Name	Chemical Formula	pH_{dis}	Molar mass
Formic acid		3.8	46.03 g mol ⁻¹
Acetic acid		4.8	60.05 g mol ⁻¹
Oxalic acid		1.3	126.07 g mol ⁻¹
Tartaric acid		3.0	150.09 g mol ⁻¹
Citric acid		3.1	210.14 g mol ⁻¹

3.1.1 Importance of LMWOAs for Soil and Plants

In the view of their high solubility, they are highly bioavailable and based on the high turnover rates of LMWOAs, they are an important member in the soil carbon cycle representing source of labile carbon (Fisher, 2010). LMWOAs have a significant role in the pedogenic processes, particularly in the weathering of soils (Ettler et al., 2009) and in the translocation of Fe and Al (Lundstrom et al., 2000).

Through the acidification effect, chelation and oxidation-reduction reactions, LMWOAs can within the rhizosphere influence the metal solubility in soils and plants uptake (Zhang et al., 2005). It is possible that genetic variation in the capacity to secrete organic anions can be exploited to beneficially manipulate the rhizosphere (Neumann et al., 2009). Analogously same may be applied even for phytoremediation purposes.

Deprotonated LMWOAs, in the form of organic anions, play an important role in the plant uptake of many nutrients (e.g., P, Fe, Mn, Zn, K) essential for the proper functioning of the organism. Higher plants evolved mechanisms of elements uptake, distribution and accumulation, which because of the shared similar chemical and physical properties are also applicable for non-essential metals/metalloids (e.g., Cd, Pb, As) (Kutrowska and Szelag, 2014).

In recent years, much research work has concentrated on the effect of LMWOAs, often identified as dissolved organic carbon (DOC), as these dissolved substances tend to chelate metals/metalloids and to inhibit their adsorption from the solid surfaces, thus increasing the metal availability (Antoniadis et al., 2005). However, increased metal adsorption by soil in the presence of organic ligands was also observed (Schwab et al., 2008).

In case of desorption of trace metals/metalloids from a contaminated soil, the potential of natural, aliphatic or aromatic LMWOAs to provide metal concentrations in solution that are environmentally safe and high enough to increase the efficiency in plant uptake seems very promising for phytoextraction method but it is also limited (Nascimento, 2006).

Many of scientific papers are devoted to characterize and understand the LMWOAs effects in the soil environment. Next chapters deal only with a small fraction of this topic emphasizing their role in the mobility of inorganic contaminants in the soil environment. For understanding

the chemical reactions that toxic contaminants in contact with the soil environment are exposed to, it is therefore important at first to characterize LMWOAs more into the details and review their life cycle.

3.1.2 Classification and Chemical Properties of LMWOAs

Present carboxylic (alkanoic) acids practically trivial named from Table 1 belong to the aliphatic (fatty) series of organic compounds and naturally contain at the end of a carbon chain at least one carboxyl functional group written as $-\text{CO}_2\text{H}$ or $-\text{COOH}$. Next to this studied group there are other important functional groups of LMWOAs, for example, $-\text{CH}=\text{CH}-\text{OH}$, $\text{Ar}-\text{OH}$, $-\text{CH}_2-\text{OH}$, $-\text{CH}_2-\text{O}-\text{CH}_2-$ and $-\text{CH}_2-\text{NH}_2$.

As shown in Table 1, their molecular masses can range from 46.03 g mol^{-1} for formic acid up to $210.14 \text{ g mol}^{-1}$ for citric acid. LMWOAs size is smaller than 1 nm (van Hees et al., 2005). The effect of LMWOAs depends on the distance (concentrations) that they can diffuse away from the rhizoplane (Singh and Mukerji, 2006). These substances act as both Bronsted-Lowry acids (proton donors) and Lewis bases (electron pair donors). Carboxyl group is involved in the solubility and the acidity of the organic acid by releasing hydrogen so it is present in the soil as an easily reactive anion (Strobel, 2001).

Carboxyl group and the carboxylate anion are stabilized by the resonance structures, but the stabilization of the carboxylate anion is much greater and induces dissociation contributing to the acidity character of carboxylic acids by releasing a proton as Bronsted-Lowry acids. In Table 1, there are presented pH values, at which the most acidic carboxyl group has a 50% probability to be dissociated, and are right equal to their dissociation constants (pKa).

Under the acidic conditions, pH lower than the pKa, the acid will occur more in its neutral form. However, in this state LMWOAs can react as a ligand and form complexes by donating a free electron pair as Lewis base. The carboxylates are dissociated at the cytosolic pH of root cells and exuded to the surrounding soil as anions. Therefore their contribution to the rhizosphere acidification thus largely depends on a net influx of excess cations, while alkalization occurs for a net influx of excess anions over cations (Hinsinger et al., 2009).

Through chelation and H^+ promoted reactions LMWOAs enhance the dissolution of soil minerals and facilitate the plant uptake of dissolved elements (Ettler et al., 2009). Depending on the degree of dissociation (efficiency), and the number of carboxylic groups, ligands of LMWOAs have negative charges, thereby enabling the complexation of nutrient cations in the soil solution and their relocation from the soil (Jones and Darrah, 1994; Drzewiecka et al., 2012).

Behaviour of investigated formate, acetate (monovalent anions), oxalate, tartrate (divalent anions), and citrate (trivalent anion) in soil differs. Trivalent anions have a high tendency to be absorbed into the soil solid phase (Jones et al., 2003). Citric acid, as a tricarboxylic acid, is one of the most effective in enhancing the dissolution (Ettler, 2004).

3.1.3 LMWOAs Life Cycle and Fate in Soil

The amount and composition of organic acids exuded into the rhizosphere varies with the different plant species, cultivar, age of plant, and environmental conditions including soil properties (Robert and Berthelin, 1986). For example, plants growing in soil rich in NH_4^+ produce lower amounts of organic acids than plants growing in soil rich in NO_3^- (Jones, 1998). Total concentration of organic acids in the soil solution ranges from 10 to 5000 $\mu\text{mol L}^{-1}$ ($=\mu\text{M}$) and therefore is low (Sposito, 2008). In case of LMWOAs, concentration rises even only up to 1000 $\mu\text{mol L}^{-1}$ due to removal of LMWOAs by many concurrent processes (Strobel, 2001; van Hees et al., 2005).

There are 44 studies of citric acid in soil solutions with 75% of these having citric acid levels less than 20 μM with some occasional exceptions in the 300 to 650 μM range (Strobel, 2001). The highest concentrations of LMWOAs are present in the upper soil layers and correspond, as explained, to plant roots activity and associated microorganisms, where LMWOAs carbon concentration represents up to 10 % of DOC (Strobel, 2001). It is just in the close vicinity of the sites firstly exposed to dispersion and deposition of potentially toxic metals/metalloids in form of fine-grained tailings, driven by water and wind erosion as reported in the area of Berg Aukas.

Low molecular-weight exudates are secreted in the zone of some 10 mm behind the root cap and this is the site of maximum nutrient absorption by the root (Lavelle and Spain, 2001). Besides the rhizodeposition, other main sources of LMWOAs in the soil environment are decomposition of plant and microorganism residues, as well as, humified organics (Fisher et al., 2010). Once LMWOAs enter the soil solution, they face a variety of fates, mainly microbial utilization and decomposition to CO₂, sorption by mineral particles and soil organic matter, or leaching (Fisher et al., 2010).

Despite LMWOAs potential instability in the soil environment they significantly affect dissolution and alteration processes (Jones, 1998). Even so rapid mineralization of LMWOAs, such of those present in Table 1, caused by microbial biodegradation and other mentioned processes leading to very short half-lives of a few minutes to few hours in the soil solution, they are continually replenished by the incessant life cycles of microorganisms and plants (Sposito, 2008). However, the turnover time might slow down when the LMWOAs exudates are associated with metals (Arwidsson et al., 2010).

3.1.4 Main Element Fluxes and Pools within Soil

Open pores between the soil particles and roots form a net system filled by gases and soil solution, allowing material exchange between solid and liquid phases, and plants too (Harrison, 1999). The basic view over the major organic acid fluxes and pools associated with rhizosphere processes is shown in Figure 1 and allows understanding of fundamental interrelations in processes discussed below.

It is clear that the huge majority of these processes are happening through the soil solution. Knowledge about what elements are dissolved or can be dissolved under certain environmental conditions in soil solution is a key factor for both managing agronomic plant nutrition and phytoremediation practices.

Importance of liquid fraction as the medium where contact occurs between soil reservoir of nutrient ions, trace metal/metalloids ions and plant roots is long recognized, but it is thought that the metal speciation and ionic activity play more significant role than the total amount of

a dissolved metal in determination of plant metal uptake (Wu et al., 2003). In the form of free ions, ion pairs, ions complexed with organic anions and ions complexed with organic macromolecules and inorganic colloids, there are present most easily plant available elements in the soil solution (Kidd et al., 2009).

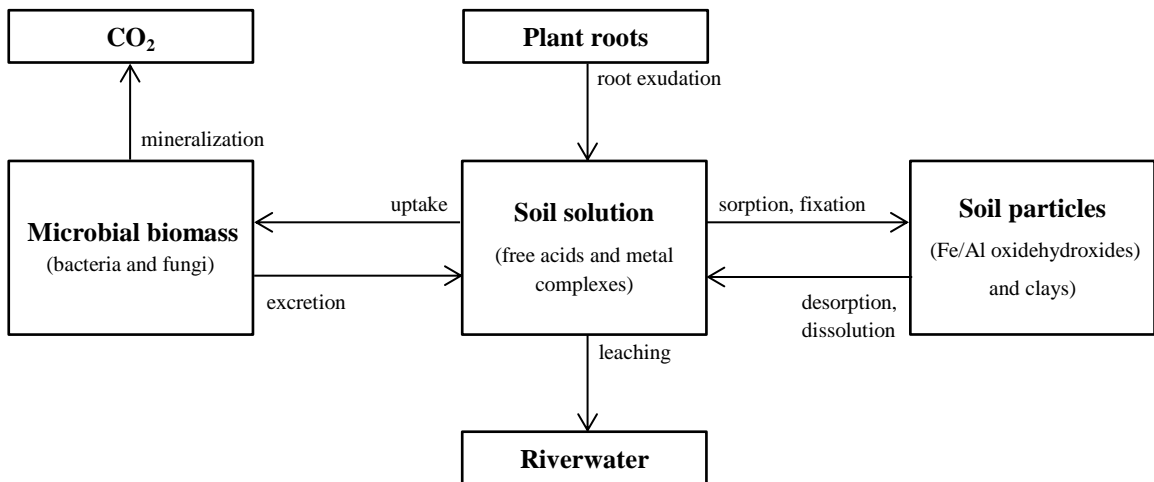


Fig. 1: Schematic diagram showing the major organic acid fluxes, pools and related processes in soil (Jones, 1998).

Metals complexed by organic matter, sorbed onto or occluded within oxides and clay minerals, co-precipitated with secondary minerals (e.g., Al-, Fe-, Mn-oxides, carbonates and phosphates, sulfides) representing so called exchange complex are important metal pools from solid phase (Markert, 2009; Kidd et al., 2009). The least readily bioavailable metals/metalloids are tightly bound to the soil structure, for example as a secondary component of the crystal lattices of primary minerals (Markert, 2009).

3.1.5 Rhizosphere Soil

The term rhizosphere, a word originating in part from the Greek word rhiza (ρίζα), meaning root, was originally proposed in 1904 by German agronomist and plant physiologist Lorenz Hiltner for the area of bacterial growth around legume roots (McNear, 2013). His observa-

tions were initially based on the growth of symbiotic nitrogen-fixing bacteria stimulated by the nitrogen released from nodules of legume root (Kennedy and Luna, 2005; Herlihy, 2008).

Rhizosphere is next to the upper soil horizons a major soil site involved in the transfer of matter and the energy in the soil humification and the weathering processes. The rhizospheric microenvironment represents the habitat with specific ecological advantage for those organisms that are exclusively associated with the roots of plants (Reuben et al., 2008). Pursuant to Hiltner it is the “Einflusssphäre der Wurzel” (Hinsinger et al., 2009).

Rhizosphere is a narrow zone of soil surrounding and influenced by the roots of vascular plants, in which the kinds, numbers, or activities of microorganisms considerably differ from that of the bulk soil (Foth, 1990; Kennedy and Luna, 2005), as indicated by the rhizosphere/soil ratio for a soil in Table 2. It is dynamic microenvironment within the soil, where there are fluxes of energy, nutrients and molecular signals between the plant roots, the soil constituents, and the soil microorganisms.

Tab. 2: Microbial diversity of major groups in the rhizospheric and nonrhizospheric zones of soil (Giri et al., 2005).

Organism	Rhizosphere soil (microbes/g dry soil)	Nonrhizosphere soil (microbes/g dry soil)	R/S ratio
Bacteria	1200 10 ⁶	53 10 ⁶	23
Actinomycetes	46 10 ⁶	7 10 ⁶	7
Fungi	12 10 ⁵	1 10 ⁵	12
Algae	5 10 ³	27 10 ³	0.2

Microenvironmental conditions in the rhizosphere are generally characterized by high microbial activity, increased carbon dioxide, decreased oxygen, decreased water and nutrient content, and decreased pH developed by intense biological activity owing to the release of root exudates, which may increase the activity and populations of most soil microorganisms (Conklin, 2005; Kennedy and Luna, 2005). Due to the inherent complexity and diversity of plant root systems, the rhizosphere is not a region of definable size or shape, but instead, consists of chemical, biological and physical gradients forming the properties varying both radially and longitudinally along the root (McNear, 2013).

Present region is thus a poorly defined space extending some <1–2 mm from the root surface for microbial populations and immobile nutrients, to one extending some >10–20 mm in the case of some mobile nutrients and water, or to even farther distances for volatile compounds released from roots (Herlihy, 2008; Gregory, 2006a; Kennedy and Luna, 2005).

Depending on the factor considered, its size differs spatially and temporally and may range from a fraction of mm to several tens of mm (Gregory, 2006b). Therefore a significant proportion of the soil volume may be comprised by the rhizosphere and be an important source of functional diversity within the soil (Lavelle and Spain, 2001). At this soil-root interface the root environment is rapidly changing especially in the respect to soil physical conditions such as mechanical properties, moisture, aeration and temperature (Gliński et al., 2008).

Due to the influx of plant-derived labile organic matter into the soil, there is a proliferation of microorganisms in the rhizosphere (Herlihy, 2008). Whole range of organic substances, released by the roots and providing a rich source of the nutrients for the microbial community, cause one of a major gradient in the rhizosphere and arises from those cells involved in the cell elongation and the lateral root formation (Kennedy and Luna, 2005).

Microbial population in the rhizosphere differ quantitatively as well as qualitatively from the surrounding bulk soil and its abundance, activity, community composition and diversity depends on a number of abiotic and biotic factors of that particular ecological niche (Ranganayaki et al., 2006), and is especially associated with the plant species (Herlihy, 2008).

Interactions of microorganisms with biotic and abiotic soil components results in multitude of chemical transformations. Root-inhabiting rhizosphere microorganisms have a major influence on plant nutrition as well as concomitant metal/metalloids circulation. Associated biogeochemical cycling of metals, and related elements, can result in their mobilization and immobilization depending on the process involved (Gadd, 2005). This issue is introduced and described in next chapters. Despite the potential consequences of physical changes inherent to the rhizosphere systems for the movement of water and solutes, they have been much less studied than biological or chemical changes (Gregory, 2006b).

Even in the terms of transformation and control of soil contaminants by phytoremediation practices, better understanding of the rhizosphere processes is a vital precondition for manag-

ing plants abilities in the modification and the control of local environments to achieve objectives useful for humankind and the ecosystems involved.

3.2 Risks Associated with Ore Processing

Although negative impacts from mining activities are inevitable everywhere, the limited capacity of local African communities to administer and monitor the sector, together with inadequate legal, regulatory, and administrative frameworks interlinking unmanaged environmental impacts, human rights violations, and obstacles to sustainable development in mining, even more obstruct adopting relevant prevention and mitigation measures (UN ECA, 2011).

Due to the economic pressures and lower environmental awareness, African communities are particularly exposed to the detrimental effects on public health, agriculture, and environment from legacy of soil contamination generated by the former mining and metallurgical industry (UN ECA, 2011; Mapani and Kříbek, 2012). General lack of waste management across the developing countries adds mine waste and tailings to the serious environmental problems as well as limits available land use options (UN ECA, 2011).

All previously mentioned weaknesses may then lead to even additional and unnecessary new environmental burdens. Such situation is documented in Berk Aukas itself, where by-produced slag and partly tailings from the ore processing are used for the construction of local roads causing wide dissemination of these contaminated materials throughout the area of southeastern and southern part of the adjacent agricultural fields and old Berg Aukas farm houses (Mapani et al., 2009).

3.2.1 Metals/Metalloids Contamination

Past mining activities together with associated processes remobilized and redistributed in the large local scales quantities of trace metals/metalloids within the Earth's crust, thus extremes in trace elements variation can be gradually transmitted from soil via food chain, with often

undesirable consequences for human and animal health, through water and food crops (Davies and Mundalamo, 2010).

In soil there is sometimes even natural content of trace metals/metalloids, mostly in the form of minerals and/or oxides not easily available to microorganisms, plants or animals, present in the big amounts (Haider and Schäffer, 2009). But those generated via man-made processes tend to be more mobile, hence bioavailable than pedogenic or lithogenic ones (Kuo et al., 1983; Kaasalainen and Yli-Halla, 2003).

Soils accumulating trace metals/metalloids above the defined background values (i.e. adaptation of the concrete ecosystem to the ambient background concentrations) pose risks to human health, plants, animals and ecosystem media. Some elements have no biological relevance and others are essential trace elements for plant, animal or human nutrition, that become toxic when present beyond a certain concentration level (Kamal et al., 2010). Despite part of them belongs into the vital group of essential or beneficial minerals for living organisms, they may cause serious environmental contamination and pollution (D'Amore et al., 2005).

Widely used term heavy metals, associated with contamination and potential toxicity or ecotoxicity, has wide range of meanings given by different authors, so it is effectively meaningless to use (Duffus, 2001). The primary environmental concerns connected to the historic ore processing focus on unmanaged remnants of waste material deposited in spacious waste rock heaps, slag deposit and tailings dams with elevated levels of trace elements as present in Berg Aukas locality.

Metal/metalloids pollution in the soils has become one of the most serious environmental threat (Alkorta et al., 2004). These wastes contain significant amounts of trace metals/metalloids, which might be possibly mobilized with all related consequences for the attached ecosystem compartments (Mapani and Křibek, 2012). The main processes and attributes, originating in physical, chemical and biological interfacial interactions, influencing metals/metalloids bioavailability and mobility are (Violante et al., 2008):

- i) sorption or desorption processes on/from soil compartments and soils;
- ii) metals/metalloids precipitation and reduction-oxidation reactions in soil solution and onto surfaces of soil components;
- iii) their chemical speciation, fractionation and bioavailability.

Concerns about the additional direct or indirect input of metals/metalloids contaminants into the soil environment followed by transfer to other ecosystem compartments and the food chain are related to their toxicological potential connected with (Haider and Schäffer, 2009):

- i) impact on soil organisms and plants;
- ii) effects on aquatic organisms due to runoff by surface and ground waters;
- iii) and uptake via food chain potentially affecting humans by reducing food quality of crops and animal products;
- iv) impact on animal health through accumulation in organs of cattle, birds, mammals.

3.2.2 Mineral Processing Wastes

Before any metallurgical extraction the metalliferous ore is mined and then treated in a physical process so called beneficiation or mineral processing as shown in Figure 2. Wastes generated by Zn–Pb–V operations are mine water, waste rock and tailings (EC JRC 2004). Their constituents may include base metals, sulfides, or other elements found in the ore, and any chemical additives used in mineral processing. Most wastes from beneficiation are disposed of in tailings impoundments (US DOE, 2002).

Large amounts of overburden and mine development rock detached to reach the ore is returned underground or stored on the site as waste rock heaps (Foth, 1990). Present study tested environmental stability of the floatation wastes derived by sulfide ore separation in Berk Aukas locality, therefore this chapter emphasises review of mineral processing wastes to the disposed tailings coming from a mill, washery or concentrator that removed their economically valuable parts (i.e. ore mineral concentrate) to be processed by pyrometallurgical methods such as smelting (US DOE, 2002; Gallaway and Palmer, 2004).

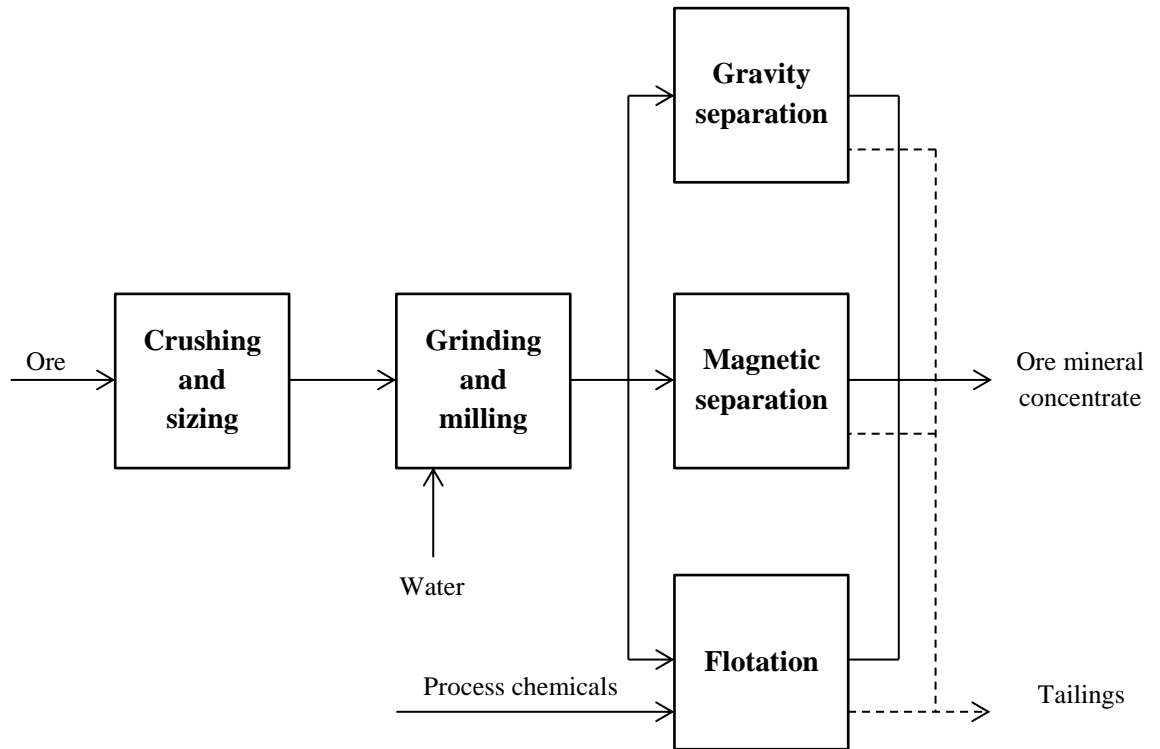


Fig. 2: Simplified flow-chart of a mineral processing operation, in which ore is processed to yield an ore mineral concentrate and tailings (Lottermoser, 2010).

During the operations, surface and underground water collecting in mine workings are pumped out of the site as necessary to allow access to the ore body for extraction and partly used in beneficiation operations (Lottermoser, 2010). Potential exists for water exposed to the sulfur-bearing minerals in an oxidizing environment to acidify, known as acid mine drainage (AMD), also referred to as acid rock drainage, when pumping stops upon exposure to oxidizing conditions. This may cause trace metals/metalloids mobilization in the remaining ore body exposed by mining and contamination of surface and ground water (US DOE, 2002).

Metal contamination having its origin in AMD depends both on the type and amount of sulfide mineral oxidized, as well as the type of gangue minerals. The primary ingredients for acid generation are as follows (Akcil and Koldas, 2006):

- i) sulfide minerals;
- ii) water or a humid atmosphere;
- iii) and an oxidant, particularly oxygen from the atmosphere or from chemical sources.

Residual material from one flotation circuit is often used as feed for a subsequent float to concentrate another mineral as in the case of former Zn–Pb–V mining district Berk Aukas (US DOE, 2002). Flotation tailings are disposed of on the surface and stored in the engineered structures so called tailings storage facilities or tailings dams at mine workings (Jantzer, 2008). They are pumped in the form of solution or as sediment slurry to these specially built and sealed areas to prevent seepage to the surrounding environment, where they are usually spread out to dry (Gallaway and Palmer, 2004; Wuana and Okieimen, 2011).

3.2.2.1 Tailings Characteristics

Characteristics of tailings diverge due to the variations in origin, mineral processing of the ore and deposition methods. As 70-99% of the ore is leftover (Jantzer, 2008) and recoveries of valuable minerals are never 100% efficient, tailings represent one of the most voluminous waste at mine operation and always contain small amounts of valuable minerals. The bulk quantity of tailings is very fine ground barren rock with significant amounts of trace elements present in the mined ore and substantial quantities of added compounds used during extraction (Mileusnic et al., 2004).

The particulate suspension of these fine-grained sediment-water slurries consist of process chemicals, tailings liquids and tailings solids (20-40 wt.%), and vary considerably in their chemical and physical characteristics (US DOE, 2002). For froth floatation, as a common beneficiation technique, frothers (e.g. pine oil, propylene glycol, aliphatic alcohols, cresylic acid) and collectors (e.g. amine, fatty acids, xanthates) are used to recover sulfides (EC JRC, 2004).

Tailings liquids are highly variable, change over time, and contain strongly elevated concentrations of various elements and process additives. Evaporative concentration causes secondary mineral precipitation at and below the surface (Lottermoser, 2010). Tailings grain size ranges from 2 μm to 2 mm and tailings solids often consist of 70-80 wt.% sand-sized particles and 20-30 wt.% finer clay-sized particles (Jantzer, 2008). Grain size parameter determines rate of wind and water erosion, substantially their resistance to them, and also influences settling of particles in tailings dams (Ettler, 2012).

Two principal primary minerals containing Zn and Pb are sphalerite (ZnS) and galena (PbS) frequently found together along with other sulfide minerals (US DOE, 2002). As the result of beneficiation tending to change the physical and chemical characteristics of extracted ore and attempt of tailings compartments to reach the equilibrium through almost endless chain of reactions, tailings significantly differ to the mined ore not only in terms of grain size, but also in mineralogy and chemistry (EC JRC, 2004).

In addition, tailings are exposed to compaction, cementation, recrystallization, mineral dissolution and formation through physical and biological processes assisted by microorganisms. Therefore, tailings liquids contain elements as dissolved species and composition of tailings solids, in potentially soluble or insoluble forms, may consist of (Lottermoser, 2010):

- i) primary ore and gangue minerals;
- ii) secondary minerals formed during weathering;
- iii) chemical precipitates formed during and after mineral processing;
- iv) and chemical precipitates formed after disposal in the tailings storage facility.

Despite limiting nutrient deficiency and high availability of Pb and Cd in base material, flotation tailings provide an unusual diversity of base and parent materials, and when left to their own fate as in Berk Aukas area, they undergo certain soil development enhanced by partial topdressing with a layer of soil transported from surrounding area by wind and/or water providing a favourable base for the natural vegetation succession process (Lavelle and Spain, 2001). However, in arid and semiarid environments these sites do not develop normal soil structure or support desirable establishment of a plant cover (Ramírez-Andreotta et al., 2011).

3.2.2.2 Environmental Impacts of Tailings

Mine wastes generally introduce anthropogenic weathering profiles to the critical zone with absence of vegetation cover lasting decades after mining cessation, which makes them vulnerable to wind and water dispersion of particulate matter to adjacent ecosystems and residential communities (Hayes et al., 2014). These redistributed concentrations of metals/metalloids persist in soils and tailings after their introduction for a long time.

However, changes in their chemical forms with varying bioavailability, mobility and toxicity are possible (Wuana and Okieimen, 2011). Environmental and human health risks assessment of contaminated sites is not based only on persistence and bioaccumulation of metals/metalloids soil contaminants anymore, but focuses also on their solubility, toxicity, natural occurrence (concentrations above/added to background), essentiality (deficiency/excess), speciation and bioavailability (Chapman, 2008).

The physical and chemical characteristics of tailings favor metal/metalloids mobilization to the environment. Considering thesis topic, two main environmental concerns with tailings are wind and water-borne dispersion of tailings particles. Tailings, small in grain size, including inhalable size fraction of diameters generally below 10 μm (PM10), contain chemicals and metals/metalloids, which may be environmentally harmful when released by oxidation and weathering reactions (Jantzer, 2008).

Fine tailings, which enhance metals/metalloids adsorption while enhancing sulfide oxidation, can more rapidly generate acid and are more likely to be distributed by wind and water (Plumlee and Nash, 1995). In fact, the size of particles, having influence on specific surface area of tailings, produced by milling and beneficiation processes can dramatically affect the extent of environmental impact. Due to high specific surface area, tailings tend easily to oxidize and leach out then waste rocks (Ettler, 2012).

Reclamation techniques of closure sites by covering with moraine (i.e., dry cover) or with a high water table (i.e., wet cover) are aimed to prevent ingress of water and oxygen into the tailings and avert wind and water erosion (Prasad et al. 2005). Spread of tailings particles from uncovered repositories, through a combination of wind dispersion and water erosion, result in measurable elevated levels of trace metals/metalloids in wildlife and humans even large distances from the tailings site (Ramírez-Andreotta et al., 2011).

Human health effects and toxicity vary with particle size, and in general, particles greater than PM10 impact back of throat and digestive tract, but particles smaller than PM10 are breathed into and can accumulate in lungs (Ramírez-Andreotta et al., 2011). Exposure over a longer period of time (i.e., chronic) to trace metals/metalloids is normally due to food chain transfer, while immediate (i.e., acute) poisoning is rare, but possible through ingestion or dermal contact (Sherameti and Varma, 2010).

Impact of trace metals/metalloids on soil and the surrounding environment is not proportional to their total concentrations (Vaněk et al., 2005). Only the soluble and mobile fraction has the potential to leach or to be taken up by plants and enter the food chain (Robinson et al., 2005). That is why the chemical form (i.e., species), in which trace metals/metalloids are displaced into the receiving environmental system, may render it more bioavailable than their concentrations (D'Amore et al., 2005).

The most threats come from trace metals whose forms in soil are positively charged cations (e.g. Pb, Cd, Zn) and metalloids whose forms in soil are combined with oxygen and are negatively charged (e.g. As) (Sherameti and Varma, 2010). Pb and Cd have no function within organism and can be tolerated at low concentrations while being toxic at higher concentrations; Zn is necessary for the function of enzymes and also essential as growth factor (Haider and Schäffer, 2009). Although several metals are essential for biological systems as it is present Zn, obtained concentrations from soil contaminated sites frequently exceed those required as nutrients or background levels (McGrath et al., 2001).

In case of Zn high values may cause phytotoxicity or injury to soil microorganisms while increased levels of non-essential Cd represent human and animal health risk for contaminating food crops by transfer from soil (Zhao et al., 2003). Cd in soils attracts wide concern because of its easy bio-assimilation together with high toxicity (Wang et al., 2013). Zn and Cd are ubiquitous pollutants that tend to occur together at many contaminated sites (Alkorta et al., 2004). Cd rarely inhibits plant growth (Poniedziałek et al., 2010). As is associated with skin damage, higher risk of cancer and problems with circulatory system (Wuana and Okieimen, 2011).

3.2.3 Metals/Metalloids Mobilization by LMWOAs

Bioavailability and bio-toxicity of trace metals/metalloids are alleviated or enhanced by adsorption or desorption, in which the main mechanisms involve chelating or complexing with LMWOAs (Xiao and Wu, 2014). LMWOAs (citrate) have significantly greater effects on increased mobilization of metals/metalloids contaminants in soil than high-molecular-weight organic acids (fulvic acid, peat water) (Ettler et al., 2009). In the two inter-linked ways

LMWOAs may affect the metals/metalloids distribution in contaminated soils by metal mobilization through forming soluble metal complexes and by present enhanced bioactivity in general through the inherent production of biodegradable compounds with easily accessible carbon source for the soil microorganisms (Arwidsson et al., 2010).

LMWOAs anions function as organic ligands and they can regulate metal/metalloids speciation and bioavailability through increased mobilization of them from contaminated soils by (Kim, 2013):

- i) replacing adsorbed metals at the soil surface through ligand-exchange reactions;
- ii) dissolving metal-oxides from surfaces that adsorbed metals;
- iii) and forming metal-organic complexes in solution.

Generally, trace elements are very reactive, able to interact or bind with different organic ligands composed of C, H, O, N, P or S (Kutrowska and Szlag, 2014). The affinity of ligand to metals to make a complex depends on the type of metal; for example the affinity for metal cations complexed by organic matter is in the following order: $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Fe}^{2+} > \text{Pb}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Mn}^{2+} > \text{Zn}^{2+}$ (Adriano, 2001). With increasing pH, carboxyl, phenol, alcohol and carbonyl functional groups in soil organic matter dissociate, thereby increasing their affinity for metal cations (Hartemink et al., 2008).

In contrast, in the event of anthropologically introduced metals/metalloids contaminants, which mostly do not undergo unlike organic contaminants microbial or chemical degradation and persist for a long time (Bolan et al., 2008), entailing potential environmental and human health risks, immobilization might be desirable. Reducing the mobility of contaminants in the soil and hence their availability to plants includes adsorption onto the surface of minerals, formation of stable complexes with organic ligands, ion exchange, precipitation (particularly salts) and co-precipitation (Kumpiene et al., 2008).

Adsorption occurs when a charged solute species (ions) are attracted to the charged soil surface by electrostatic attraction and/or through the formation of specific bonds (Mott, 1981). Formation of stable complexes can also contribute to metal/metalloids retention in soil. Precipitation appears to be the predominant process of metal/metalloids immobilization in alkaline soils with high pH in the presence of anions such as sulphate (SO_4^{2-}), carbonate (CO_3^{2-}), hydroxide (OH^-) and phosphate (HPO_4^{2-}) (Hartemink et al., 2008).

It depends on the actual combination of many factors and it is extremely difficult to predict which effects plants actually have on element mobilization/immobilization under a given set of conditions (Jacob and Otte, 2003). The bioavailability of metal/metalloids in the soil to plant is driven by the result of such a set of qualities and quantities associated mainly with soil properties itself, pollutant characteristics and effects of plant roots and the associated microbial community (Wenzel, 2009).

It primarily regards metal contents, chemical forms of metal compounds, soil properties as organic matter content, carbonate, or phosphate content, granularity, pH and environmental conditions as temperature and humidity, concentrations of other trace elements and relative biological activities (Zhao et al., 2012). Chemical solubility of trace elements is a prerequisite for their physical mobility and bioavailability for organisms within/from the soil environment (Robinson et al., 2005).

4 Materials and Methods

4.1 Berg Aukas

Investigated former mining district is situated in the Otavi Mountain Land (northern Namibia). The Berg Aukas mine, famous for excellent and large descloizite crystals, is located approximately 19 km east of the town of Grootfontein. Presence of zinc on top of the hill now known as Berg Aukas Mine Kopje (GPS: S 19° 30' 40.89", E 18° 15' 40.45") was discovered in 1913 (Figure 3). Zn–Cu–Pb vanadate ores (descloizite, mottramite and vanadinite) in the Otavi Mountainland once were considered the greatest vanadium deposits in the world (Boni et al., 2007). First mining activities started in 1920 and stopped in 1928 by reaching groundwater level.



Fig. 3: Eastern view over the abandoned mine and metallurgical complex at Berg Aukas (Weatherly International, 2011: <http://goo.gl/YhgN2e>).

The Zn–Pb–V Berg Aukas mine was then operating from 1958 with a very small scale of operations, milling only 11,000 t of ore monthly, as a low tonnage high grade producer of lead, zinc and vanadium (Misiewicz, 1988). In 1978 the mine was due to economic factors, when

price of zinc fell to \$550 per ton, abandoned and flooded despite significant documented mineralization still in situ – the ore reserves at the time of mine closure were estimated as 1.65 Mt at an average grade of 17% Zn, 5% Pb and 0.6% V₂O₅ (Misiewicz, 1988).

Principal ore minerals include (von Bezing et al., 2008; CAR, 2014):

- sphalerite (ZnS; 64% Zn, low in Fe, trace Cd and Ge);
- willemite (Zn₂SiO₄; 59% Zn), smithsonite (ZnCO₃; 52% Zn);
- galena (PbS; 87% Pb, with Ag);
- pyrite (FeS₂);
- descloizite ((Pb, Zn)₂(OH)VO₄; 51% Pb, 16% Zn, 12.6% V);
- cerussite (PbCO₃; 78% Pb, <1% of ore minerals);
- minor mottramite (PbCu(VO₄)(OH));
- and vanadinite (Pb₅(VO₄)₃Cl).

4.1.1 Site Description

After the end of mining activities unmanaged remnants of spacious waste rock heaps, slag deposit and tailings dams were left behind (Tab. 3). Today, the facilities of former mine are used as training center of the National Youth Service. In order to be self-sustaining, the organization is involved in crop production within 308 ha of agricultural fields located adjacent to the tailings dams and southward from the former mine. Local people and trainees consume a great part of grown white and yellow maize, vegetables (spinach, cabbage, onions, green peppers) and fruits (water melons) (Křibek and Kamona, 2006).

Tab. 3: Areal extent and volume of anthropogenic deposits in the Berg Aukas area (Křibek and Kamona, 2006).

Type of anthropogenic deposit	Area	Volume
Waste rocks deposit I	11 460 m ²	91 680 m ³
Waste rocks deposit II	1 300 m ²	5 200 m ³
Slag deposit	35 211 m ²	1 756 055 m ³
Tailings dam I	53 000 m ²	265 000 m ³
Tailings dam II	15 700 m ²	78 500 m ³

Berg Aukas is situated in flat-lying topography with elevations ranging from 1,350 m to 1,380 m above mean sea level (CAR, 2014). Two mine tailings were built using downstream wet deposition method and process water drained later in semiarid conditions (Šrůček et al., 2014). Tailing storage facilities in the form of unfenced and uncontrolled paddocks are located in the north out of former mine in the close vicinity of water reservoirs and agricultural fields, and are one of the main sources of pollution for surrounding area. No remediation practice has been carried out and the remobilization of fine wastes has led to the significant contamination of local soils and vegetation (Mapani et al., 2010).

4.1.2 Environmental Conditions

The total volume of flotation tailings is estimated at 343,500 m³ in the area of 68,700 m² and their height is about 15 m (Mapani et al., 2010). Slopes are about 30° steep and on the top there are flat areas partly covered by scattered vegetation. Around mine tailings there are not any permanent water bodies. The groundwater analysis is available only for mine shaft located southeast of mine tailings. Groundwater is of Ca–Mg–HCO₃ type with alkaline pH, Zn concentration of 2.34 mg L⁻¹, V concentration below 0.005 mg L⁻¹ and is used for irrigation (Mapani et al., 2010).

The eastern part of the tailings dam is partly covered by self-seeding grass and acacia which may point at its earlier origin. During the rainy season, fine-grained tailings are being washed in larger quantities into adjacent ephemeral streams, therefore in many sites the area is highly water eroded (Křůbek and Kamona, 2006). Most precipitation falls with a long-term annual average of 556 mm from December to March. However, in the 2010/2011 season precipitation reached 956 mm. In the meanwhile top of the mine tailings can be temporarily flooded, but in the course of sampling in June 2012 such situation was not observed.

The Grootfontein District has a dry semi-arid climate of subtropical latitudes with typical hot summers and mild winters. The annual mean temperature for Grootfontein is 26°C with the mean monthly temperature varying from 25° to 16°C throughout the year (CAR, 2014). The maximum average temperature in Berg Aukas is in October reaching almost 32.1 °C (Šrůček et al., 2014). The wind direction is predominantly south westerly with average speeds of be-

tween 3 and 5 m s⁻¹ blowing 40% of the time (CAR, 2014). A zone of high risk to human health was delineated due to severe trace metals/metalloids contamination of surface soils, as well as high accumulation of trace elements in crops, south and east of the abandoned mining district (Mapani et al., 2010).

4.2 Flotation Waste from Berg Aukas

4.2.1 Sampling of Mine Tailings

A mixed sample of reddish tailings from the surface layer (0–20 cm) of flotation waste dams was collected using a hand-drilling auger with an inner diameter of 4 inches, as the top of fine-grained tailings outwash tends to be deposited in local ephemeral drainage streams, especially during the dry season. The samples were preserved in polyethylene (PE) bags.

4.2.2 Geochemical and Mineralogical Composition of Flotation Waste

There are no data on composition of flotation waste during or shortly after deposition. Additional data on geochemistry and mineralogy of studied waste material were provided by colleagues from Faculty of Science of the Charles University in Prague.

4.2.2.1 Bulk Composition of Solid Samples

In order to determine bulk element concentrations in the samples, a pseudo-total digest according to the standardized *aqua regia* extraction protocol (ISO 11466:1995) was performed. A flame atomic absorption spectrometer (FAAS, Varian SpectrAA 280 FS, Australia) was used for element determination; three replicates were applied.

During the analytical procedure, deionized water (Milli-Q Element, Millipore, France) and chemicals of analytical grade (Lach-Ner, Czech Republic) were used. The quality control

(QC) was evaluated using the standard reference material (CRM 7001, Analytika, Czech Republic) with the RSD <10%.

To determine CEC, the soil was saturated with Ba²⁺ cations using 0.1 M BaCl₂. Barium was subsequently released using MgSO₄ (ISO 11260:1994). Excess Mg present in the solution was determined using FAAS. The concentrations of TIC and total S (S_{tot}) were determined by catalytic oxidation (1350 °C) using Metalyt CS 500 and Metalyt CS 530 elemental analyzers (ELTRA, Germany). Particle size distribution was determined by the hydrometer method (Gee and Bauder, 1986). The pH at the point of zero charge was assessed by the immersion technique of Fiol and Villaescusa (Fiol et al., 2009).

Table 4 shows detailed data relating to the physico-chemical characteristics. The textural analysis of contaminated soil shows the preponderance of sand fraction (82%), followed by silt (16%), then clay (2%). Table 5 gives an overview of the bulk concentrations. Major contaminants in the waste are Zn, Pb and Cd, with a maximum for Zn (>5 wt.%). Clay as the potentially most reactive fraction in relatively low content.

Tab. 4: Physico-chemical parameters of the flotation waste.

Clay (%)	2	pH_{H2O}	8.25	CEC (cmol kg⁻¹)	0.90
Silt (%)	16	pH_{KCl}	7.63	TIC (%)	8.35
Sand (%)	82	pH_{ZPC}	7.70	S_{tot} (mg kg⁻¹)	8.0

Tab. 5: Chemical composition of the flotation waste (mg kg⁻¹) (n = 3).

Fe	18,700 ± 900	Pb	11,900 ± 500	Cu	148 ± 23	V	808 ± 73
Mn	429 ± 50	Zn	58,500 ± 700	Cd	320 ± 19	As	138 ± 36

4.2.2.2 X-ray Powder Diffraction (XRD) of Heavy Fraction of Sediments

Data on waste mineralogy (Table 6) were obtained using the X-ray diffraction method (PANalytical X'Pert Pro diffractometer, Netherlands) applied on bulk and pre-concentrated samples (separated in 1,1,2,2-tetrabromethane as a heavy liquid with a density of 2.96 g

cm⁻³). The analyses were performed under the following conditions: CuK α radiation, 40 kV, 30 mA, step scanning at 0.02°/150 s in the range of 5–80° 2 θ . Qualitative and semiquantitative analysis was performed with X'Pert HighScore software 1.0d, equipped with the JCPDS PDF-2 database (ICDD, 2003).

Tab. 6: Mineralogical composition of the flotation waste.

Dolomite	CaMg(CO ₃) ₂	45%
Calcite	CaCO ₃	7%
Quartz	SiO ₂	41%
Magnesite	MgCO ₃	4%
Willemite	Zn ₂ SiO ₄ 3%	3%
Goethite	FeOOH	*
Hematite	Fe ₂ O ₃	*
Descloizite	(Pb, Zn) ₂ (OH)VO ₄	*
Smithsonite	ZnCO ₃	*

The reference intensity ratio (RIR) method was used for the abundance estimation (%) of major crystalline phases. Contaminant-bearing trace phases detected in heavy mineral fraction are indicated (*) below without an indication of abundance.

Flotation waste consist of 56% carbonates, mainly dolomite, (CaMg(CO₃)₂) accompanied by calcite (CaCO₃) and magnesite (MgCO₃). In the latter part is 41% quartz (SiO₂) and 3% willemite (Zn₂SiO₄). In the heavy mineral fraction of this material, apart from willemite, other metal-bearing phases derived from primary or weathered ore are also present, namely smithsonite (ZnCO₃), descloizite (Pb,Zn)₂(OH)VO₄) as well as primary/secondary Fe oxides goethite (FeOOH) and hematite (Fe₂O₃).

4.2.3 Leaching Experiments and Speciation Modeling

4.2.3.1 Leaching of Samples

Experimental approach was adopted from Ettler et al. (2009). Batch leaching experiments were performed at a solid-to-liquid (S/L) ratio of 1/10 (2 g of air dried waste in 20 mL of solution) in 500 μ M LMWOAs to study environmental stability of flotation waste. Citric, oxalic

and acetic acids were used to simulate environment of rhizosphere as these acids commonly occur in rhizospheric soil solutions (Evangelou et al., 2008; Jones, 1998). Value of 500 μM was selected to simulate the higher concentration range observed in soil solutions (Jones, 1998). Deionized water was used as the fourth leaching medium for comparison.

LMWOAs solutions were prepared from chemicals of analytical grade (Lach-Ner, Czech Republic) and deionized water. Set of leaching experiments was conducted at a constant laboratory temperature of 21 ± 3 °C in acid cleaned 50-mL centrifugation tubes (PP) shaken on an end-overend shaker for 0.5, 1, 2, 12, 24, 48 and 168 h and then sampled. Shaker was covered with aluminium to prevent LMWOA photodegradation.

The experiments were performed in two replicates for all sampling times and treatments. At each sampling time, the suspensions were centrifuged for 5 min (at 3500 rounds min^{-1}) and the pH and temperature were measured immediately using a pH-meter handylab pH 11 (Schott, Germany).

Leachates were then filtered to 0.45 μm using nylon syringe filters (Nalgene, USA) and analyzed for major and trace elements (Ca, Fe, Mn, Zn, Pb, Cd, Cu, As) and anions (Cl^- , F^- , NO_3^- , PO_4^{3-} , SO_4^{2-}) using a combination of FAAS and IC (ICS 1600, Dionex, USA). The quality of the FAAS measurements was controlled using the standard reference material NIST 1640a (National Institute of Standards and Technology, USA); the accuracy was <10% RSD.

The residual LMWOA concentrations in the leachates were analyzed using IC (ICS 1600, Dionex, USA). Alkalinity was measured by back titration using a Schott TitroLine Easy (Schott AG, Germany) automatic microtitrator and 0.05 M HCl.

4.2.3.2 Geochemical Modeling

All of the analytical data were further used for speciation modeling and element complexation. The PHREEQC-2 speciation-solubility code (Parkhurst and Appelo, 1999), version 2.18 for Windows, was used to determine the metal and As speciation in the experimental solutions and the saturation indices (SI) of possible solubility controlling phases. The minteq.dat

database was used for all the calculations and was supplemented by stability constants of Me-LMWOA complexes from Smith et al. (2004).

Results

4.3 Leaching of Flotation Waste

Results of leaching experiments are given in Figure 4, which shows the time-dependent patterns of pH and concentrations of Zn, Pb and Cd in LMWOAs leachates (500 μM) and deionized water. In citric suspensions obtained maximum metal concentrations were distinctly in the decreasing order $\text{Zn} > \text{Pb} > \text{Cd}$. In general, the highest metal concentrations were observed during first 2 h of leaching. Concentrations of Zn and Cd reached maximum after 1 h of leaching in all tested solutions followed by their gradual decrease. In the case of elevated concentrations of Pb, effect of citric acid suspension exceeded others and showed significant dependence of Pb mobilization on presence of citrate.

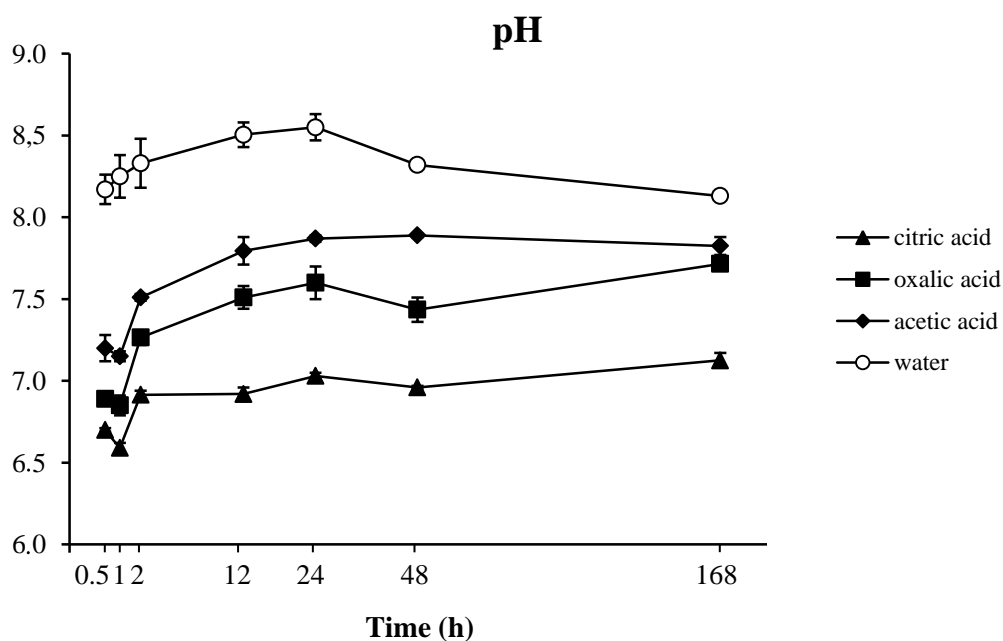


Fig. 4: Time-dependent patterns of pH and concentrations of Zn, Pb, and Cd in LMWOA leachates; i.e., in 500 μM solutions of citric, oxalic and acetic acids and deionized water as a control. Depicted values are means and standard deviations of 2 replicates.

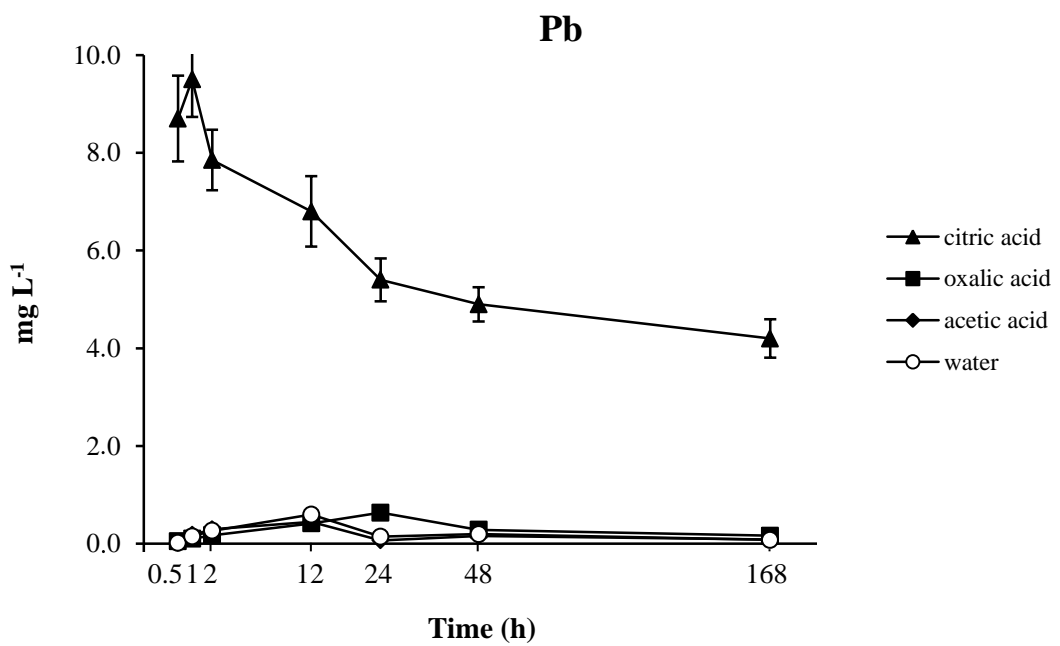
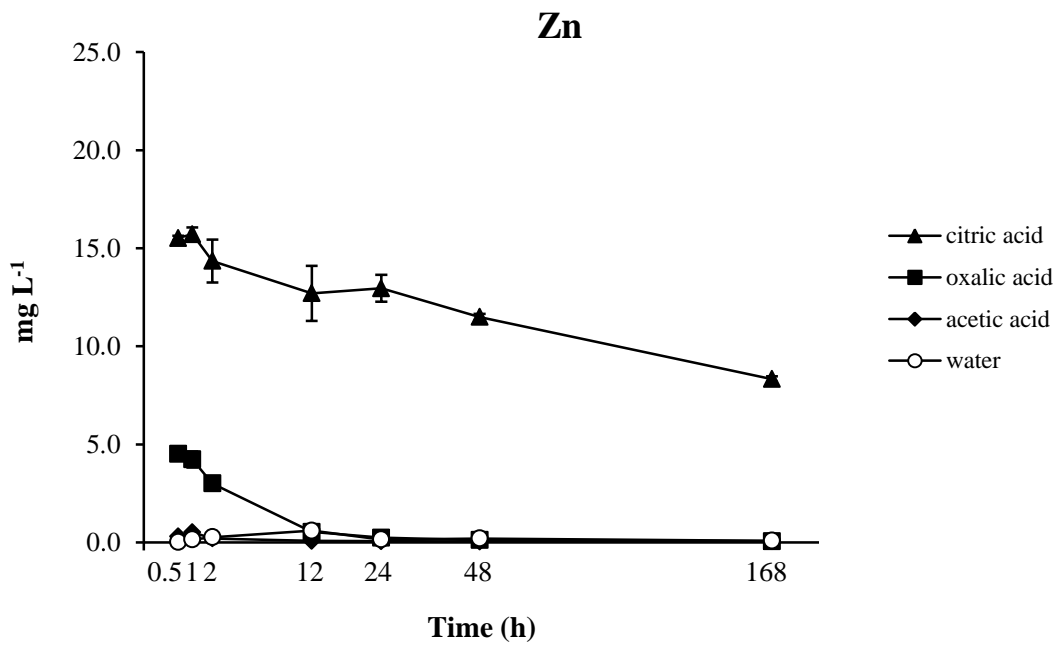


Fig. 4: (continued).

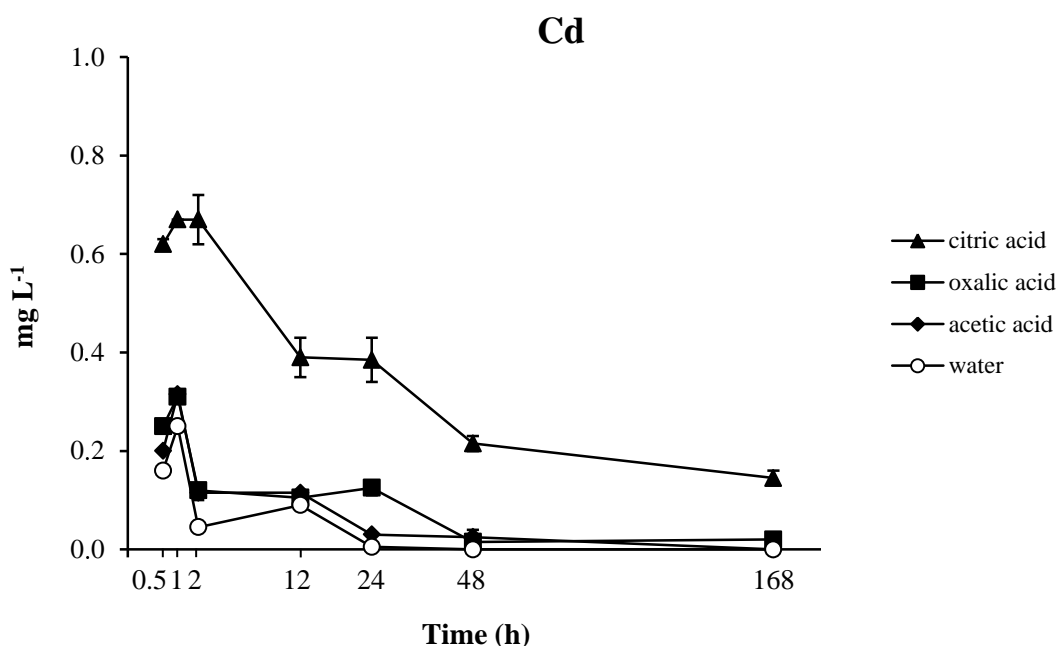


Fig. 4: (continued).

Generally, distinct effect of citrate on metal mobilization could be observed in all cases. The maximum concentrations accounted for 16 mg Zn L⁻¹, 10 mg Pb L⁻¹ and 0.6 mg Cd L⁻¹. Interestingly, the amount of metals mobilized by oxalate and acetate were negligible or very low, and there was also no difference compared with water solution. Despite a relatively large amount of V in the material (~800 mg kg⁻¹) mentioned in Table 5, very low V concentrations were present in the leachates (<0.2 mg L⁻¹).

The initial pH values of the suspensions (i.e., after 1 h of leaching) were significantly lower in the LMWOAs solutions compared to water (8.3) and reached 6.6 (citrate), 6.9 (oxalate), 7.2 (acetate). There was slight increasing pH trend observed in LMWOAs solutions until 24 h of leaching, when values were rather stable; with a minimum for the citrate (7.0). At the end of experiment (after 168 h), the pH values of all samples ranged between 7.1 and 8.1. The lowest pH (7.1) could be observed for the citrate. This findings indicated close-to-neutral or slightly alkaline conditions in all suspensions.

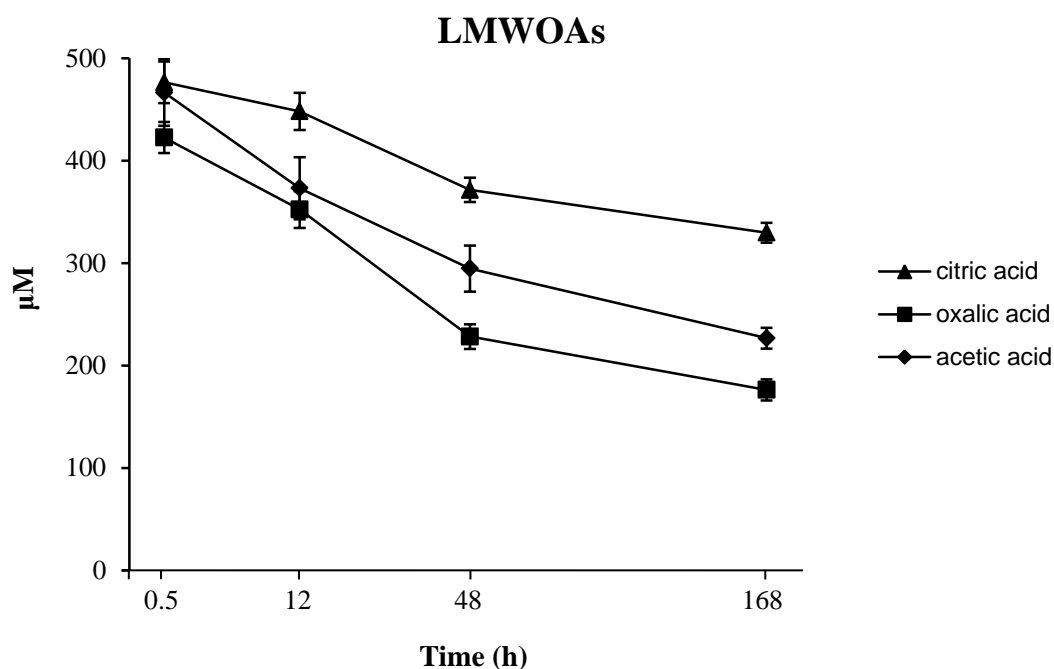


Fig. 5: Concentration of free LMWOAs (citrate, oxalate and acetate; determined by IC) during the waste leaching as a function of time. Depicted values are means and standard deviations of 2 replicates.

Figure 5 shows time-dependent degradation of all the acids and their residual concentrations during soil samples leaching, which have in common gradual slight decrease with time. After 48 h more than 25% of citrate, 40% of acetate and 50% of oxalate were decomposed. Concentration of oxalate and acetate followed the same trend. In the end of experiment after 168 h up to 60% for oxalate, 50% for acetate and only 30% for citrate were degraded.

Table 7 shows concentration of inorganic and organic ligands after 12 h of leaching. Inorganic ligands were found at similar portions in all leachates as they origin in soil; with the highest concentration of SO_4^{2-} ($\sim 90 \text{ mg L}^{-1}$) and Cl^- ($10\text{--}19 \text{ mg L}^{-1}$). Concentrations of organic ligands decreased from citrate to acetate (85 mg L^{-1} , 31 mg L^{-1} and 22 mg L^{-1} respectively).

Tab. 7: Concentration and limit of detection (LOD) of inorganic/organic ligands (mg L⁻¹) as determined by IC after 12 hours of leaching (mean, n = 2).

LMWOA	Citrate	Oxalate	Acetate	LOD
F ⁻	0.55	0.18	0.27	0.004
Cl ⁻	18.91	15.66	10.23	0.010
NO ₂ ⁻	<LOD	0.04	<LOD	0.018
NO ₃ ⁻	5.56	6.21	12.68	0.031
SO ₄ ²⁻	90.72	85.49	87.31	0.020
PO ₄ ³⁻	0.34	0.22	0.53	0.082
Citrate	84.70	<LOD	<LOD	0.064
Oxalate	<LOD	31.01	<LOD	0.022
Acetate	<LOD	<LOD	22.01	0.027

<LOD – below the limit of detection

4.4 Speciation Calculations

The calculations estimate the fate of trace elements and ligands in the leachates at certain conditions and gives limited information about the possible compounds in solutions and their ratio amounts. The most important results of speciation modeling using a chemical analysis of a water to calculate the distribution of aqueous species by employing an ion-association aqueous model are SI for minerals, which indicate whether a mineral should dissolve or precipitate (Anderson 2009):

- i) minerals with a SI equal to zero are said to be in equilibrium with the liquid phase.
- ii) those with positive SI are termed supersaturated, indicating they are favored to precipitate from solution;
- iii) and those with negative SI termed unsaturated, indicating that they are favored to dissolve in solution.

SI for predicted solubility controls in the leachates are reported in Table 8 which clearly indicates whereas no secondary Zn-bearing or Cd-bearing phases were predicted. In citrate leachates saturation indices were slightly negative for anglesite (PbSO₄), ferrihydrite (Fe(OH)₃) and strengite (FePO₄·2H₂O), but they might also indicate equilibrium when analytical errors are considered. Citrate solution was unsaturated with respect to calcite (CaCO₃)

and smithsonite (ZnCO_3). In contrast, citrate leachate was saturated or supersaturated by Pb-bearing phases, Fe-bearing phases and hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$).

Tab. 8: Mean saturation indices ($n = 2$) of selected solubility-controlling phases as calculated by PHREEQC-2 for leachates obtained after 12 h of extraction. Oversaturation of the leachates with respect to the solid phases is indicated in bold.

Phase	Formula	Citrate	Oxalate	Acetate
Anglesite	PbSO_4	- 0.24	- 2.25	- 3.24
Calcite	CaCO_3	- 2.26	- 1.45	0.06
Cerussite	PbCO_3	0.92	- 0.11	0.20
$\text{Fe}(\text{OH})_{2.7}\text{Cl}_{0.3}$	$\text{Fe}(\text{OH})_{2.7}\text{Cl}_{0.3}$	4.76	6.63	6.70
Ferrihydrite	$\text{Fe}(\text{OH})_3$	- 0.10	1.97	2.18
Goethite	FeOOH	4.29	6.36	6.57
Hematite	Fe_2O_3	13.58	17.73	18.16
Hydrocerussite	$\text{Pb}(\text{OH})_2 \cdot 2\text{PbCO}_3$	2.02	- 0.85	- 0.63
Hydroxyapatite	$\text{Ca}_5(\text{PO}_4)_3\text{OH}$	1.30	3.04	6.63
Lanarkite	$\text{PbO} \cdot \text{PbSO}_4$	1.22	- 1.59	- 2.97
Lepidocrocite	FeOOH	3.42	5.49	5.70
$\text{Pb}(\text{OH})_2$	$\text{Pb}(\text{OH})_2$	0.83	0.02	- 0.38
$\text{Pb}_3(\text{PO}_4)_2$	$\text{Pb}_3(\text{PO}_4)_2$	8.00	3.30	1.80
PbHPO_4	PbHPO_4	1.16	- 0.78	- 1.33
Pyromorphite	$\text{Pb}_5(\text{PO}_4)_3\text{Cl}$	23.95	15.82	12.90
Strengite	$\text{FePO}_4 \cdot 2\text{H}_2\text{O}$	- 0.53	0.41	0.47
Smithsonite	ZnCO_3	- 2.32	- 1.89	- 1.66

Table 9 depicts distribution of contaminant species in leachates after 12 h. Speciation calculations using PHREEQC-2 indicates that Zn was predominantly (92%) present as a negatively charged Zn-citrate⁻ complex in the citrate media, with Zn²⁺ accounting only for little portion (7%) of the total speciation. In contrast, Pb occurred in the citrate solution mainly as Pb²⁺ (43%) and negatively charged carbonate (26%) and sulfate (12%), whereas Pb-citrate⁻ accounted for only 9% of the total speciation. Cd in the citrate leachate was mainly present as Cd-citrate⁻ (62%), Cd²⁺ (31%) and to a lesser extent as neutral CdSO₄⁰ complex.

Tab. 9: Distribution of contaminant species (%) as calculated by PHREEQC-2 for leachates obtained after 12 h of leaching (mean, n = 2).

Cd	Citrate	Oxalate	acetate
Cd ²⁺	31.16	71.87	35.33
CdSO ₄ ⁰	4.64	10.32	4.62
Cd(SO ₄) ₂ ²⁻	0.04	0.10	0.04
CdCO ₃ ⁰	0.27	5.71	49.58
CdHCO ₃ ⁺	0.35	1.87	8.62
CdCl ⁺	1.21	2.32	0.71
CdCitrate ⁻	62.33	0.00	0.00
CdOxalate ⁰	0.00	7.82	0.00
CdAcetate ⁺	0.00	0.00	1.10
Pb	Citrate	Oxalate	acetate
Pb ²⁺	42.84	9.20	1.00
PbSO ₄ ⁰	12.41	2.57	0.26
Pb(SO ₄) ₂ ²⁻	0.06	0.01	0.00
PbCO ₃ ⁰	25.67	50.12	95.95
PbHCO ₃ ³⁺	3.01	1.51	1.55
PbCl ⁺	0.70	0.12	0.01
PbOH ⁺	5.70	4.75	0.95
PbNO ₃ ⁺	0.19	0.05	0.01
PbCitrate ⁻	9.42	0.00	0.00
PbOxalate ⁰	0.00	31.67	0.00
PbAcetate ⁺	0.00	0.00	0.27
Zn	Citrate	Oxalate	acetate
Zn ²⁺	7.20	51.06	38.55
ZnSO ₄ ⁰	0.88	6.01	4.15
Zn(SO ₄) ₂ ²⁻	0.01	0.04	0.03
ZnCO ₃ ⁰	0.05	3.26	43.63
ZnHCO ₃ ⁺	0.08	1.34	9.53
ZnCl ⁺	0.01	0.05	0.02
ZnOH ⁺	0.05	1.51	2.11
Zn(OH) ₂ ⁰	0.00	0.55	1.46
ZnCitrate ⁻	91.71	0.00	0.00
ZnOxalate ⁰	0.00	36.18	0.00
ZnAcetate ⁺	0.00	0.00	0.53

5 Discussion

The characteristic low water through-flux and episodic wet–dry cycles in such arid environments are expected to uphold the persistence of acidity and sulfate that would be leached with AMD at higher pore volume hydrologic flux (Hayes et al. 2014). However, the reddish colour of studied samples and no evidence of original primary sulfides like galena or sphalerite in waste point out that the alternation period after the termination of mining activities (>30 years) was sufficient enough to promote significant natural weathering of mine tailings in surface layer (0–20 cm).

Šráček et al. (2014) actually observed that their oxidation progressed at least to the maximum depth of sampling carried out down to 2.4 m. Major contaminants (Table 5) in the waste were Zn, linked to primary willemite, descloizite and secondary smithsonite, Pb and Cd, with a maximum for Zn (>5 wt.%).

The content of Fe in solid phase was low as a consequence of limited initial presence of Fe-sulfides with accessory of Fe which supports the contention that most of sphalerite was removed from mined ore during mineral processing by flotation. Conversely in case of Pb, dissolution of galena is relatively fast in oxidizing environments (Dold, 2010), therefore Pb present in tailings was partly associated to primary descloizite, while latter portion adsorbed onto or co-precipitated with ferric oxyhydroxides through transformation.

There are slight inconsistencies between chemical and mineralogical data (Table 5 and 6) which apply particularly to Zn and Pb constituents. This finding could be a complex result of three following causes:

- i) relatively high detection limit of XRD for majority of crystalline phases ($\geq \sim 5$ wt.%);
- ii) a portion of trace metals associated (co-precipitated) with primary carbonates and oxides;
- iii) and/or the presence of amorphous/poorly crystalline phases undetectable by XRD and enriched in trace metals.

Prevailing carbonates forming the mineral matrix (Table 6) keep alkaline conditions in the mine tailings (pH 8.3 in water suspension) so as the result tailings are carbonate-neutralized

through evaporation as an important mechanism in the formation of mineral salts. Carbonate minerals play a key role in acid buffering capacity of tailings (Lottermoser, 2010). This finding, together with very low sulphur content, virtually eliminates future environmental risk of AMD that is usually connected with negative impacts on ecosystems through acidity, ferric ion (Fe^{3+}) precipitation, oxygen depletion and release of trace metals such as aluminum (Al^{3+}) or zinc (Zn^{2+}) (Akcil and Koldas, 2006):

In contrast, as carbonate minerals are readily soluble in body liquids, oral ingestion or inhalation of dust containing secondary-carbonate minerals such as smithsonite or cerussite could be harmful to living organisms (Jamieson, 2011; Mapani et al., 2009). Considering results on particle size distribution (Table 4) derived flotation waste is classed as loamy sand with clay as potentially most reactive fraction present in relatively low content (2%), whereas particles generated by ore crushers are generally larger in size than those generated by smelters (Ettler et al., 2012).

The vast majority of Zn, Pb and Cd were present within studied flotation waste in water insoluble forms and their potential release depends on how significantly water soluble LMWOAs in given chemical and mineralogical conditions of tailing samples are capable to transfer them into water soluble metal-LMWOAs complexes (Jones, 1998). The pH of zero point charge (7.7) suggests preferential adsorption of cations at alkaline conditions due to negatively charged surfaces. Very low cation-exchange capacity (0.9 cmol kg^{-1}) is probably connected with small specific areas of present primary phases (Table 6).

An important factor affecting desorption of trace metals in soils is pH as it can change the affinity of sorption sites for metals, the forms of metals and the quantity and species of organic ligands (Qin et al., 2004). The values of time-dependent patterns of pH in tested leachates (6.6 in citrate, 6.9 in oxalate, 7.2 in acetate and 8.3 in water) after 1 h of flotation waste leaching proves through common drop in pH the initial acidic behavior of applied LMWOAs (Figure 4), followed by the pH increase associated to carbonate ion concentrations increase, which are responsible for the buffering capacity of tailings.

However, potential for a partial pH change (i.e., pH increase) is still left through various dissociation/protonation reactions, pH-dependent oxidation/reduction reactions or (re)precipitation of new phases. After 24 h from the beginning of experiment the pH values in all sus-

pension were rather uniform with a minimum for citrate (7.0) and maximum for water (8.1) (Figure 4). Concentrations of organic ligands decreased in order citrate > oxalate > acetate after 12 h of leaching (Table 7).

The detected gradual slight decrease of LMWOAs concentrations shows their time-dependent degradation (Figure 5); up to 60% of oxalate was decomposed after 168 h, whose trend almost identically shows typical resistance between 0.5-12 h as Van Hees et al. (2005) and Oburger et al. (2009) documented. Considering the results of previous study (Vaněk et al., 2012), when up to 90% of individual LMWOAs were degraded accompanied with higher pH increase, it can be suggest that the microbial decarboxylation of organic anions consuming H^+ and liberating OH^- and CO_2 in soils with $pH > 7$ plays a minor role (Yan et al., 1996). However, such a conclusion could be additionally verified by comparison of non-sterile and sterile treatments.

The leaching behaviour of Zn, Pb and Cd, being the main contaminants in the flotation waste, generally shows that the highest metal concentrations were detected in LMWOA solutions after 1 h of leaching (Figure 4), with a distinct effect of citrate on metal mobilization. As far as mobilization of Zn, Pb and Cd is concerned, their maximum measured concentrations in the leachates were 16 mg Zn L^{-1} , 10 mg Pb L^{-1} and 0.7 mg Cd L^{-1} . In contrast, the amounts of metals mobilized by oxalate and acetate were negligible or very low and there was also no difference when compared with water (Figure 4).

Nevertheless, oxalate extracted higher amounts of metals than acetate proving its theoretically higher metal complexation strength. In short, the differences between the complexing abilities of tested LMWOAs, related to their chemical structures (ions of acetate can only form monodentate complexes with metals, while ions of citrate carrying two or three $-COO$ groups can form chelates with 5- or 6- membered ring structure), with trace metal contaminants may be one possible reason for the different trend of metal desorption by LMWOAs in response to pH change related chemical structures (Qin et al., 2004).

Surprisingly, even relatively large amount of V found in the flotation waste ($\sim 800 \text{ mg kg}^{-1}$), very low V concentrations were identified in LMWOA and water leachates ($< 0.2 \text{ mg L}^{-1}$). This limited V release indicates both high stability of V bearing phases and minimum V solubility in the demonstrated rhizosphere-like solution. A significant fraction of V within mine

tailings remains in descloizite, overgrowing other primary minerals such as dolomite and willemite, while mobilized part of V is adsorbed on or co-precipitated with ferric oxyhydroxides (Šrámek et al., 2014).

In short, results of leaching in citrate media (Table 9) show that there were Zn present mainly as a negatively charged Zn–citrate[−] complex (92%), Pb in forms of Pb²⁺ (43%) and negatively charged carbonate and sulfate complexes (26% and 12%, respectively) and Cd as both Cd–citrate[−] (62%) and Cd²⁺ (31%). SI (Table 8) clearly indicates that whereas no secondary Zn-bearing or Cd-bearing phases were predicted, a series of Pb-bearing phases such as cerussite (PbCO₃), lanarkite (PbO·PbSO₄), Pb(OH)₂ and Pb-phosphates could be partially responsible for the time-dependent decrease of Pb concentration in the leachate.

Further possible re-adsorption of metallic species to solid phases in the tailings will depend also on speciation. The key mechanism responsible for the gradual decrease of metals in tested LMWOAs as a function of time (Figure 4) is probably related to the adsorption to newly formed phases, namely Fe (hydr)oxides, which were predicted to precipitate from all the leachates (Table 8) and are typical for neutral or alkaline soil systems in the tropics (Rieuwerts, 2007).

Due to such a close-to-neutral or slightly alkaline conditions (Figure 4) they will as presumably negatively charged surfaces attract positively charged metallic species from the solutions for adsorption. For this reason the decrease of Pb and Cd in citrate solutions could be related to re-adsorption on these phases, whereas Zn will be adsorbed to a lesser extent, because it occurs as negatively charged citrate complexes (Figure 4, Table 9).

A similar phenomenon can be suggested for oxalate and acetate leachates. As Zn and Cd in oxalate leachates were predominantly occurring as free cationic species (Table 9), they could be easily adsorbed to surfaces of Fe (hydr)oxides (Figure 4). Cd in acetate solution reflected the same behavior, because it was mainly present as Cd²⁺ (Table 9, Figure 4). In contrast, Pb predominantly formed neutral complexes in oxalate and acetate solutions (PbCO₃⁰ and/or Pb-oxalate⁰) (Table 9) and this denotes that its leaching behavior is not controlled by sorption, but rather by precipitation of Pb-bearing phases and its leaching curves for all the media are rather flat (Figure 4, Table 8).

6 Conclusion

The effectiveness of LMWOAs (citrate, oxalate and acetate) in mobilizing trace metals (Zn, Pb, Cd), being the main contaminants in the Berg Aukas flotation waste, from contaminated tailings was investigated subject of thesis. Relatively low concentrations of metals were released from the studied flotation waste in the presence of model LMWOA solutions, as expected. However, enhanced metal leaching abilities were observed for citric acid solutions; the maximum portions of mobilized contaminants corresponded up to 2% (Cd), 0.8% (Pb) and 0.3% (Zn) of their total amounts, i.e., associated with the solid phase.

Therefore, citric acid was the most effective extracting agent and significantly contributed to the flotation waste alteration, while the precipitation of Fe oxides led to metals stabilization in LMWOA solutions through their re-adsorption on them. Contrastingly, the effect of oxalic and acetic acids on the complex process of contaminant release was usually negligible and comparable with water. The only exception was found for Zn, which was also slightly mobilized by oxalic acid solution.

Generally, the effectiveness of LMWOAs to mobilize and complex trace metals from flotation waste increased with higher concentrations of organic ligand and decreased with their time-dependent degradation. The precipitation of newly formed Fe (hydr)oxides followed by adsorption of Pb, Cd and eventually Zn (if present as free Zn^{2+}) from the solutions seems to be the principal mechanism, which leads to the stabilization of metals, as predicted by speciation modeling.

Therefore, hypothesis of LMWOAs, potentially released by plants growing on mine tailings, inducing trace element solubilisation and thus causing metal leaching to subsoil layers or groundwater is only partially true. While the present study simulate “short-term” mobility and mobilization mechanisms of metals associated with the specific mine wastes when interacting with LMWOAs, the role of LMWOAs in the rhizosphere systems, where root activity and acid production are continuous during the vegetation season, will presumably be more pronounced in the long-term.

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List of Abbreviations

The following list describes the significance of various abbreviations and acronyms used throughout the thesis.

Abbreviation	Description
AMD	Acid mine drainage
°C	Degree Celsius
CAR	China Africa Resources
CEC	Cation-exchange capacity
cm	Centimeter
cm ³	Cubic centimeter
cmol	Mole of cations
DOC	Dissolved organic carbon
EC JRC	European Commission Joint Research Centre
g	Gram
GPS	Global Positioning System
h	Hour
ha	Hectare
kg	Kilogram
L	Liter
LMWOA	Low-molecular-weight organic acid
LOD	Limit of detection
m ²	Square metre
m ³	Cubic meter

mg	Milligram
ml	Milliliter
mol	Mole
nm	Nanometer
pKa	Dissociation constant
PM10	Particulate matter of diameter generally below 10 μm
s	Second
SI	Saturation index
S _{tot}	Content of total sulphur
TIC	Total inorganic carbon
UN ECA	United Nations Economic Commission for Africa
US DOE	United States Department of Energy
wt. %	Weight percentage
μM	Micromolar
μm	Micrometer
μmol	Micromole