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The Microbiology of Metal Mine Waste: Bioremediation Applications and Implications for Planetary Health

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Key Points:

- Microbes colonize and inhabit mine wastes, they tolerate high concentrations of metals and contribute to soil functioning and plant growth
- Microbes transform metal speciation and environmental mobility, through metabolism, biogeochemical cycling and metal resistance mechanisms
- Beneficial microbial activity can be stimulated to remediate metal-containing mine wastes, but more long-term field studies are required

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Abstract

Mine wastes pollute the environment with metals and metalloids in toxic concentrations, causing problems for humans and wildlife. Microorganisms colonize and inhabit mine wastes, and can influence the environmental mobility of metals through metabolic activity, biogeochemical cycling and detoxification mechanisms. In this article we review the microbiology of the metals and metalloids most commonly associated with mine wastes: arsenic, cadmium, chromium, copper, lead, mercury, nickel and zinc. We discuss the molecular mechanisms by which bacteria, archaea, and fungi interact with contaminant metals and the consequences for metal fate in the environment, focusing on long-term field studies of metal-impacted mine wastes where possible. Metal contamination can decrease the efficiency of soil functioning and essential element cycling due to the need for microbes to expend energy to maintain and repair cells. However, microbial communities are able to tolerate and adapt to metal contamination, particularly when the contaminant metals are essential elements that are subject to homeostasis or have a close biochemical analog. Stimulating the development of microbially reducing conditions, for example in constructed wetlands, is beneficial for remediating many metals associated with mine wastes. It has been shown to be effective at low pH, circumneutral and high pH conditions in the laboratory and at pilot field-scale. Further demonstration of this technology at full field-scale is required, as is more research to optimize bioremediation and to investigate combined remediation strategies. Microbial activity has the potential to mitigate the impacts of metal mine wastes, and therefore lessen the impact of this pollution on planetary health.

Plain Language Summary

Mine waste is a serious global environmental issue. Poorly managed mine wastes are responsible for polluting our environment with toxic metals and metalloids. Microbes can live in mine wastes, even when they contain high levels of metals. These microbes can lessen the environmental impact of mine wastes by helping them become colonized by plants, and by changing the metals into forms that are less mobile in the environment. For example, some microbes can make minerals that stop metals dissolving into rainwater, and therefore prevent them from ending up in rivers. But on the other hand, some microbes can increase the amount of metals that dissolve into waters by producing acidity. This article describes the impact of microbial activity on the metals most commonly found in mine wastes, and how we can encourage beneficial microbial activities to reduce the environmental impact of mine wastes.

1. Introduction

Mine wastes are the unwanted by-products left behind after the ores of economic interest have been extracted, and can be solid, liquid or gaseous (Lottermoser, 2010). Mining has occurred for thousands of years, and almost every country has a legacy of mine waste that contains toxic materials including various metals and metalloids (Hudson-Edwards et al., 2011). It has been estimated that 20–25 Gt of solid mine wastes are produced globally every year (Lottermoser, 2010). These contain waste rock, poorly extracted ore minerals, gangue minerals, tailings, processing chemicals and residues that are stored at or near mine sites, or in the past were discharged to rivers or wetlands (Hudson-Edwards et al., 2011). Pollution of the environment by metals and metalloids from mine wastes is a global environmental issue due to their widespread distribution and potential toxicity to humans, plants and wildlife. To improve planetary health we need interdisciplinary solutions to limit the impact of soil and water pollution; for mine wastes this has to involve geochemical, mineralogical and microbiological considerations.

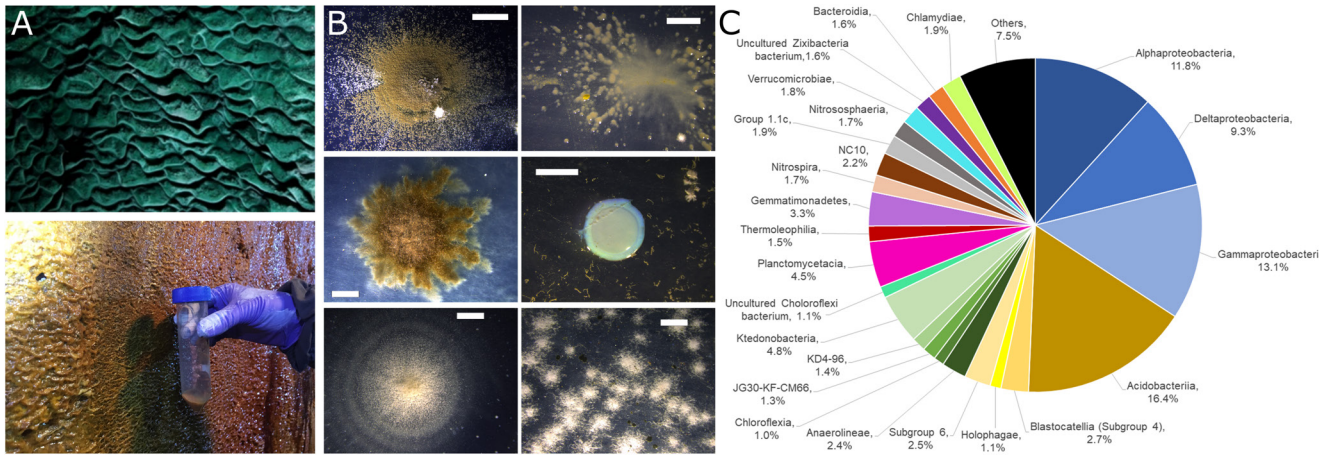

Figure 1. Diverse range of microorganisms found in a former metal mine (Cornwall, UK). (a) Secondary mineral coatings forming within the mine. (b) Range of organisms isolated from the secondary mineral coatings. Scale bars 2 mm. Image source: T. Sbaffi. (c) Composition of the prokaryotic community in the secondary mineral coatings. Image source: Bakes, 2020.

The fate and transport of metals and metalloids in mine wastes are controlled by physical, chemical and biological processes. Microorganisms colonize and inhabit mine wastes (Figure 1), they can tolerate high concentrations of metals and metalloids, and transform/detoxify them through metabolism or resistance mechanisms. This review focusses on the impact of microbiological activity on the behavior of metals in the environment, and how microorganisms can be used to remediate metal and metalloid contaminated mine wastes. We review microbial interactions with the most common potentially toxic metals and metalloids found in mine wastes, together with how microbial processes influence their environmental mobility. We also describe the effect of these contaminants on the essential microbial activity that contributes to soil functioning, and the impact of biogeochemical cycling on the fate of metals and metalloids. Throughout this review we have referred to metals and metalloids found in mine wastes as "metals." We discuss specific field sites and how microbial processes can be enhanced to mitigate the impacts of metal pollution to improve planetary health (Hudson-Edwards, 2016). Phytoremediation, that is growing plants to stabilize mine tailings, or the detoxification of mine wastes by hyperaccumulators (e.g., Wang et al., 2017) is not covered.

Section 2 of this review describes microbe-metal interactions including microbial metabolisms, how microbial oxidation and reduction impact metal mobility, metal complexation by microbially generated ligands, microbial metal resistance mechanisms and biosorption. Section 3 then covers how microbes interact with arsenic, cadmium, chromium, copper, lead, mercury, nickel, and zinc. Section 4 of this review describes case studies where microbial metabolism has been stimulated to remediate metal contamination at mine sites with acidic, neutral and alkaline wastes.

2. Microbe-Metal Interactions

Microbial activity can solubilize and/or precipitate metals through metabolic processes, changing the pH or redox conditions, secreting chelating agents and/or through passive sorption. These processes can be used by microbes to gain energy, or they may require energy and form part of metal uptake or resistance mechanisms. For reference, microbially precipitated metals are sometimes referred to as biominerals, and the processes of formation is called biomineralization (Konhauser, 2007). The process of solubilizing metals is often referred to as bioleaching, or if undertaken for industrial purposes, biomining.

2.1. Microbial Metabolism

To understand microbe-metal interactions we first need to understand how microbes metabolize. Like all living organisms, microbes need to make energy to grow and reproduce. There are two main ways of making energy; from light "phototrophy" or from the oxidation of inorganic or organic chemicals "chemotrophy" (Pepper & Gentry, 2015). Phototrophs such as algae and some bacteria contain light-sensitive pigments

that absorb energy from sunlight and generate electrons from water (oxygenic) or H_2S, S(0), $S_2O_3^{2-}$, H_2, or Fe(II) (anoxygenic; Konhauser, 2007). In most cases of phototrophy and chemotrophy it is the movement of electrons through the electron transport chain that generates proton motive force and ATP, the biochemical unit of energy.

Chemotrophs make energy during a series of redox reactions in which electrons are transferred from a primary electron donor to a terminal electron acceptor through a series of intermediate steps catalyzed by enzymes. Oxygen is the most energetically favorable electron acceptor and is used in aerobic respiration by fungi, protozoa, bacteria and archaea. If oxygen is available, microbes that are capable of respiring oxygen are likely to grow quickly and outnumber those that cannot. In a diffusion-limited setting such as water-logged soils, oxygen will be used up and anaerobic respiration will take over; microbes that can reduce alternative electron acceptors will predominate, such as archaea and bacteria. In order of most energy available these terminal electron acceptors include nitrate, Mn(IV), Fe(III), and sulfate. Certain metals and metalloids in mine waste can also act as electron acceptors and be transformed by microbial metal reduction (Section 2.3). Beyond sulfate reduction, methanogenesis is often the last step in anaerobic metabolism. Strictly anaerobic archaea can gain energy from the disproportionation of acetate or methyl-containing compounds to produce methane, or by producing methane from the reduction of bicarbonate coupled to the oxidation of H_2 (Konhauser, 2007). It is fairly common for bacteria to be able to use multiple metabolic pathways to function under different environmental conditions, such as switching from aerobic respiration to nitrate reduction in the suboxic zone (facultative anaerobes), or H_2 oxidising bacteria switching to a heterotrophic metabolism when organic compounds are available (facultative chemolithoautotrophs), or fermenting organic matter when terminal electron acceptors are limited (Konhauser, 2007; Pepper & Gentry, 2015). This flexibility allows these bacteria to profit from the most energetically favorable metabolisms under changing environmental conditions.

Chemoheterotrophs gain energy from using organic compounds as electron donors, oxidising them to CO_2 or CH_4 coupled to the reduction of a terminal electron acceptor (or light for photoheterotrophs). The availability of organic matter can therefore be a limiting factor for aerobic and anaerobic respiration. Some bacteria do not require organic matter in their metabolism; chemolithoautotrophs gain energy from oxidising inorganic compounds such as H_2, sulfur or Fe(II). In mine waste Fe(II) and sulfur oxidising bacteria break down sulfide minerals, generating acidity and consequently control metal behavior in these environments (Section 2.2). While heterotrophs obtain their C and energy from organic matter, chemolithoautotrophs and photoautotrophs use energy to fix C from inorganic sources for example, CO_2. While microbial metal reduction and oxidation can clearly affect metal behavior in mine waste, even the simple metabolism of organic carbon by aerobic heterotrophs can conceivably impact metal mobility. For example, the mineralization of organic carbon generates organic acids (Section 2.4.1) which are eventually broken down to CO_2; these all increase the acidity which can cause metals to dissolve from minerals. Calcium carbonate minerals are particularly susceptible to acid attack. Coupled to the metabolism of organic C is the respiration of O_2, which under diffusion-limited conditions causes the redox potential to decrease, leading to sub-oxic or anoxic conditions and potentially changing the solubility of metal oxide minerals.

As well as requiring energy and carbon in order to grow, microbes need essential nutrients such as nitrogen, phosphorus, iron, sulfur; biogeochemical cycling of these elements is crucial for all life on Earth. Microbial activity in mine waste can be limited by the availability of these essential nutrients (Craw & Rufaut, 2017; Rashid et al., 2016). Some bacteria and archaea can fix N_2 from the atmosphere, while other microbes require it in other forms such as ammonium, nitrate or organic N. Most microbes require P in the form of soluble inorganic orthophosphate, which can be obtained from organic P compounds using phosphatase enzymes. Trace metals that are essential elements for growth are mostly obtained by active uptake mechanisms that require energy, although passive diffusion will contribute somewhat. The mechanisms used by microbes to obtain essential nutrients for example, secreting chelating agents, can also impact on metal behaviour in mine waste (Section 2.4). Although microorganisms have a range of mechanisms to deal with metal toxicity (Section 2.5), metal contamination can impact soil functioning, by adversely affecting microbial activity. Evidence for this is obtained by measuring soil enzyme activities; microbial enzymes mediate nutrient cycling in soils (e.g., dehydrogenases for C cycling, ureases for N cycling, phosphatases for

P cycling, sulfatases for S cycling etc.) and these are used as indicators for soil health, along with microbial biomass and diversity, basal and substrate respiration rates etc (Alkorta et al., 2003).

2.2. Oxidation Processes and Their Impact on Metal Mobility

As mentioned above, certain prokaryotes are able to gain energy from oxidising Fe(II) and sulfide, generating acidity and acid mine drainage (AMD) as part of the process. This impacts on metal mobility by solubilizing metals associated with reduced minerals such as pyrite (FeS_2). On the other hand, microbial oxidation of Fe(II) and Mn(II) leads to the precipitation of Fe(III) and Mn(IV) oxide minerals that can sequester metals from solution.

Iron-oxidising microorganisms gain energy from oxidising Fe(II) to Fe(III), even under conditions where chemical Fe(II) oxidation is very fast for example in circumneutral oxygenated waters (Hedrich et al., 2011; Ilbert & Bonnefoy, 2013; Neubauer et al., 2002; Stumm & Morgan, 1981). At pH ~7, there are a number of potential electron acceptors as well as oxygen; for example, some prokaryotes couple Fe(II)-oxidation to nitrate reduction and are able to oxidize Fe(II) under microaerophilic or anoxic conditions (Hedrich et al., 2011). Dissimilatory Fe(II)-oxidation is undertaken by bacteria and archaea; some are able to fix CO_2 via the ribulose-1, 5-biphosphate carboxylase-oxygenase (RuBisCo) enzyme, others need the presence of organic C to grow (Hedrich et al., 2011; Ilbert & Bonnefoy, 2013).

At low pH (less than 4), chemical Fe(II) oxidation by oxygen occurs very slowly, and extremely slowly at the very low pH values commonly encountered in sulfidic mine wastes. However, in such low pH environments, the rate of Fe(II) oxidation actually increases with decreasing pH (and increasing Fe[III] solubility), demonstrating the significant contribution of microbial Fe(II) oxidation to the formation of AMD (Larson et al., 2014). The redox potential of the O_2/H_2O couple makes oxygen the more favorable electron acceptor to oxidize Fe(II) at low pH (Hedrich et al., 2011). Iron oxidation pathways are well studied and summarized in Ilbert and Bonnefoy (2013). In acidophilic bacteria, the iron oxidation systems involve: several cytochromes that conduct electrons from Fe(II) located outside of the cell to the electron acceptor located inside, a cytochrome oxidase that reduces the electron acceptor (i.e., oxygen), a high potential iron-sulfur protein (HiPIP) and a rusticyanin (e.g., *Acidithiobacillus ferrooxidans*). In acidophilic archaea, the pathways differ from those found in acidophilic bacteria and include different cytochromes, HiPIP, copper proteins and oxidases (Ilbert & Bonnefoy, 2013).

Microbial Fe(II) oxidation is the main cause of AMD (Figures 2 and 3). AMD is a global environmental issue causing serious pollution of terrestrial and aquatic environments due to the low pH values and high concentrations of metals, metalloids and sulfate. As just one example, the Parys Mountain former mine (Anglesey, Wales) discharges 24 tonnes of Zn and 10 tonnes of Cu to the Irish Sea each year (Johnston et al., 2008), and this has caused high concentrations of metals to accumulate in local wildlife (Chalkley et al., 2019). AMD forms when microorganisms gain energy from the oxidation of Fe(II) present in iron sulfide minerals (e.g., pyrite), which solubilizes Fe as well as other metals and metalloids. Microbial activity has been shown to increase the rate of iron oxidation by five orders of magnitude at low pH conditions (Nordstrom et al., 2015; Singer & Stumm, 1970). This process generates acidity, driving the pH to very low values, and keeping metals in solution.

The high concentrations of Fe(III) in AMD, together with other factors such as pH, lead to the precipitation of secondary minerals for example, schwertmannite ($Fe_8O_8[OH]_{8-2} \times [SO_4] \times [x = 1–1.75]$), or jarosite ($KFe_3[SO_4]_2[OH]_6$), etc., even at low pH (e.g., 1.8). These secondary Fe minerals sequester metals, removing them from solution (Ahoranta, 2016; Khamphila et al., 2017; Shu et al., 2019). Burgos et al. (2012) compared the sequestration of metals by schwertmannite formed at low pH (2.5–4.0) by biological Fe(II) oxidation to the chemical formation of ferrihydrite ($Fe_{10}O_{14}[OH]_2$) at higher pH (4.4–8.4). Their experiments showed that more metals adsorbed to ferrihydrite than to schwertmannite. The adsorption of metals to Fe(III) minerals is of increased interest due to their potential for remediating contaminated waters, by decreasing the mobility of metals (e.g., Cu, Zn, and Pb) and other toxic elements such as As (Fan et al., 2018; Xie et al., 2018). The combination of As(III) and Fe(II) oxidation has been proposed for remediating As-contaminated soils and watercourses (Section 3.1.2).

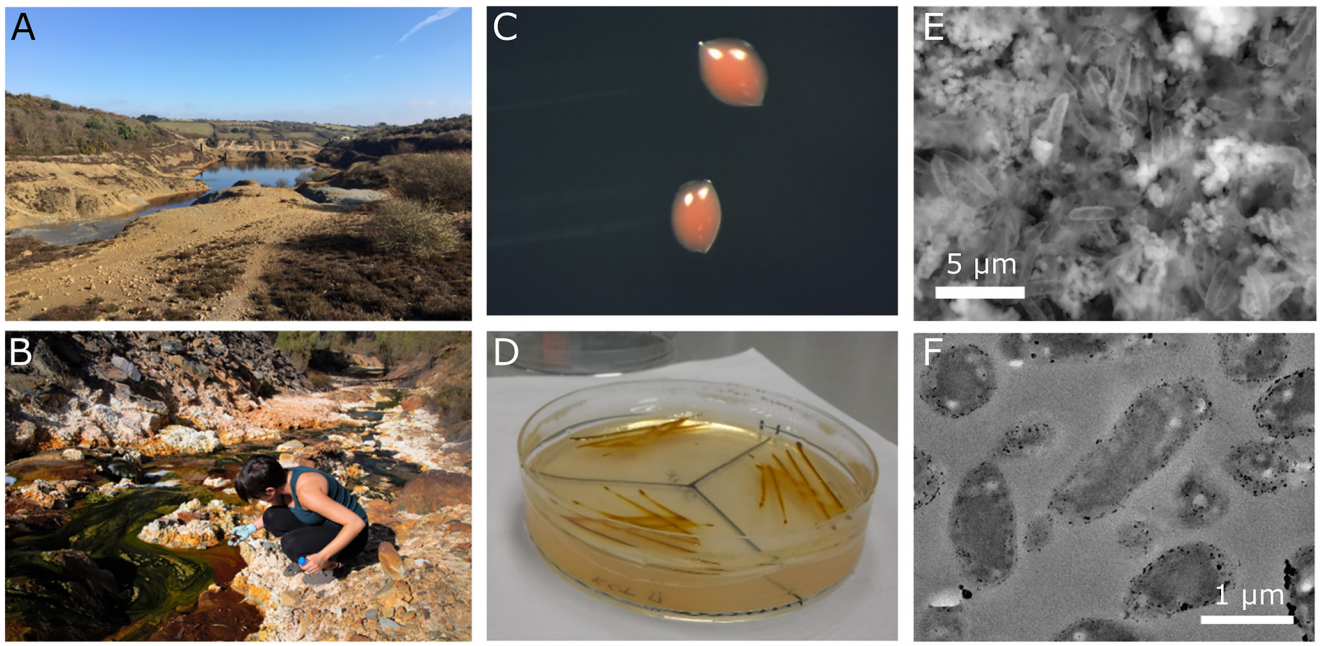

Figure 2. Environments impacted by acid-generating mine waste and examples of the microbes responsible. (a) Sulfide-rich mine tailings and acid mine drainage at an abandoned site, Cornwall, UK. Image source: L. Newsome. (b) Sampling microbial communities in highly acidic mine drainage, Huelva, Spain. Image source: A. Roman-Gonzalez. (c) Colonies of *Acidicapsa ferrireducens*^{T} isolated from an acidic pit lake in the Iberian Pyrite Belt. Magnification of colonies 10–20X. (d) Iron oxidising microorganisms growing on solid medium (note: the colonies have the distinctive color of oxidized iron). (e) Scanning electron microscopy image of bacterial cells and precipitates formed in a sulfidogenic bioreactor irrigated with acidic synthetic mine water rich in aluminum. (f) Transmission electron microscopy images of cell sections of *Acidibacter ferrireducens*^{T} growing in the presence of iron and producing extracellular deposits. Image source (c–f): Falagán (2015).

Microbial oxidation of reduced sulfur compounds (i.e., H_2S, S[0], sulfite, thiosulfate, and tetrathionate) coupled to the reduction of oxygen is ubiquitous in the environment. Organisms able to oxidize reduced sulfur compounds are referred to as S-oxidizers hereafter. Phototrophic S-oxidizers oxidize reduced sulfur compounds anaerobically to fix CO_2 and produce S(0), which is accumulated intra- or extracellularly, or sulfate (Fike et al., 2016). Other S-oxidizers can use alternate electron acceptors such as nitrate for example, *Thiobacillus denitrificans* (Fike et al., 2016) or Fe(III) for example, *A. ferrooxidans* (Osorio et al., 2013). Some S-oxidizers produce sulfuric acid when reduced sulfur compounds are oxidized; this is of importance in mine wastes where there are minerals that are susceptible to acid dissolution (e.g., sphalerite [ZnS], chalcocite [Cu_2S]). Some microorganisms can oxidize the sulfur present in pyrite (Figure 3) further contributing to the formation of AMD and metal dissolution (Sasaki et al., 1998). There are several molecular

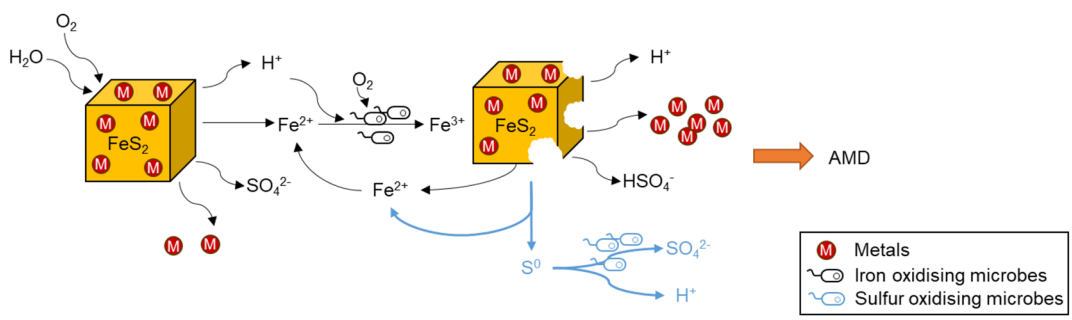

Figure 3. Simplified schematic of acid mine drainage (AMD) formation. The oxidation of pyrite starts when in contact with oxygen and water releasing ferrous iron, this is oxidized by oxidising microorganisms and the generated ferric iron oxidizes further the pyrite. The blue lines and letters indicates an alternative Fe(III) oxidation route of pyrite where the sulfur is partially oxidized to elemental sulfur that is oxidized by sulfur oxidising microorganisms. The overall oxidation of pyrite causes the pH to decrease, the release of metals and sulfate into solution generating what is known as AMD.

pathways related to the oxidation of reduced sulfur compounds, which are shared among microorganisms, within those, the Sox pathway appears most important (Dahl et al., 2008). A recent review summarizes the different pathways involved in the oxidation of reduced sulfur compounds by *Acidithiobacillus* spp. (Wang et al., 2019), these include enzymes for S(0) oxidation, thiosulfate oxidation, sulfide oxidation, and sulfite oxidation.

The formation of Mn(III)/Mn(IV) oxides by Mn(II) oxidising bacteria and fungi can sequester metals from solution. Microbial Mn(II) oxidation can occur at rates five orders of magnitude greater than abiotic oxidation, so much so that most naturally occurring Mn oxides are thought to be biogenic, although abiotic Mn(II) oxidation becomes more favorable at pH > 9 (Nealson, 2006; Tebo, 1991). Microbial Mn(II) oxidation occurs during heterotrophic metabolism via the formation of superoxide, or directly via heme peroxidases or multicopper oxidases (Anderson et al., 2009; Romano et al., 2017; Tebo et al., 2004, 2005), although recently the first autotrophic Mn(II) oxidising bacterium was discovered (Yu & Leadbetter., 2020). Mn(III)/Mn(IV) oxides have a strong affinity for metal cations and are known to sorb and incorporate many contaminants for example, Cr, Hg and Pb (Section 3).

2.3. Reduction Processes and Their Impact on Metal Mobility

Some bacteria and archaea are able to reduce certain forms of metal oxides or sulfate as the terminal electron acceptor coupled to the oxidation of an electron donor, and in doing so gain energy for growth. This process can impact on metal mobility indirectly by solubilizing oxidized minerals that contain metals such as Mn(IV)- and Fe(III)-oxides, or by precipitating reduced mineral phases that sequester metals such as Fe(II) minerals or sulfides. These microorganisms can also directly reduce redox-sensitive metals which impacts on their environmental mobility. Most metals tend to be less mobile under reducing conditions, but arsenic is a notable exception (Section 3.1). Indeed, the microbial reduction of metals and sulfate is the key process that occurs in constructed wetlands to facilitate the bioremediation of metal-impacted minewaters (e.g., Section 4.2). Although metal-reduction is predominantly performed by prokaryotes, some fungi can reduce metalloid cations to form elemental nanoparticles including Ag(I) to Ag(0), Se(VI) and Se(IV) to Se(0) and Te(IV) to Te(0) (Espinosa-Ortiz et al., 2015; Gade et al., 2008; Ollivier et al., 2011; Rosenfeld et al., 2017).

Dissimilatory microbial Mn(IV)- and Fe(III)-reduction is a ubiquitous respiratory pathway in the environment and is undertaken by a phylogenetically diverse range of bacteria and archaea (Lovley, 2006), hereafter referred to as metal-reducing microorganisms. It requires an electron donor which can be $H_{2,}$ or fermentation products from sedimentary organic matter for example, simple organic acids like acetate (Lovley et al., 2004). The products Fe(II) and Mn(II) can be soluble, sorb to surfaces, or form minerals such as magnetite (Fe_3O_4; Lovley et al., 1987). Metal-reducing microorganisms can be facultative anaerobes (e.g., *Shewanella* spp.) that can also grow with alternative electron acceptors such as oxygen or nitrate, or be obligate anaerobes (such as *Geobacter* spp.). At the near-neutral pH conditions commonly found in most environments, Mn(IV) and Fe(III)-oxide minerals are insoluble, therefore metal-reducing microorganisms must be able to transfer electrons to solid phases via extracellular electron transport mechanisms. These include direct physical contact between the mineral and *c*-type cytochromes in the cell membrane or nanowires (Malvankar et al., 2012; Pirbadian et al., 2014; Yalcin & Malvankar, 2020), or secretion of extracellular electron shuttles (Canstein et al., 2008). Under acidic conditions found in many sulfidic mine wastes, high concentrations of Fe(III) are present in solution, and acidophilic microorganisms such as *A. ferrooxidans* can grow by reducing aqueous Fe(III) to Fe(II) coupled to the oxidation of H_2 or S(0), again with *c*-type cytochromes implicated (Das et al., 1992; Ohmura et al., 2002). Microbial Fe(III)-reduction can also occur at alkaline pH, demonstrated with organic-amended pH 11.8 sediments collected from a legacy lime works (Williamson et al., 2013). Natural Mn(III)/Mn(IV)- and Fe(III)-oxides have a strong affinity for metals; for example manganese oxides such as birnessite (δ-MnO_2) can sorb and incorporate large quantities of As, Cu, Co, Cd, Hg, Ni, Pb, Se, Sn, U, Zn (Tebo et al., 2004) and iron oxides such as ferrihydrite and goethite (FeOOH) can sorb Cd, Cr, Cu, Hg, Ni, Pb, and Zn (Ugwu & Igbokwe, 2019). Microbial reduction of these minerals will lead to the release of sorbed metals to solution, although they may subsequently be sequestered for example, in Fe(II) minerals.

Dissimilatory sulfate reduction can be undertaken by certain bacteria and archaea; energy is gained by oxidising organic compounds (organic acids, fermentation by-products and hydrocarbons; (Rabus et al., 2006)) or H_2 as electron donors coupled to the reduction of sulfate to sulfide. This is undertaken by a phylogenetically diverse range of prokaryotes and is widely distributed (Wagner et al., 2005). Sulfate-reducers are strict anaerobes although some can tolerate oxygen for short periods of time (Rabus et al., 2006). Sulfate reduction occurs intracellularly via an 8 step electron transfer process, generating a series of intermediates that for the most part of the process are not excreted (Rabus et al., 2006). Sulfate-reducing prokaryotes can be detected in environmental samples by the presence of two conserved genes; dissimilatory (bi)sulfide reductase (*dsrAB*) and adenosine-5'-phosphosulfate reductase (*apsA*; Wagner et al., 2005), with *dsrAB* used as a phylogenetic marker for sulfate-reduction (Müller et al., 2015). Sulfate-reduction can occur at a wide range of pH values, from pH 2.5–4.0 (Florentino et al., 2019; Sánchez-Andrea et al., 2013; van der Graaf et al., 2020), to pH 11 in soda lakes (Sorokin et al., 2011). Stimulating sulfate reduction is beneficial as contaminant metals can be precipitated as insoluble sulfide minerals and it also generates alkalinity that helps to treat acidic mine waters (Guy Riefler et al., 2008). Sulfidogenic bioreactors have been implemented at the laboratory scale to remove metals from contaminated mine waters (Christensen et al., 1996; Holanda & Johnson, 2020; Sánchez-Andrea et al., 2014), and microbial sulfate-reduction plays a key part in constructed wetlands used to treat acid mine drainage and other metal-impacted mine waters (Guy Riefler et al., 2008; Moreau et al., 2013).

2.4. Metal Complexation by Microbially Generated Ligands

Microorganisms produce chelating compounds and ligands either as a by-product of their metabolism, or to specifically bind with metals and enhance their transport under metal-limiting conditions. These complexing agents include organic acids and siderophores which can mobilize metals from minerals present in mine waste and consequently increase metal bioavailability. On the other hand, some microorganisms secrete complexing agents that can precipitate with metals and remove them from solution, such as oxalates and phosphates.

2.4.1. Organic Acids

Organic carboxylic acids are produced during microbial metabolism. These dissociate to generate acidity which can increase the solubility of metals, while the deprotonated organic anions (sometimes described as volatile fatty acids) can act as chelating agents to increase metal solubility. Organic acids (oxalic, malic, succinic, and citric) applied directly to contaminated soils were shown to chelate 29%–60% of As, Cr and Cu after 6 h (Uwumarongie-Ilori & Okieimen, 2010). Bidentate (e.g., oxalic) and tridentate (e.g., citric) organic acids are more effective at chelating and solubilizing metals cations from minerals compared to monodentate organic acids (e.g., acetic; Welch & Ullman, 1993).

Some organic acids are produced from fermentation reactions, for example, acetogenic bacteria generate acetate chemolithoautotrophically from CO_2 and H_2. However, more significant is the production of organic acids during glucose metabolism. Pyruvate is produced from glucose via glycolysis, and can then either be fermented to produce lactate, acetate and formate, or respired via the citric acid cycle to produce citrate, succinate, fumarate, and malate, amongst other intermediates and products. In one example, microbial metabolism of glucose in anaerobic sediment microcosms caused the pH to decrease from 8.0 to below 6.5 and the accumulation of acetate, lactate and formate, enhancing the mobility of cobalt (Newsome et al., 2020). Subsequent microbial respiration of lactate can then produce propionate and acetate (Newsome, Morris, Shaw, et al., 2015). Analysis of field samples showed that organic acids are produced by microbial fermentation of sedimentary organic matter in aquitards, and these are consumed by microbial respiration in aquifers, driving the development of anoxic conditions (McMahon & Chapelle, 1991).

Fungi are particularly effective at producing organic acids and the ability to produce oxalic and citric acids is widespread (Gadd, 1999). Over-production of oxalic acid by fungi can solubilize metal phosphate, sulfide, carbonate, and oxide minerals, and precipitate the metals as highly insoluble oxalate minerals (Fomina et al., 2005). Various fungi were shown to leach cobalt and nickel from low grade laterite ores via the production of organic acids (Valix et al., 2001). Fungal organic acids can also leach metals from metal-contaminated mine tailings and soil (Arwidsson et al., 2009; Ilyas et al., 2013; Seh-Bardan et al., 2012). As fungi

require aeration and a carbon source, they will be more appropriate for bioleaching metals in engineered bioreactors rather than for *in situ* applications (Gadd, 1999). However, fungal activity will still influence metal behavior in surficial soils in the environment through organic acid secretion.

2.4.2. Siderophores

Iron is an essential element for many biological processes; it is used in heme-containing proteins and in FeS cofactors in enzymes. In the near-neutral aerobic conditions present in most surface environments Fe is present as highly insoluble Fe(III) oxides, although Fe can be soluble (and potentially available for uptake) under acidic conditions (<pH 5) and under reducing conditions as Fe(II) (Hem & Cropper, 1962; Sandy & Butler, 2009). Under Fe-limiting conditions microbes will use energy to obtain it by making and secreting siderophores. Siderophores are multidentate organic ligands that chelate insoluble Fe(III) and allow it to be taken up into the cell, where it is then reduced by assimilatory ferric reductases to Fe(II), which can be incorporated into proteins (Schröder et al., 2003). These ligands include catecholate (such as in enterobactin), hydroxamate (such as in desferrioxamine), and/or α-hydroxy-carboxylate residues (such as in achromobactin); bacteria and fungi can secrete one or more of these which have different affinities for Fe binding depending on the pH (Haas, 2014; Kurth et al., 2016; Sandy & Butler, 2009). Hundreds of different siderophores have been identified.

As well as Fe, siderophores can bind with metals and mobilize them from soils, and it has been proposed that they could be used to remediate metal contaminated environments (Ahmed & Holmström, 2014; Hernlem et al., 1999). The presence of other metals can stimulate or inhibit the production of siderophores. The mechanism for this process is unknown but it has been suggested that increased siderophore production may contribute to metal resistance as metals bound by siderophores can be prevented from entering cells, and catecholates may offer protection from oxidative stress (Braud et al., 2010; Johnstone & Nolan, 2015; Schalk et al., 2011). Although producing siderophores requires energy, this does not disadvantage siderophore producers in microbial communities; a shift toward siderophore producers was observed following copper contamination, with the growth of siderophore-producers less inhibited by Cu (Hesse et al., 2018).

2.4.3. Phosphates and Carbonates

Immobilizing metals as phosphate minerals is desirable due to their low solubility products. The orthophosphate (PO_4^{3-}) anion is well known to form complexes with transition metals (Van Wazer & Callis, 1958). Phosphate compounds can be applied directly to soils impacted by metals and mine waste to form insoluble metal phosphate minerals (Andrunik et al., 2020; Cotter-Howells & Caporn, 1996). In addition, phosphate applied to mine waste can form metal phosphate coatings on sulfide minerals, preventing them from being oxidized, and thus, the formation of acid and dissolution of metals, although this had little impact on metalloid mobility (Harris & Lottermoser, 2006). This technology has been trialled in both *in situ* and *ex situ* field applications with varying degrees of success, using phosphoric acid, rock phosphate and biosolids (Interstate Technology & Regulatory Council, 2010).

Microorganisms express the phosphatase enzyme to release orthophosphate from organic phosphate compounds; this ability is widespread as it ensures that phosphate is available for uptake as an essential nutrient. In laboratory experiments, microorganisms that overexpress phosphatase have been shown to precipitate metals from solution as phosphate minerals. For example, when supplied with organic phosphate compounds a *Serratia* bacterium was able to precipitate cadmium (Section 3.2), lead (Section 3.5) and uranium from solution as phosphate minerals (Macaskie and Dean, 1984, 1987; Newsome, Morris, & Lloyd, 2015). Similarly some fungi were able to precipitate lead as pyromorphite ($Pb_5[PO_4]_3Cl$; Liang, Csetenyi, &Gadd 2016; Liang, Kierans, et al., 2016) and uranium as uranyl phosphate (Liang et al., 2015). Microbial phosphatase activity is likely to contribute to the remediation of mine waste when organic phosphate compounds such as biosolids are applied, and also could potentially be designed for use in bioreactors.

The formation of metal carbonate minerals has also been proposed as a remediation technology. Photosynthetic microorganisms such as Cyanobacteria can facilitate carbonate mineral precipitation by using bicarbonate as their carbon source, producing hydroxyl ions and shifting the equilibrium toward carbonate; they also provide reactive surfaces for mineral nucleation (Konhauser, 2007). Urea ($CO[NH_2]_2$) can be used to stimulate the precipitation of carbonate minerals; microorganisms break down urea to form ammonium and carbonate; a process is known as ureolysis which is widespread in the environment. Ureolytic bacteria

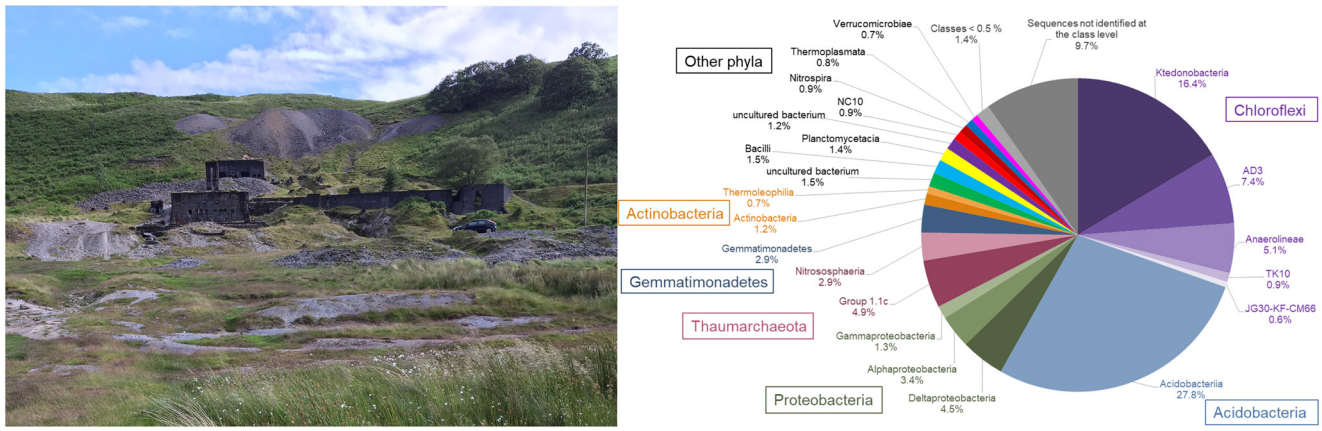

Figure 4. Metal-impacted tailings from a former Pb/Zn mine (Ceredigion, Wales) and the composition of the prokaryotic community inhabiting the tailings (unpublished data). Image and data source: L. Newsome, University of Exeter.

such as *Sporosarcina pasteurii* can precipitate large volumes of calcite ($CaCO_3$) *in situ* (Ferris et al., 1996; Tobler et al., 2011). This process can remediate metal contamination by co-precipitation with calcite for example, Cd, Cu (Bhattacharya et al., 2018; Chen & Achal, 2019), or by precipitation of metal carbonate minerals for example, Pb (Kang et al., 2015). Laboratory experiments showed that contaminated soils can be augmented with *S. pasteurii* and urea to stabilize Pb, Zn, and Cd (P. Liu, et al., 2020). Carbonate-rich supernatants produced by ureolytic fungi can form copper carbonate nanoparticles, offering potential for remediation applications (Li & Gadd, 2017).

2.5. Metal Resistance Mechanisms

Metals enter microorganisms by active uptake through metal transport systems or they can passively diffuse through porins (Z. Ma et al., 2009). For essential elements microorganisms balance uptake and efflux mechanisms to ensure homeostasis, although excess concentrations may overwhelm efflux capacity and cause toxicity. For metals with no biological function, microbes will not have specific efflux mechanisms to deal with them, although some may be sufficiently similar to essential metals to be transported into or out of cells. Metal resistance mechanisms involve preventing the uptake of metals from the environment, binding metals intracellularly to decrease their toxicity, or removing unwanted metals by pumping them back to the environment. These strategies are employed by bacteria and fungi to survive in high metal environments (Figures 1 and 4). The genes for metal resistance can be encoded on chromosomes or plasmids.

"General metal resistance mechanisms" defined by Roane et al. (2015) do not require metal stress and include: biosorption to extracellular polymeric substances (Section 2.6); production of siderophores that bind to metals and reduce their bioavailability (Section 2.4.2); or releasing metabolic by-products such as sulfide or phosphate which precipitate metals from solution (Sections 2.3 and 2.4.3). "Metal-dependent resistance mechanisms" defined by Roane et al. (2015) occur under metal stress and include: using energy dependent efflux pumps (such as the metal-exporting ATPases CadA and ZntA) to remove metals from within a cell into the environment; binding of metals with metallothioneins (these are reported to be present in plants, algae, yeast and fungi but do not appear to be widespread in prokaryotes, Blindauer, 2011); or methylation of metals to enhance diffusion of metals out of the cell. Frequently metal resistance mechanisms in bacteria involve P-type ATPase efflux systems (Borremans et al., 2001). Intracellular compartmentation is also used by some eukaryotes (algae and fungi) as a mechanism of metal tolerance (Gadd, 2010).

Nies (2003) assigned the mechanisms for metal resistance to three layers (which are found in all kingdoms of life): the RND (resistance, nodulation and cell division) protein family that exports cations including metals; the CDF (cation diffusion facilitator) protein family that includes metal transporters involved in metal-resistance; and P-type ATPases, a protein family involved in metal homeostasis that can import and efflux metal cations. For full details of these proteins and the genes that encode them the reader is referred to Nies (2003). Metal resistance mechanisms are discussed for each metal individually in Section 3.

However, metal-resistant prokaryotes often use multiple resistance mechanisms in combination with each other, such as reduction of a metal followed by removal from the cell via an efflux pump, and these need not be specific to a particular metal.

2.6. Biosorption of Metals

Many metals can be removed from solution via sorption to biomass, in a process termed biosorption. This is a passive process, with metals binding similarly to living or dead biomass. Metal sorption to cell walls offers some protection for living microbes against metal toxicity. Microbes are particularly sorptive as they have a relatively large surface area that is typically negatively charged and attracts metal cations electrostatically. The bacterial cell envelope, extracellular polymeric substances, and fungal cell walls and hyphae also contain anionic carboxyl, phosphoryl, and hydroxyl functional groups that bind metals through chemical sorption (Beveridge & Murray, 1980; Fomina & Gadd, 2014). Sorption of metals to microorganisms provides surfaces for mineral nucleation and chemical reactions to occur (Gadd, 2010). Bacteria, algae, and fungi have been studied intensively for their ability to sorb metals, with algae and fungi particularly of interest due to their rapid sorption of metal cations, coupled with their abundance, ease of growth and availability in waste products (Fomina & Gadd, 2014; He & Chen, 2014). Applying sorptive biomass to recover metals from contaminated mine waters has been a subject of research. Biosorption of metal cations is less effective under acidic conditions due to the protonation of cell surfaces, and therefore is unlikely to be significant in environments impacted by the oxidative weathering of sulfidic mine wastes. Moreover, sorption to biomass is not a long term sink for environmental metals as cells will die and decay, releasing their sorbed metals back to the environment. As such biosorption is not considered to have a significant impact on the overall fate of metals in mine wastes.

2.7. Summary of Microbe-Metal Interactions

Microbial metabolism and strategies for metal resistance can both create and solve problems with metals in mine wastes, with associated implications for planetary health. Microbial oxidation of Fe(II)- and sulfide-bearing minerals is responsible for liberating metals from sulfide mine wastes and generating acid mine drainage; this is a global environmental problem contributing substantial levels of metal pollution to the terrestrial and aquatic environments. Organic acids produced during respiration and fermentation can also generate acidity, and microbial chelating agents may also enhance the mobility of metals. However, it may be possible to stimulate these processes in a controlled manner to decontaminate mine waste (Section 4.1) or even to recover valuable metals from tailings.

On the other hand, microbial activity can remove metals from the aquatic environment, so limiting their impact on human health and wildlife. Microbes can sequester metals from solution by precipitating them as sulfide, phosphate, carbonate and oxalate minerals, and also in association with Mn and Fe oxides. Encouraging their formation by constructing wetlands to treat mine waters (Section 4.2), or even applying organic amendments (such as C and P) directly to mine waste to stimulate mineral precipitation will benefit the environment. The latter approach may also improve planetary health by contributing nutrients that are lacking in mine waste-impacted soils, and assist with subsequent soil development.

Section 3 describes microbial interactions with key contaminant metals, and then Section 4 reviews how microbial activity has been harnessed in bioremediation technologies to mitigate the impact of mine waste contamination and improve planetary health.

3. The Geomicrobiology of Metals and Metalloids Found in Mine Waste

Geomicrobiology, as defined by Henry Lutz Ehrlich, is “the study of the role that microbes play, or have played in specific geological processes” (Ehrlich, 1990). This section focuses on how microbes influence the environmental behavior of the key contaminant metals and metalloids found in mine waste, namely arsenic, cadmium, copper, chromium, lead, mercury, nickel and zinc. For each metal in turn we review their (a) geochemistry, (b) mechanisms for uptake and toxicity in microorganisms, (c) direct and indirect microbial

metal resistance mechanisms, (d) impact on soil microbial processes and microbial communities and (e) behavior during biogeochemical cycling.

Studies where metals were added to soil communities are unlikely to represent conditions encountered in the field, where metals often accumulate over prolonged time periods, and in different chemical forms to a soluble metal salt (Giller et al., 1998). This was demonstrated experimentally by Renella et al. (2002), who showed that acute exposures to metals are a poor representation of the response to chronic metal stresses that occur in the environment. Therefore where possible we describe the results of field studies over laboratory experiments, studies that assess long-term metal exposure (i.e., many months to years) in preference to short-term (i.e., days to many weeks), and studies that focus on metal-impacted mine wastes rather than metal salts or other metal-contaminated wastes such as sewage sludge or electronics.

3.1. Arsenic

Arsenic is ubiquitous in the environment and as such nearly all living organisms have As detoxification pathways (Garbinski et al., 2019). Arsenic is highly toxic from both acute and chronic exposure, and is carcinogenic. However, As is essential for some animals and potentially also for the human diet in very low quantities (Chen et al., 2013; Vasiliu & Dixon, 2016).

3.1.1. Arsenic Geochemistry

Arsenic is present in the Earth's crust at around 3.4 mg kg^{-1}, commonly as sulfide minerals such as realgar (As_4S_4) or orpiment (As_2S_3), or oxides such as arsenolite (As_2O_3; Agency for Toxic Substances & Disease Registry, 2007). Arsenic is a common contaminant in waste from sulfide ore mines, often in the form of arsenopyrite (FeAsS). In the environment As is typically found as As(V) under oxidising conditions or As(III) under reducing conditions; As(V) is less mobile and less toxic compared to As(III). As(V) sorbs to Fe(III) oxyhydroxides and under oxidising conditions is poorly mobile (Lafferty & Loeppert, 2005). Under reducing conditions As is released to solution as a result of the dissolution of Fe(III) and Mn(IV) oxides by metal-reducing bacteria. Microbially mediated As redox transformations occur much faster and are therefore more environmentally important than abiotic reactions (Ahmann et al., 1997; Gihring et al., 2001; Huang, 2014; Meng et al., 2002; Newman et al., 1997).

3.1.2. Microbial Interactions With Arsenic

3.1.2.1. Uptake Mechanisms and Mode of Toxicity

Specific uptake mechanisms for As do not exist. As(V) is taken up via inorganic phosphate uptake systems due to the similarities of the arsenate and phosphate oxyanions (Garbinski et al., 2019; Rosenberg et al., 1977). Aquaglyceroporins (water channels) can transport As(III) as arsenite ($As[OH]_3$) due to its physical and chemical similarity with the glycerol molecule (Bienert & Chaumont, 2013; Sanders et al., 1997). As(III) toxicity primarily occurs via strong binding with sulfhydryl/thiol groups in proteins, which impacts on their ability to function, while As(V) toxicity occurs by interfering with phosphate metabolism and oxidative phosphorylation (Oremland & Stolz, 2003), or by intracellular reduction to As(III).

3.1.2.2. Direct Resistance Mechanisms

Arsenic detoxification occurs via efflux, intracellular sequestration or methylation. In most cases arsenic efflux proceeds first by the reduction of As(V) to As(III), which can then be transported extracellularly via a number of efflux proteins. In prokaryotes the *ars* operon is widely distributed and includes arsenic resistance (*ars*) genes (*arsR*, *arsC*, *arsB*, *arsA*, and *acr3*) that encode for a sensor/repressor ArsR, an As(V) reductase ArsC and an As(III) efflux transport protein; either the ion transport protein ArsB (which in conjunction with ArsA, an ATPase stimulated by As(III), forms the ArsAB efflux pump), or the arsenite efflux permease Acr3 (Achour et al., 2007; Shi et al., 2018; Zhou et al., 2000). Eukaryotes do not have ArsB efflux; in fungi the arsenite efflux permease Acr3 confers resistance to *Saccharomyces cerevisiae* (Bobrowicz et al., 1997; Maciaszczyk-Dziubinska et al., 2014), *Aspergillus niger* was reported to reduce As(V) to As(III) as a detoxification mechanism (Cánovas et al., 2003) and AcrA, an arsenite efflux transporter located in the plasma membrane of *A. niger* (and a homolog to Acr3) conferred resistance to As(V) (Choe et al., 2012). Fungi are also able to sequester arsenic in vacuoles as a mechanism of As resistance, with links

between glutathione biosynthesis and vacuolar arsenic sequestration observed in a range of fungi (Cánovas et al., 2004; Choe et al., 2012; Ghosh et al., 1999; Khullar & Reddy, 2020; L. Li et al., 2021).

Both bacteria and fungi can transform As to methylated forms which are then lost by volatilization. This occurs via the Challenger mechanism of biomethylation where As(V) is reduced to As(III) followed by a series of methylation-oxidation and reduction reactions to eventually form trimethylarsine which is volatile and can be lost to the environment (Dombrowski et al., 2005). This is generally considered to be a detoxification process, despite some methylated forms of As being more toxic than inorganic forms (Ben Fekih et al., 2018). Fungal arsenic methyltransferase genes enhance biomethylation and volatilization and confer As resistance (J. Li et al., 2018; Qin et al., 2006; Verma et al., 2016).

3.1.2.3. Indirect Resistance Mechanisms

Respiratory As(V) reduction has been documented in anaerobic bacteria and archaea (Ahmann et al., 1994; Huber et al., 2000; Newman et al., 1997). Dissimilatory As(V) reduction is different to when As(V) is reduced to As(III) by ArsC as part of the energy-dependent detoxification mechanism described above; instead As(V) is reduced as the terminal electron acceptor to gain energy coupled to the oxidation of organic compounds or H_2. Dissimilatory arsenate respiration uses the *arr* (arsenate respiratory reduction) operon which contains a two gene cluster (*arrA* and *arrB*; Saltikov & Newman, 2003). The dissimilatory arsenic reductase genes are highly conserved and encountered in many environmental samples (Malasarn et al., 2004). Most dissimilatory As(V) reducers are heterotrophs and can gain energy from oxidising a range of organic compounds (Niggemyer et al., 2001; Saltikov et al., 2003), although autotrophic As(V) reduction has also been documented (Hoeft et al., 2010). Microbes can respire both aqueous and solid associated As(V), but respiration of aqueous As(V) is much faster than that of As(V) sorbed to iron oxides (Langner & Inskeep, 2000; Zobrist et al., 2000). The rate of arsenate reduction in the environment is likely to be limited by the availability of As(V) in solution for example, by desorption from minerals (Glasser et al., 2018; Huang, 2018).

Bacteria can also conserve energy by oxidising As(III) to As(V), with As(III) acting as an electron donor coupled to O_2 or nitrate reduction and with C obtained from CO_2 or bicarbonate (Hoeft et al., 2007; Muller et al., 2003; Santini et al., 2000). Anaerobic photoautotrophic As(III) oxidisers have been isolated from a hyperalkaline lake (Budinoff & Hollibaugh, 2008; Kulp et al., 2008). In contrast to energy conserving autotrophic As(III) oxidation, heterotrophic As(III) oxidation is considered to be a detoxification mechanism (Oremland & Stolz, 2003). Two systems for arsenite oxidation in bacteria have been identified; the most common is the aerobic arsenite oxidase *aio* (previously referred to as *aox, aso*, or *aro* (Lett et al., 2012)), while *arx* genes encode for microaerophilic or anaerobic As(III) oxidation coupled to nitrate reduction (Amend et al., 2014; Zargar et al., 2012).

3.1.2.4. Impact on Soil Microbial Processes and Microbial Communities

Although arsenic has been intensively researched, only a few studies could be found that directly assess the impact of As on soil microbial processes or microbial communities. Overall the impact of As contamination on soil functioning in appears to be varied, while limited effects on microbial communities have been observed in field studies.

A 25-year field study of soils spiked with up to 300 mg kg^{-1} sodium arsenate showed that microbial diversity was similar to the unamended control soils (2.6 mg kg^{-1} As; Lorenz et al., 2006). The As-contaminated soils had similar xylanase, invertase, protease, urease, and phosphatase activities compared to the control, while the sulfatase activity was significantly lower. A comparison of soils with elevated As (up to 36 mg kg^{-1}) against a background soil (11 mg kg^{-1}) showed significantly lower microbial biomass carbon and nitrogen and basal and substrate induced respiration (Ghosh et al., 2004), as well as decreased urease, phosphatase, β-glucosidase and sulfatase activities, which correlated with increased concentrations of water soluble or exchangeable As (Bhattacharyya et al., 2008). A study of agricultural soils with total As up to 417 mg kg^{-1} showed As had an adverse effect on fungal biomass and dehydrogenase, phosphatase, β-glucosidase and sulfatase activities, but not on bacterial biomass or urease activity (Das et al., 2013). Analysis of soils collected in the region of a former As mine containing up to 4,008 mg kg^{-1} As found phosphatase, β-glucosidase and dehydrogenase activities increased with increasing As concentration (Z. Wang et al., 2020). In this study soil enzyme kinetics were used to derive a mean ED_{10} (ecological dose value that causes a 10% decrease in

activity) of 35 mg kg^{-1} As. The dehydrogenase activity in soils collected on a transect from a mine tailings facility (up to 3,322 mg kg^{-1} As) to a relatively unaffected area (12 mg kg^{-1} As) was only slightly negatively correlated with total arsenic (Fernández et al., 2005).

Regarding microbial communities, a study of agricultural land in an arsenic mining area (16–1023 mg kg^{-1} As) showed that land use and pH were the most significant factors affecting the bacterial communities rather than As concentrations (Wu et al., 2016). No correlation was observed between As concentrations (from around 4 to 35 mg kg^{-1}) and fungal colony forming units (Singh et al., 2015). A study comparing contaminated soils near an As mine to unpolluted soils found a higher number of viable colonies of bacteria, actinomycetes and fungi in contaminated upland soils (459 mg kg^{-1} As) compared to unpolluted upland soils (43 mg kg^{-1} As; Hiroki, 1993). In the same study, the number of viable bacteria and actinomycetes were similar in contaminated (391 mg kg^{-1} As) and unpolluted (32 mg kg^{-1} As) paddy soils, but fungi were considerably higher in the contaminated soils.

3.1.2.5. Impact of Biogeochemical Cycling

Given that As(V) is less mobile in the environment compared to As(III), microbial reduction of As(V) to As(III) via respiration or detoxification has the effect of increasing the environmental mobility of As, while As(III) oxidation decreases its environmental mobility. As well as these direct redox transformations of As, because As(V) strongly sorbs to iron(III) oxide minerals, iron biogeochemistry plays a crucial role in mediating the environmental behavior of As. Under anaerobic conditions sediment bacteria can enzymatically reduce Fe(III) to aqueous Fe(II) coupled to oxidation of organic electron donors (Lovley et al., 2004), which in As-impacted sediments causes As(V) to be released to solution (Islam et al., 2004). These redox effects were demonstrated in a field study of a contaminated aquifer, where near-surface sediments contained As(V) and groundwater was low in As, while at depth sediments contained As(III) and groundwater As concentrations were elevated (Gnanaprakasam et al., 2017). Whether microbial Fe(III) or As(V) reduction controls the release of As associated with Fe-oxides to the aqueous phase is debated. Some studies have shown that Fe(III)-reduction occurs first, releasing As(V) to solution which is then reduced to As(III) (Newsome et al., 2018; Revesz et al., 2016), while in others they occurred simultaneously (Huang, 2018; Smeaton et al., 2012). Overall it is clear that in the environment, microbial communities will be capable of reducing both Fe(III) and As(V), and therefore microbial activity will increase the mobility of As if the geochemical conditions are suitable, that is, there is sufficient electron donor available and limited oxygen transfer.

Should conditions be sufficiently reducing to stimulate sulfate reduction, this will favor the removal of As from solution. As(III) can become incorporated into iron sulfide minerals, as demonstrated in mesocosms designed to simulate wetlands (Zhang et al., 2017). The formation of A_2S_3-like complexes associated with mackinawite (FeS) has also been observed in flooded soil and As-doped Fe oxide microcosm experiments (Burton et al., 2013, 2014). Bacterial arsenate and sulfate reduction can precipitate As from solution as sulfide minerals coupled to oxidation of organics such as ethanol or lactate (Newman et al., 1997; Rodriguez-Freire et al., 2014). As(V) reduction preceded sulfate reduction, with subsequent As(III) removal from solution occurring when sulfide was formed (Newman et al., 1997). In this study, abundant orpiment precipitates were formed extracellularly, as well as some intracellular nanoparticles observed near the cytoplasmic membrane. These processes are environmentally relevant: microbial formation of As sulfide minerals such as realgar has been shown to occur under strictly anaerobic conditions in wetland soils (Drahota et al., 2017; Falteisek et al., 2019) and As sulfide minerals found in salt flats were confirmed to have a microbial origin (Demergasso et al., 2007). A sulfate-reducing consortium supplied with glycerol was able to completely remove As from acid mine drainage at pH 4 by precipitation as orpiment and realgar (Le Pape et al., 2017).

The other side of iron redox cycling is microbial oxidation of Fe(II), forming Fe(III) oxide minerals that can sequester As. Stimulating Fe(II) oxidation has been proposed as a means to treat As contaminated waters (Section 4.1). Nitrate was used to stimulate microbial Fe(II) and As(III) oxidation in anaerobic sediment columns, and As was removed from solution as As(V) sorbed to Fe(III) oxyhydroxides (Sun et al., 2009). Iron oxides (ochres) precipitated from mine drainage could be used to treat arsenic-contaminated soils (Doi et al., 2005) although it appears they are better at removing As from solution rather than improving contaminated soils (Olimah et al., 2015). Co-precipitation of As(V) and Fe(III) minerals mediated by bacteria removed up to 75% of As and 13% of Fe (Casiot et al., 2003). Microbially mediated As(III) oxidation

and schwertmannite formation could be applied to treat highly contaminated soils, removing up to 99% of As (Yang et al., 2017). Manganese(IV) oxides can effectively oxidize As(III) to As(V) (Fischel et al., 2015; Oscarson et al., 1981). Mn(IV) oxides are also preferentially reduced before As(V)-bearing iron oxides and therefore will delay the release of As to solution under reducing conditions (Ehlert et al., 2016).

The volatilization of As via methylation will in principle lower the As content of contaminated soils, and this is favored under reducing conditions (Frohne et al., 2011). Methanogenic conditions also slightly favor the methylation of As (Webster et al., 2016). Arsenic methylation is widespread in the environment, including in mining environments (Héry et al., 2014; Ngegla et al., 2020). However, the significance of this process to the overall fate of As is questionable, with relatively low proportions of soil arsenic volatilized.

3.1.3. Implications for Mine Waste Containing Arsenic

Mine waste contaminated with arsenic is a relatively common problem, with very high concentrations (g kg^{-1}) found at some mine sites. Arsenic poses particular challenges to human health due to its toxicity. However, the impact of As on the soil environment appears to be less severe. In terms of soil functioning, As contamination has a variable impact, with some effects observed at relatively low concentrations (30–40 mg kg^{-1}) while other studies showed limited effects or even As-induced stimulation at high concentrations. Studies of contaminated field samples appear to show that As contamination does not adversely affect microbial communities, which perhaps is unsurprising given the multiple arsenic resistance mechanisms that are widespread amongst prokaryotes and fungi, including detoxification and methylation.

Microbial activity can control the mobility of arsenic in the environment. Immobilization of As in insoluble minerals decreases the likelihood of human exposure via aquatic pathways or plant uptake. Oxidising conditions favor As(V) which sorbs strongly to iron oxide minerals, which can form abiotically or by microbial activity. The genes for these processes are widely distributed in environmental samples indicating that they are likely to occur when the geochemical conditions are suitable (e.g., microaerophilic, redox interfaces, or low pH). Maintaining oxidising conditions and the presence of Fe(III) minerals is beneficial for minimizing As mobility in the environment.

The presence of reducing conditions is likely to favor the formation of the more mobile and toxic As(III), via the desorption of As(V) from iron oxides during microbial Fe(III)-reduction, and via respiratory As(V) reduction. These processes are stimulated by a wide range of electron donors and organic compounds that are commonly available in the environment. However, if the conditions become more reducing to stimulate sulfate reduction, As can be removed from solution in association with iron sulfide minerals and directly as As-sulfide. The significance of this compared with the release of As to solution during the reduction of Fe(III) oxides is not yet clear. The presence of microbial As sulfide minerals in the environment under strictly anoxic conditions suggests that strongly reducing conditions will also limit the mobility of As in the environment.

3.2. Cadmium

Cadmium has no known biological function, it bioaccumulates in plants and animals, and is toxic and carcinogenic to humans

3.2.1. Cadmium Geochemistry

Cadmium is typically present in the Earth's crust at 0.1–0.5 mg kg^{-1} but is concentrated in Cu, Pb and Zn ores and wastes (Agency for Toxic Substances & Disease Registry, 2012a). Generally Cd is immobilized in soil through binding strongly to organic matter, although it remains bioavailable in this form, particularly under acidic pH conditions (Agency for Toxic Substances & Disease Registry, 2012a). Cd is not redox active, it is mobile in waters as Cd^{2+} ions or forming water-soluble complexes with anions, humic acids and dissolved organic matter (Kubier et al., 2019).

3.2.2. Microbial Interactions With Cadmium

3.2.2.1. Uptake Mechanisms and Mode of Toxicity

Cadmium can enter cells via the Mn^{2+} and Zn^{2+} transport systems (Hao et al., 1994; Laddaga & Silver, 1985). Cd toxicity is caused primarily by DNA damage through binding to sulfhydryl groups in proteins, but it can occur via cell membrane disruption, inhibition of translation, cell division, and enzymatic activity, and protein denaturation (Roane et al., 2015).

3.2.2.2. Direct Resistance Mechanisms

Cadmium resistance is often achieved in prokaryotes via the use of efflux pumps, such as the plasmid encoded *cadA* gene from *Staphylococcus aureus* (Nucifora et al., 1989), or through biosorption of Cd to functional groups in the cell wall (Manasi et al., 2014). Cd binding to metallothioneins has been identified in the cyanobacterium genus *Synechococcus*, although metallothioneins are more commonly found in eukaryotes (Blindauer, 2011; Olafson et al., 1979). Fungi can sequester Cd as a glutathione complex in the vacuole (Y. Li et al., 1997).

Transcriptomics and proteomics have been used to investigate the molecular response to Cd. Following exposure of a wastewater consortium to 10 mg L^{-1} Cd, the expression of >100 proteins changed relative to controls, and the results varied depending on the length of time after exposure (15 min compared to 2 h; Lacerda et al., 2007). Differential expression of bacterial proteins known to be involved in response to Cd shock included ATPases, dehydrogenases, ribosomal proteins, oxidoreductases, catalase, superoxide dismutase, inorganic pyrophosphatase and transcriptional regulators. A proteome study of *S. cerevisiae* found that Cd exposure induced expression of the sulfur amino acid biosynthetic pathway and caused increased glutathione and cysteine biosynthesis; this may contribute to Cd-resistance via chelation and transport into the vacuole (Vido et al., 2001). The authors concluded that the glutathione and thioredoxin redox systems are important contributors to cellular Cd detoxification in yeast.

3.2.2.3. Indirect Resistance Mechanisms

Indirect Cd resistance can occur via the precipitation of Cd biominerals, such as phosphates, carbonates and sulfides. Cd was immobilized from solution via the formation of phosphate minerals, using glycerol phosphate to stimulate the phosphatase activity of a *Serratia* sp. (Macaskie & Dean, 1984). A Cd-resistant *Geobacter* sp. was shown to be able to reduce Cd-doped Fe(III)-oxide ferrihydrite and precipitate dissolved Cd from solution as an otavite ($CdCO_3$), siderite ($FeCO_3$) and calcite mixed mineral phase (Muehe, Obst, et al., 2013). Microbial sulfate reduction can precipitate Cd from solution; *Desulfovibrio desulfuricans* and *Desulfococcus multivorans* oxidized lactate and reduced sulfate in the presence of up to 0.5 mmol L^{-1} Cd, with Cd minerals accumulating intracellularly and in the periplasm (suggested to be due to binding to a metallothionein homologs; Naz et al., 2005). In a separate study the growth of a mixed culture biofilm of sulfate-reducing bacteria was not inhibited by 0.2 mmol L^{-1} Cd, with CdS granules observed to accumulate within the biofilm (White & Gadd, 1998). However in some cases it appears that the presence of Cd may inhibit bacterial sulfate reduction at 0.1–0.18 mmol L^{-1} (Gonzalez-Silva et al., 2009; Hao et al., 1994; Medírcio et al., 2007). Microorganisms have also been shown to facilitate the precipitation of CdS nanoparticles under non-sulfidogenic conditions. This can occur due to bacterial extracellular polymeric substances acting as a nucleation surface in the presence of a cadmium salt and Na_2S (Raj et al., 2016; Sakpirom et al., 2019; Sweeney et al., 2004), or by the activity of cysteine desulfhydrase producing S^{2-} to generate CdS nanoparticles which can then be transported extracellularly (Bai et al., 2009; Cunningham & Lundie, 1993). CdS nanoparticles can also be synthesized by yeasts and fungi (Ahmad et al., 2002; Dameron et al., 1989), for example, intracellular CdS formed in *Candida* spp. cultures under non-growth conditions (Cuéllar-Cruz et al., 2017).

3.2.2.4. Impact on Soil Microbial Processes and Microbial Communities

A 25-year field study of soils spiked with up to 250 mg kg^{-1} $CdCl_2$ showed decreased microbial diversity and fewer respiratory quinones compared to unamended control soils (5 mg kg^{-1} Cd; Lorenz et al., 2006). The soils with the highest Cd concentrations had lower protease, urease, phosphatase and sulfatase activities compared to the control, but higher xylanase activity, this was suggested to be due to an increased requirement for C for maintenance and repair processes caused by metal contamination. Another long-term

field study contaminated soils with up to 40 mg kg^{-1} $Cd(NO_3)_2$ and analyzed soil enzyme activities after 11–13 years (Renella et al., 2005). Compared to uncontaminated soils, Cd contamination led to higher metabolic quotients (CO_2-C respired to ATP ratio) and lower hydrolase activities, indicating that microbial metabolism was less efficient in the presence of Cd. At the higher concentrations of Cd, soils also had lower phosphatase, glucosidase, protease and sulfatase enzyme activities, but urease activity was not affected. The microbial communities present in soils from abandoned farmlands contaminated with unspecified industrial wastes including Cd (up to 47 mg kg^{-1}) were compared (X. Li et al., 2017). The Shannon diversity indices and number of operational taxonomic units were not significantly different, but some differences in microbial community composition were observed.

The soil microbial community has been shown to affect Cd bioavailability; metal-hyperaccumulating *Arabidopsis halleri* plants accumulated 1.9 times less Cd when grown on gamma irradiated "sterile" soil compared to untreated soil, suggesting microbial activity may contribute to Cd uptake (Muehe et al., 2015). Inoculating contaminated soils with a phosphate-solubilizing bacterium significantly increased Cd uptake in plants compared to the non-inoculated controls, but it also enhanced plant growth (Jeong et al., 2012). Microbes can also decrease Cd uptake by plants; inoculating contaminated soils with Cd-resistant bacterial isolates decreased Cd uptake by mung bean, due to intracellular and periplasmic accumulation of Cd by the isolate SB21 (Saluja & Sharma, 2014).

3.2.2.5. Impact of Biogeochemical Cycling

As well as transforming aqueous Cd, sulfate-reducing microorganisms can decrease the bioavailability of Cd in mine waste. A column study amended Cd-contaminated mine waste (67 mg kg^{-1} Cd) with organic carbon and sodium sulfate, and showed that the Cd was initially present as a mixture of carbonate, sulfate, nitrate and hydroxide phases, but after 252 days it comprised 39% Cd-sulfide and 61% Cd-carbonate (Karna et al., 2018). The sulfur-cycling genes *dsrB* and *dsrA* were significantly more abundant compared to the unamended control, and far less Cd was released to the aqueous phase (Karna et al., 2016), leading the authors to conclude that constructed wetlands are beneficial for stabilizing Cd in mine waste materials. Non-sulfidogenic metal-reducing conditions were shown to decrease the bioavailability of Cd in anoxic soil microcosms, and more so when the activity of indigenous Fe(III)-reducing bacteria was stimulated by adding an organic electron donor (Muehe, Adaktylou, et al., 2013). The authors suggested that Cd was immobilized primarily within a mixed Fe(II)/Fe(III) mineral such as magnetite, with a minor fraction associated with carbonate and sulfide phases.

3.2.3. Implications for Mine Waste Containing Cadmium

Cadmium-contaminated mine waste is a fairly uncommon environmental problem, but it does pose a serious risk due to its toxicity. Microbial activity can decrease the mobility of Cd in the environment and consequently the likelihood of it causing adverse effects, and therefore bioremediation has the potential to improve planetary health. It appears that stimulating the development of metal-reducing and sulfate-reducing conditions by adding organic C to sediment microbial communities may stabilize Cd in the solid phase, and/or precipitate it from the aqueous phase, via the formation of sulfide or Fe(II)-containing minerals. Although different microbial processes have been shown to increase or decrease Cd uptake by plants, overall it appears that the formation of anoxic conditions is likely to limit Cd bioavailability in the environment. Remediation of Cd by applying organic amendments such as waste materials has been the subject of a number of studies, and has been shown to immobilize Cd by increasing sorption to soils, increasing the pH and decreasing Cd bioavailability, although adverse side effects such as water pollution by N and P and the presence of other metals in organic wastes should be taken into account (Khan et al., 2017).

3.3. Chromium

Chromium is highly toxic and non-essential for microorganisms (Cervantes et al., 2001). Cr(III) is a micronutrient for mammals, however Cr(VI) is highly toxic and carcinogenic (Agency for Toxic Substances & Disease Registry, 2012b).

3.3.1. Chromium Geochemistry

Chromium is typically present in the Earth's crust at 100–300 mg kg^{-1} (Cervantes et al., 2001). Cr is mined in several locations around the world as chromite ($FeCr_2O_4$) or in association with other minerals. Cr bioavailability and toxicity vary depending on its oxidation state; Cr(VI) is more toxic and soluble and forms oxyanions, while Cr(III) is less toxic and soluble, it forms oxides, hydroxides or sulfates, and binds to organic matter (Agency for Toxic Substances & Disease Registry, 2012b). The solubility of Cr is dictated by pH; Cr(III) precipitates under neutral to basic pH conditions, while at low pH it tends to remain in solution; Cr(VI) is soluble under all pH conditions. Cr in soils is subject to redox cycling, but when oxidative conditions predominate, Cr(VI) can persist for years (Cervantes et al., 2001; Kimbrough et al., 2010; Oliveira, 2012).

3.3.2. Microbial Interactions With Chromium

3.3.2.1. Uptake Mechanisms and Mode of Toxicity

Cr(III) does not enter the cell and accumulates extracellularly by binding to the cell wall (Flemming et al., 1990). Active uptake of Cr as Cr(VI) occurs via the sulfate transport system in prokaryotes and eukaryotes (Cervantes et al., 2001). Inside the cell Cr(VI) is reduced to Cr(V), Cr(IV), free radicals and Cr(III). During the reduction process reactive oxygen species are produced, deteriorating normal physiological functions, and intracellular Cr(III) alters enzymatic activity and structure and interferes with DNA replication (Cervantes et al., 2001).

3.3.2.2. Direct Resistance Mechanisms

Transformation of Cr(VI) to the less toxic form Cr(III) is considered to be a resistance mechanism. Several bacterial and fungal species are able to reduce Cr(VI) to Cr(III) using direct mechanisms, or indirectly by producing reducing agents extra- or intracellularly (Ramírez-Díaz et al., 2008). Several Cr(VI) reductases have been identified and characterized (e.g., chromate reductases Gh-ChrR, YieF, and Nema); a comprehensive list of these enzymes can be found in Thatoi et al. (2014). It has been suggested that the reduction of Cr(VI) is a secondary function as in the case of the nitroreductases NfsA/NfsB (Ramírez-Díaz et al., 2008); the Cr(VI) reducing activity of these enzymes is an adaptation to the prolonged exposure to Cr(VI). Tolerance to Cr depends greatly on its oxidative state, the minimum inhibitory concentrations for Cr(III) for *A. ferroxidans* and *Acidithiobacillus ferridurans* were 50–100 mM, but only 5 μM for Cr(VI; Johnson et al., 2017). The moderate halophilic *Nesterenkonia* sp. strain MF2 was able to tolerate up to 600 mM chromate (Amoozegar et al., 2007).

Resistance in yeast is mostly due to the limited Cr uptake, by direct transformation of Cr(VI) to Cr(III) or by secreting reducing agents that reduce Cr(VI). A yeast isolated from industrial wastewater (*Candida tropicalis*), showed the ability to uptake Cr(VI) and reduce it to Cr(III; Ilyas et al., 2020). The yeasts *S. cerevisiae* and *Pichia guilliermondii* were able to reduce Cr(VI) and produce a chelating agent that trapped Cr(III) extracellularly when grown in the presence of Cr(VI) (Ksheminska et al., 2006). In another study, *S. cerevisiae* was used to remove 85% Cr(VI) from tannery wastewater optimally at pH 3.5; the authors found evidence that Cr sorbed to the cell walls (Mahmoud & Mohamed, 2017).

3.3.2.3. Indirect Resistance Mechanisms

Other resistance mechanisms relate to the production of enzymes involved in the protection against oxidative stress, DNA damage, sulfur metabolism, and iron binding. Ramírez-Díaz et al. (2008) summarizes the different resistance mechanisms found in bacteria. Protecting against oxidative stress includes the activation of certain enzymes, such as producing thioredoxin and glutaredoxin in *Caulobacter crescentus* or *Shewanella oneidensis* MR-1 (Chourey et al., 2006; Hu et al., 2005). The presence of the plasmid pMOL28 in *Cupriavidus metallidurans* encodes a chromate efflux pump and two other proteins involved in chromate resistance (Nies et al., 1990). The presence of Cr(VI) is known to induce the generation of repair systems in *Pannonibacter phragmitetus* strain BB; 361 proteins were upregulated including enzymes involving extracellular reduction (Chai et al., 2019).

3.3.2.4. Impact on Soil Microbial Processes and Microbial Communities

The presence of Cr(VI) in soils has a negative impact on the microbial community in soils. CrO_4^{2-} reduced the microbial activity measured as ^{3}H-leucine incorporation (Shi et al., 2002). Soils heavily contaminated

with Cr(VI) had different microbial communities and functioning compared to uncontaminated soils, with Cr(VI) reduction ability higher in heavily contaminated soils (Pei et al., 2018). Increasing the Cr(VI) concentration (up to 100 mg kg^{-1}) was shown to substantially decreases dehydrogenase, alkaline phosphatase and fluorescein diacetate activity (Dotaniya et al., 2017). Catalase activity was reduced when soil experiments were amended with Cr(III) and Cr(VI) at 2, 5, 10, and 20 mg kg^{-1}; at the maximum concentration catalase activity decreased by 83% and 68% for both Cr(III) and Cr(VI) (Stêpniewska et al., 2009). The soil enzymatic activity (dehydrogenase activity and alkaline phosphatase) in Cr-contaminated mine soils was negatively correlated with Cr content, however urease activity was higher in the contaminated mine soils when compared with control soils (Pradhan et al., 2020).

3.3.2.5. Impact of Biogeochemical Cycling

The ability of some organisms to reduce Cr(VI) to Cr(III), either aerobically or anaerobically, could be used to bioremediate contaminated soils or wastes (Dhal et al., 2013). There are several microbial species that can reduce Cr(VI) to the less soluble form Cr(III). *Pseudomonas mendocina* reduced up to 90% of the Cr(IV) in soil to Cr(III) in 12 h (Salunkhe et al., 1998). The use of *Bacillus* PSB10, a Cr(VI)-reducer and plant growth-promotor increased the growth of chickpea plants in the presence of Cr and reduced uptake (Wani & Khan, 2010). Although at high pH values Cr(VI) reduction is slower than at lower pH, the isolation of alkaliphilic *Halomonas* spp. able to reduce Cr(VI) at pH 10 opens the possibility of *in situ* bioremediation of chromium ore processing residue under alkaline conditions (Watts et al., 2015). Under certain conditions and in the presence of O_2 or Mn oxides, Cr(III) can be oxidized to Cr(VI) although this is uncommon; most Cr(III) will not be oxidized to Cr(VI) even in the presence of Mn oxides (Zayed & Terry, 2003).

The production of Mn oxides and Fe oxides by microorganisms influences the fate of Cr via the reduction and/or adsorption of Cr(VI), although there are few studies focusing on this topic (Whitaker et al., 2018; Xia et al., 2019). In microcosms with alkaline soil contaminated with Cr, the presence of Fe(II) caused the reduction of Cr(VI) to Cr(III) (Whittleston et al., 2011). Iron reducing microorgansims were found in this soil, and the authors in the study suspected that members of the Firmicutes were responsible for the reduction of Fe(III) and the regeneration of Fe(II). Further evidence of Cr(VI) being reduced by Fe(II) produced by microbial Fe(III) reduction has been observed (Ding et al., 2016; Whittleston et al., 2011, 2013). In acid pit lakes, microbial Fe(III) and sulfate reduction have been linked to the precipitation of aluminum oxyhydroxides, through increasing the pH and providing nucleation surfaces; these Al minerals also effectively removed Cr and other metals from solution via sorption and co-precipitation (Sánchez-España et al., 2016).

3.3.3. Implications for Mine Waste Containing Chromium

Most Cr contamination is produced by industrial processes other than mining; therefore mining itself is not the most significant contributor to Cr(VI) pollution and the risk it poses to planetary health. However, chromite ore processing residue poses significant environmental problems, albeit on a localized scale, and it is difficult to treat due to its alkaline pH. Promoting the development of conditions that favor Fe(III)-reducing microorganisms that are already present in contaminated soils/waste could be a feasible long-term way of immobilizing Cr as $Cr(OH)_3$. As Cr(VI) reduction can take place under oxic and anoxic conditions, it seems that the probability that this process occurs naturally is high, given the availability of sufficient electron donor the mobility and bioavailability of Cr will naturally diminish. On the other hand, promoting iron oxidation would also help the removal of Cr from contaminated waters as iron oxides adsorb several metals, including Cr.

3.4. Copper

Copper is an essential element that is required for the functioning of many enzymes in all domains of life, although it can be toxic at high concentrations, as well as deficient at low concentrations. As such, intracellular concentrations of Cu are carefully balanced by homeostasis; the regulation of acquisition, sequestration and efflux mechanisms.

3.4.1. Copper Geochemistry

Copper is typically present in the Earth's crust at an average concentration of 50 mg kg^{-1} (Agency for Toxic Substances & Disease Registry, 2004). Copper speciation is influenced by pH, redox potential and the

presence of other ions for example, Cl^-, OH^-, SO_4^{2-}, and CO_3^{2-} (Cuppett et al., 2006). Temperature has a weaker effect on Cu speciation (Casas et al., 2000). It can be found as Cu^+ or Cu^{2+} in aqueous solutions, although Cu^+ is unstable and easily oxidized to Cu^{2+}. In nature it also exists as elemental Cu, and as Cu(II) or Cu(I) in minerals for example, chalcopyrite ($CuFeS_2$), chalcocite, malachite ($Cu_2[CO_3]\,[OH]_2$). Chalcopyrite is very common in mine wastes, it is a recalcitrant Cu sulfide mineral that dissolves slowly generating Cu-rich acid mine drainage. Cu mining generates large quantities of solid wastes for example, tailings and aqueous acid mine drainage (Milu et al., 2002).

3.4.2. Microbial Interactions With Copper

3.4.2.1. Uptake Mechanisms and Mode of Toxicity

As Cu is part of many biological functions, maintaining intracellular Cu concentrations at the right level is of major importance for organisms. There are several proteins in bacteria involved in the active transport of Cu: porins, TonB-dependent transport systems, and chalkophores (Cu-binding metallophores; Andrei et al., 2020; Argüello et al., 2013). Proteins involved in the transport of Cu from the periplasm to the cytoplasm include major-facilitator-superfamily type transporters and chalkophores (Andrei et al., 2020). Copper transport in eukaryotes (e.g., *S. cerevisiae, Aspergillus fumigatus*) is carried out by the membrane-associated Cu transporting protein (Ctr) family, Cu binding or acquisition motifs (Mets) (Antsotegi-Uskola et al., 2020; Smith et al., 2017), or low-affinity uptake systems as the Fe, Cu, and Zn transporter Fet4 in *S. cerevisiae* (Smith et al., 2017). Modes for Cu toxicity include depolarization of the cytoplasmic membrane, loss of membrane integrity, inhibition of respiration and generation of reactive oxygen species that provoke damages in the DNA and other cell structures (Warnes et al., 2012). Copper also induces oxidative stress responses at higher concentrations that oversaturate homeostasis inside the cell. Cu toxicity is also determined by pH; in acidophilic microorganism experiments Cu became more toxic as the pH increased from 1.8 to 2.2 (Falagán & Johnson, 2018), due to the positive membrane potential becoming more negative at higher pH values (Alexander et al., 1987).

3.4.2.2. Direct Resistance Mechanisms

Bacterial resistance mechanisms to Cu involve the active efflux of the metal from the cytoplasm to the periplasmic space, via enzymes such as ATPases, protein complexes and clusters (the Cus-system and Cop/Pco systems; Andrei et al., 2020; Orell et al., 2010). The presence of ATPases involved in Cu resistance in *A. ferrooxidans* and *Escherichia coli* suggests they function as efflux pumps, and they are also found in eukaryotes (Antsotegi-Uskola et al., 2020; Orell et al., 2010). Some bacterial Cu resistance is conferred by the presence of Cu-binding proteins and chaperones located in the periplasmic space that sequester Cu, decreasing its toxicity and providing Cu for biogenesis of cuproenzymes (Andrei et al., 2020). Extracellular complexation in *Vibior alginolyticus* has also been described as a resistance mechanism (Harwood & Gordon, 1994) although this organism is very sensitive to Cu in general terms as it can only tolerate up to micromolar concentrations. Microorganisms typically found in acidic environments such as *A. ferrooxidans* show similar Cu resistance mechanisms to other neutrophilic microorganisms (e.g., ATPases, chaperones). Acidophiles can resist higher concentration of heavy metals up to 300 mM (Norris et al., 2020) compared to some neutrophiles, for example the minimum inhibitory concentrations for different strains of *Pseudomonas* were far lower at 2.8–3.5 mM (Singh et al., 2010). Cu resistance mechanisms found in fungi and yeast include the sequestration of Cu by metallothioneins in *S. cerevisiae* and *Candida albicans*, extracellular sequestration and chelation agents (Antsotegi-Uskola et al., 2020; Radić et al., 2017; M. Wang et al., 2020).

3.4.2.3. Indirect Resistance Mechanisms

Interesting groups highly resistant to Cu are the acidophilic bacteria and archaea used in biomining. These microorganisms tolerate elevated concentrations of metals, including Cu, at levels (e.g., >100 mM) that are toxic for many other microorganisms (Falagán et al., 2019; Norris et al., 2020; Panyushkina et al., 2019). Their positive membrane potential provides a resistance mechanism for the accumulation of cations such as Cu in their cytoplasm (Falagán & Johnson, 2018; Orell et al., 2010).

The production of long polymers of inorganic polyphosphate may be related to Cu resistance; enzymes involved in polyphosphate production (polyphosphate kinase [PPK]) and hydrolysis have been found in several microorganisms (Orell et al., 2010; Remonsellez et al., 2006). In Remonsellez et al. (2006), the authors

relate the accumulation of polyphosphate granules to Cu resistance; in experiments with three different *Sulfolobus* species, only the polyphosphate granule producing strain *Sulfolobus metallicus* could grow in up to 200 mM of $CuSO_4$. Electron-dense granules composed of polyphosphates have also been found in other acidophiles such as *A. ferrooxidans* when grown in the presence of 10–100 mM Cu, suggesting that polyphosphates were involved in Cu resistance (Alvarez & Jerez, 2004).

3.4.2.4. Impact on Soil Microbial Processes and Microbial Communities

The presence of microorganisms alters the bioavailability of Cu. Accumulation of Cu by *Elsholtzia splendens* (a shrub of the mint family) was enhanced by the presence of bacteria isolated from the rhizosphere of the plant (Chen et al., 2005) indicating that these microorganisms possess an important role in Cu uptake by plants. Some fungi are also able to accumulate Cu (Hong et al., 2010) which reduces its bioavailability.

The presence of Cu in soils alters the microbiome towards a community dominated by Cu-resistant bacteria (Berg et al., 2005; Fagnano et al., 2020; Nunes et al., 2016; Shaw et al., 2020; Wang et al., 2007). The presence of Cu diminished the abundance and diversity of *Pseudomonas* spp. in rhizosphere soil, affecting both the microbial community and plants (Brandt et al., 2006). A long-term field study applied contaminated sludge to soils to achieve concentrations of up to 200 mg kg^{-1} Cu and then sampled the soils 10 years later to assess the effect on the microbial communities (Singh et al., 2014). In the Cu contaminated soils the operational taxonomic unit richness was reduced by 5%–10%, and the composition of functional genes (i.e., C, N, P, S cycling, antibiotic resistance, and metal resistance/reduction) was significantly shifted compared to unamended controls. Soil functioning assessed via basal respiration and glucose mineralisation was unaffected, suggesting that although Cu changed the microbial community diversity and composition, it did not have a long-term impact on soil functioning. In another study, Cu contamination up to 200 mg kg^{-1} had little effect on the enzymatic activity of terrestrial model ecosystems (i.e., dehydrogenase, urease, β-glucosidase, N-acetyl- β-glucosaminidase, acid phosphatase, and alkaline phosphatase) over a 70 day incubation. In Milosavljevic et al. (2020), the enzyme arylsulphatase was negatively correlated to Cu contamination in the soils studied and β-glucosidase was positively correlated to Cu, Fe, and Zn content. In another study, dehydrogenase, acid phosphatase and arylsulfatase enzymes were found to be the most sensitive to Cu contamination (Aponte et al., 2020).

3.4.2.5. Impact of Biogeochemical Cycling

The presence of sulfate-reducing bacteria and subsequent production of sulfide decrease the bioavailability of Cu by locking it up as a highly insoluble copper sulfide (Xu & Mills, 2018). Microorganisms have been used to bioaccumulate Cu; different strains of *Fusarium solani* and *Hypocrea lixii* were able to accumulate copper from 15 mM Cu-containing solid media in their mycelia (Hong et al., 2010), Some strains of *Pseudomonas* spp. and *Candida* spp. accumulated Cu up to 25 mg g^{-1} dry weight when grown with 2.9 mM Cu (Ahemad & Malik, 2011).

3.4.3. Implications for Mine Waste Containing Copper

Copper contamination in mine waste is a very common environmental problem. Mine tailings rich in chalcopyrite and other sulfide minerals are the main source of AMD, which causes adverse environmental impacts and poses a serious risk to planetary health. Although Cu is not particularly toxic to humans, it is highly toxic to aquatic organisms, especially fish. In terms of soil functioning, Cu does not appear to have a significant impact, although soils contaminated with Cu tend to be dominated by Cu resistant microorganisms. Nonetheless the continuous exposure to very high Cu concentrations that can be found in mine wastes will cause toxicity for most organisms. The development of anoxic environments favoring the growth of sulfate-reducing bacteria decreases the environmental mobility and bioavailability of Cu by trapping it as insoluble copper sulfide, and therefore stimulating these conditions could be applied as a bioremediation strategy.

3.5. Lead

Lead has no known biological function and is toxic to humans, exhibiting toxic effects in all organs, and it is mutagenic, teratogenic and a probable human carcinogen.

3.5.1. Lead Geochemistry

Concentrations of Pb in the Earth's crust are typically 15–20 mg kg^{-1}; galena (PbS) is the most important Pb mineral, with anglesite ($PbSO_4$) and cerussite ($PbCO_3$) also common (Agency for Toxic Substances & Disease Registry, 2020). Lead is predominantly present as Pb(II) under almost all environmental conditions. Pb is relatively immobile in soils as it sorbs strongly to soil particles such as clays, silts, Fe and Mn oxides and organic matter, but it can form mobile complexes with organic C at pH 4–6 (Agency for Toxic Substances & Disease Registry, 2020). Pb is effectively retained in soils, often due to strong binding to organic matter present in humic layers (Michopoulos et al., 2005; Siccama & Smith, 1978; Ukonmaanaho et al., 2001). Transport of Pb in rivers is largely in the solid phase as colloids, particles of Pb carbonate, oxide or other minerals, or sorbed to sediment; Pb sorbed to colloids is the most labile fraction (Agency for Toxic Substances & Disease Registry, 2020). The solubility of Pb in natural waters is limited by the formation of carbonate, hydroxide and sulfur minerals. Pb solubility increases at lower pH, in the presence of high chloride, and under reducing conditions.

3.5.2. Microbial Interactions With Lead

3.5.2.1. Uptake Mechanisms and Mode of Toxicity

Lead as Pb^{2+} can substitute for Ca^{2+} and enter cells via Ca^{2+} channels (Kerper & Hinkle, 1997). Pb can damage DNA, proteins and cell membranes via binding to sulfhydryl, phosphate and hydroxyl functional groups (Kushwaha et al., 2018; Roane et al., 2015). Pb causes toxicity to yeast by inhibiting protein synthesis and generating reactive oxygen species (Sousa & Soares, 2014; Van der Heggen et al., 2010).

3.5.2.2. Direct Resistance Mechanisms

Pb resistance in bacteria has been reported to occur via transport using the P-type ATPase efflux pumps ZntA and CadA (Binet & Poole, 2000; Rensing et al., 1998). The first report of a specific Pb-resistance mechanism was for *Cupriavidus metallidurans* CH4 (Borremans et al., 2001), which has a plasmid-located Pb resistance operon (*pbr*) that encodes for Pb(II) uptake, efflux and accumulation. Increased sensitivity to Pb(II) was shown to occur via overexpression of the PbrT protein, then cytoplasmic Pb(II) could be transported extracellularly by the PbrA Pb(II) ATPase and/or bound and accumulated by the PbrD protein. The minimum inhibitory concentration for Pb(II) in *C. metallidurans* CH4 was reported as 0.3 mmol L^{-1} (Taghavi et al., 2008). A similar plasmid-located gene cluster has since been identified in *Achromobacter xylosoxidans* and confirmed to confer Pb-resistance (Hložková et al., 2013). Some Pb-resistant bacteria can bind Pb intracellularly. *Bacillus megaterium* was shown to form nanoparticles of Pb within the cytoplasm (Roane, 1999), *Providencia vermicola* strain SJ2A bound Pb in the periplasm as lead sulfite ($PbSO_3$; Sharma et al., 2017) and *Salmonella choleraesuis* strain 4A and *Proteus penneri* strain GM10 accumulated 20 mg g^{-1} Pb (Naik et al., 2012); all three studies suggested that metallothionein-like proteins may have played a role in Pb sequestration.

3.5.2.3. Indirect Resistance Mechanisms

Microbial precipitation of Pb minerals can act as an indirect resistance mechanism. Both bacteria (*A. xylosoxidans*) and fungi (*P. javanicus*) can precipitate Pb(II) extracellularly as pyromorphite, linked to phosphatase activity (Liang, Kierans, et al., 2016; Sharma et al., 2018). *Bacillus ceres* 12–2 was shown to form Pb-hydroxyapatite ($Ca_{2.5}Pb_{7.5}[OH]_2[PO_4]_6$) both intra- and extracellularly, linked to enzyme activity (Chen et al., 2016). Some fungi can transform metallic Pb into pyromorphite, the most stable Pb mineral (Rhee et al., 2012). Indeed, phosphate has been shown to effectively immobilize Pb in soils, demonstrated via the addition of P as phosphate rock and phosphoric acid (Cao et al., 2002). As well as forming Pb-phosphate biominerals, fungi can secrete oxalic acid to precipitate Pb(II) as Pb-oxalate (Liang, Kierans, et al., 2016). *A. niger* can transform pyromorphite into Pb-oxalate (Sayer et al., 1999). *Candida* spp. were observed to precipitate Pb^{2+} as extracellular PbS under growth conditions. These studies show the importance of microbes, particularly fungi, in immobilizing Pb in soils.

Binding of Pb by siderophores may also affect its mobility. A *Pseudomonas aeruginosa* strain 4EA isolated from Pb-contaminated soils was observed to secrete more siderophores in the presence of higher Pb concentrations (Naik & Dubey, 2011). The binding of non-Fe metals by siderophores secreted by *Pseudomonas*

spp. has been investigated extensively, and it appears that metal accumulation is prevented by the activation of an ATP-dependent siderophore efflux pump rather than by limiting metal uptake (Johnstone & Nolan, 2015; Schalk et al., 2011).

3.5.2.4. Impact on Soil Microbial Processes and Microbial Communities

The impact of lead on soil microbial communities varies depending on the soil type (Doelman & Haanstra, 1979). Adding 375 mg kg^{-1} Pb to sandy soils lowered the respiration and dehydrogenase activity, this occurred to a lesser extent in clay soils, whereas no impact was observed in peat soils, demonstrating the importance of organic matter in controlling Pb bioavailability.

The microbial community in a soil that was naturally elevated in Pb (10% w/w Pb, formed from the chemical weathering of galena) was compared to an adjacent uncontaminated soil (Bååth et al., 2005). The abundance of bacteria was not significantly different between the Pb-soils and the controls, but it appeared that Gram-positive bacteria were more common in the Pb-soils. In contrast, fungi were less prevalent in the Pb-soils, which was suggested to be due to the lack of plant roots, and the composition of fungal isolates was very different to the control soils. A study of Pb-contaminated forest soils (13,750 mg kg^{-1}) involving 16S rRNA and ITS amplicon sequencing showed a similarly diverse bacteria community compared to an uncontaminated control, with no major differences seen in bacterial community structure at the phylum level (Hui et al., 2012). However, the fungal community was significantly less diverse at the contaminated site, with the Basidiomycota particularly affected. A field study of soils at varying distances from a Pb/Zn mine found a gradient in the number of culturable bacteria, bacterial community diversity, and soil enzyme activities (dehydrogenase, phosphatase, urease), with a considerable decrease in these parameters observed when concentrations exceeded 965–1575 mg kg^{-1} Pb (Qu et al., 2011).

3.5.2.5. Impact of Biogeochemical Cycling

The column study described for Cd (Section 3.2.2) where contaminated mine waste was amended with organic carbon and sodium sulfate also contained Pb (5,050 mg kg^{-1}), which was initially present as a mixture of carbonate, sulfate and phosphate phases (Karna et al., 2018). After 252 days amendment the waste comprised 62% Pb-sulfide and 38% Pb-carbonate, and far less Pb was released to the aqueous phase compared to the unamended control (Karna et al., 2016). This demonstrates that the development of reducing conditions in constructed wetlands would be beneficial for the immobilization of metals, including Pb. However, volatile and toxic tetramethyl lead can be formed in anaerobic (lake) sediments (Agency for Toxic Substances & Disease Registry, 2020), although methylation of Pb to tetramethyl lead was not found to be a significant process in a study of anoxic wetland soil (Huang & Matzner, 2005), and it would be likely to be rapidly oxidized in aerobic conditions.

Manganese oxides are known to have a strong affinity for Pb. A study of massive deposits of Mn-oxides in a karst cave system underlying a former Pb-mine works found that they contained a diverse microbial community and had accumulated a substantial amount of Pb, up to 55 wt. % (Newsome et al., 2021). Around 5% of prokaryotic DNA sequences and 10% of fungal DNA sequences was closely related to known Mn(II)-oxidizers, and active Mn(II)-oxidising bacteria were isolated. This suggested that Mn(II)-oxidising bacteria and fungi present in the cave crusts may have been responsible for Mn(IV)-oxide mineral formation and contributed to the attenuation of Pb from the former mine workings.

3.5.3. Implications for Mine Waste Containing Lead

Lead is a fairly common contaminant in mine wastes, and is highly toxic to humans, therefore has serious implications for planetary health. However, many Pb minerals are poorly soluble and therefore the likelihood that they will be transported significant distances in the environment is low, although the formation and inhalation of Pb-rich dusts near mine sites is an issue. Overall it appears that the presence of organic matter is key to controlling the mobility of lead in the environment. Pb can be immobilized by the formation of phosphate biominerals by both bacteria and fungi. It is likely that the addition of phosphate to mine waste would be beneficial for limiting Pb bioavailability, as would stimulating the development of anoxic conditions. There is an interesting aspect that warrants further investigation regarding the significance of fungi-Pb interactions, given that it appears that fungi are less prevalent in Pb-impacted mine waste, yet potentially are capable of transforming Pb into highly recalcitrant minerals. Supporting soil development

on Pb mine wastes, perhaps by adding limiting nutrients such as C, N and P and inoculating with mixed microbial communities could limit the likelihood of dust formation and inhalation of Pb.

3.6. Mercury

Mercury is a major pollutant that bioaccumulates through the food chain causing serious health effects in animals, including humans. It is very toxic in small quantities, acts as a neurotoxin and can harm the unborn child. Until recently no biological function was associated with Hg, until *Rhodobacter capsulatus* was observed to have higher growth rates in the presence of Hg and a decreased lag phase compared to Hg-free cultures (Grégoire & Poulain, 2016). The authors suggest that Hg(II) reduction was not only used as a detoxification mechanism, but also to maintain redox homeostasis. The EU has taken action to tackle mercury pollution by prohibiting mercury mining in EU countries and its export, to discourage use in other countries (European Commission, 2020).

3.6.1. Mercury Geochemistry

The Hg concentration in the Earth's crust is ~80 μg kg^{-1} (Gonzalez-Raymat et al., 2017), it occurs naturally as elemental (metallic) mercury (Hg^0), inorganic mercury (Hg salts) and organic mercury (e.g., methylmercury $[CH_3Hg]^+$). The most common Hg ore mineral is cinnabar (HgS), although Hg is found in minor quantities in other minerals. Hg can be found in spoil and waste piles and other mining environments, in conjunction with other toxic elements, such as As (Loredo et al., 1999, 2003). Mercury has three redox states, Hg(0), Hg(I), and Hg(II). Hg^0 can form amalgams with other metals, is liquid at room temperatures, and will evaporate to form Hg vapors (Agency for Toxic Substances & Disease Registry, 1999). Hg vapors can be oxidized in the atmosphere by ozone to Hg^{2+}, which is then removed by precipitation. Hg^{2+} can be reduced back to Hg^0, or undergo transformations mediated by microorganisms including reduction, methylation and oxidation.

Anthropogenic sources of Hg include mining (particularly through its use in gold mining), smelting, combustion of fossil fuels, or the chlor-alkali production (Gonzalez-Raymat et al., 2017). About 80% of anthropogenic Hg comprises Hg^0 released to the atmosphere, 15% enters the soil environment from chemicals and landfill, and 5% is present in industrial wastewater (Agency for Toxic Substances & Disease Registry, 1999). Organic mercury forms such as methylmercury are produced from inorganic mercury by microbial activity. Mercury methylation was thought to be predominantly undertaken by sulfate-reducing bacteria under anaerobic conditions (Agency for Toxic Substances & Disease Registry, 1999). However, genes associated with Hg methylation have recently been found across a range of redox gradients in seawater, suggesting that Hg methylation occurs under microaerophilic and even oxic conditions (Lin et al., 2021; Villar et al., 2020). Methylmercury is soluble, mobile and can be assimilated by plants and other organisms, it also bioaccumulates and biomagnifies in the trophic chain (Bravo et al., 2014). Mercury adsorption by soils is pH dependant, Hg is desorbed at higher pH values, while at low pH it is adsorbed. Hg^{2+} adsorption in soils is influenced by several factors including the presence of chloride, dissolved organic carbon and pH. At pH 3–5, Hg^{2+} was highly adsorbed in soils, but this decreased at higher pH in the absence of chloride (Yin et al., 1996). However, in the presence of chloride, Hg^{2+} adsorption varied with both pH and chloride concentration.

Factors affecting Hg bioavailability include the presence and type of organic acids (Gu et al., 2011), and the presence of other metals; desorption of Hg^{2+} increased in the presence of increasing concentrations of Cu^{2+} or Zn^{2+} (Hahne & Kroontje, 1973; Haitzer et al., 2003; Jing et al., 2007). Mercury can be photoreduced from Hg^{2+} to Hg^0, which is also affected by the dissolved organic carbon content (Costa & Liss, 2000; Ravichandran, 2004). The generation of Hg^0 by Hg^{2+} reduction releases mercury into the atmosphere, methylation makes mercury assimilable to other organisms that then pass through different organisms up the aquatic trophic chain (Ward et al., 2010), and to humans through seafood consumption (Rimmer et al., 2010).

3.6.2. Microbial Interactions With Mercury

Microorganisms play an important role in the fate of Hg in the environment, by being the main drivers of Hg methylation and its incorporation into the trophic chain. A detailed review of microbial Hg resistance is provided by Barkay et al. (2003) and we refer the reader to this excellent resource for further information on this aspect.

3.6.2.1. Uptake Mechanisms and Mode of Toxicity

Uptake of Hg by microorganisms has been studied in phototrophs such as algae (Beauvais-Flück et al., 2017), Cyanobacteria (Cain et al., 2008) and diatoms (Mason et al., 1996; Zhong & Wang, 2009) as well as in bacteria. Passive diffusion is thought to be the primary Hg uptake mechanism due to the capacity of neutral Hg-S complexes to diffuse into the cytoplasm (M. Ma, et al., 2019). Hg^{2+} uptake by *Geobacter sulfurreducens* is an energy-dependant process either by electrogenic or ATP-driven mechanisms (Schaefer et al., 2011), although in later work the authors suggest that the active uptake of Hg^{2+} may be accidental (Schaefer et al., 2014). Toxicity is avoided by Hg^{2+} methylation and export of the methylated Hg out of the cell (Schaefer et al., 2011, 2014). Hg^{2+} uptake in phototrophic bacteria takes place in two phases, a fast phase where Hg^{2+} absorbs into extracellular polysaccharides and proteins followed by diffusion through the membrane, and a slow phase determined by active processes that depend on cellular metabolism (Kis et al., 2017). The effect of pH on Hg^{2+} uptake by aquatic bacteria was studied by Kelly et al. (2003), who found that small changes in pH increased the uptake of Hg^{2+} and addition of dissolved organic carbon decreased the uptake.

3.6.2.2. Direct Resistance Mechanisms

The *mer* operon is the major mechanism that confers Hg resistance in prokaryotes (Dash & Das, 2012). Hg^{2+} is transported into the cytoplasm by the inner membrane protein MerT and other transporters, and then reduction is regulated by MerR. This allows the expression of the Hg resistance gene *merA*, which encodes for a mercuric reductase that uses NAD(P)H to reduce Hg^{2+} to the volatile Hg^0 that then diffuses through the membrane (Freedman et al., 2012). The mechanism involves the transport of Hg to the cytosol and the subsequent reduction by the mercuric ion reductase (Barkay et al., 2003). The *mer* operon conferring Hg resistance is broadly distributed within bacteria and archaea, indicating its potential evolution during early life on Earth (Freedman et al., 2012). Another important enzyme in mercury resistance in bacteria is merB, this encodes for a organomercurial lyase that releases Hg^{2+} from organomercurial compounds (Lello et al., 2010).

Demethylation is another pathway against Hg toxicity. Methylmercury is degraded to Hg^{2+} and CO_2 (Bridou et al., 2011) or CH_4 (Oremland et al., 1991). The studied sulfate-reducing bacteria were found to demethylate mercury to Hg^{2+} but did not produce Hg^0 as an end product that otherwise could be released out of the cell. This is interesting as Hg^{2+} is highly toxic and its accumulation has a negative impact on cell functioning. Both processes of methylation and demethylation occur in some strains of bacteria (Lu et al., 2016); whether they can be considered as detoxifying mechanisms or as alternative electron donors or acceptors is unresolved.

The *mer* operon has not been found in eukaryotic organisms. Hg detoxifying mechanisms in fungi involve bioaccumulation and biovolatilisation (Chang et al., 2020; Pietro-Souza et al., 2020; Urík et al., 2014). The yeast *Yarrozwia* sp. was found to adsorb Hg to the cell wall and in spheroplasts; it was also able to volatilize Hg but the mechanism was not described (Oyetibo et al., 2016).

3.6.2.3. Indirect Resistance Mechanisms

A mercury resistant strain of *Enterobacter* sp. was found to accumulate Hg and synthesize Hg nanoparticles (Sinha & Khare, 2011). *Bacillus* and *Candida* spp. form intracellular crystals of HgS nanoparticles under non-growth conditions (Cuéllar-Cruz et al., 2017). The extracellular polymeric substances produced by the yeast *Yarrowia* were found to adsorb Hg (Oyetibo et al., 2016).

3.6.2.4. Impact on Soil Microbial Processes and Microbial Communities

Microorganisms are able to reduce, oxidize, methylate and demethylate Hg affecting its mobility and availability to other organisms (Barkay et al., 2003). As with other metals, the presence of Hg can modify the microbial community toward a less diverse and Hg-resistant community (Müller et al., 2001; Ranjard et al., 2000). The abundance of sulfate-reducing bacteria and methanogenic archaea increased with Hg contaminated soils, suggesting that these groups were responsible for Hg-methylation (Vishnivetskaya et al., 2018). A study focused on the effect of Hg contamination in gold mine tailings found that microbial diversity was lower in the samples that contained higher (5–12 mg kg^{-1}) Hg concentrations (Ji et al., 2018).

Bacterial alpha diversity was shown to be lower in Hg contaminated soils (Mahbub, Subashchandrabose, et al., 2017; Vishnivetskaya et al., 2018).

Hg contamination has a negative impact on soil enzymatic activity. A study of the effect of Cd and Hg contamination showed the catalase, urease and dehydrogenase activities were decreased by up to 35%, 90%, and 93%, respectively when the soils were spiked with 30 mg kg^{-1} of Hg (Zheng et al., 2019). As well as this, the diversity of the bacterial community decreased, as assessed by the Shannon diversity index.

3.6.2.5. Impact of Biogeochemical Cycling

Mercury transformations mediated by microorganisms are ubiquitous, taking place in oxic and anoxic environments. There are several studies focusing on the application of microorganisms in Hg remediation. Mahbub, Bahar, et al. (2017) compiled the different strategies used for Hg remediation and divided them into physico-chemical, biological techniques and nanotechnology. Biological techniques include phytoremediation (not covered in this review), microbial remediation and biosorption. Microbial reduction followed by volatilization could be used to remove Hg from water or soils, but Hg will enter the atmosphere and remain a problem as it can be transported away from its source and be returned to water and soil. The production of nanoparticles by *Enterobacter* sp. (Sinha & Khare, 2011) may present a viable remediation strategy for Hg contaminated soils and also provide also a source of Hg to industry. The transgenic bacterial system studied by Ruiz et al. (2011) showed high Hg accumulation and avoided volatilization which would make the technology safer.

3.6.3. Implications for Mine Waste Containing Mercury

Mercury is highly toxic and highly mobile in the environment, posing a significant challenge to planetary health. Stopping Hg mining and encouraging a reduction in the use of Hg are strategies used to mitigate Hg contamination. In spite of this, Hg has even reached remote locations such as Antarctica due to the volatility of Hg^0 allowing it to be transported and deposited far from its source (Cipro et al., 2017). Developing a feasible remediation strategy for Hg-contaminated mine wastes is challenging as the mechanisms by which microorganisms interact with Hg can produce volatile Hg^0 which just transfers the problem from the soil or water environment to the atmosphere, or they can produce highly soluble and mobile methylmercury that bioaccumulates and is toxic. As such, highly engineered systems are likely to be required, and therefore efforts to remediate Hg contamination are typically focused on using physical or chemical strategies (Wang et al., 2012).

3.7. Nickel

Nickel is an essential trace element for animals, plants and some microorganisms; Ni deficiency has not been found in humans due to the low concentrations required, while Ni can be toxic at high concentrations (Anke et al., 1995; Mulrooney & Hausinger, 2003; Yusuf et al., 2011). In small amounts Ni enhances the growth of microorganisms; however, high concentrations have negative impacts on microbial communities (Cai et al., 2007). Ni is required for the functioning of certain enzymes in microorganisms, acting for example, as a cofactor in metalloenzymes (Macomber & Hausinger, 2011). These enzymes are crucial for a wide variety of microbial metabolisms and processes and include: urease that hydrolyses urea to form ammonia; Ni-Fe hydrogenase that catalyzes the reversible oxidation of H_2; enzymes involved in the reversible oxidation of CO to CO_2 under anaerobic conditions; methyl-coenzyme M reductase which is essential for methanogenesis; the cellular protection enzymes Ni-dependent superoxide dismutase, Ni-depended glyoxylase; and various others (Mulrooney & Hausinger, 2003).

3.7.1. Nickel Geochemistry

Nickel is present in the Earth's crust on average at 86 mg kg^{-1} (Agency for Toxic Substances & Disease Registry, 2005a). Nickel is ubiquitous in soils and is strongly sorbing, particularly to Fe and Mn oxyhydroxides and clays to a lesser extent (Agency for Toxic Substances & Disease Registry, 2005a). It is typically found as Ni(II), this form is stable over a broad range of pH and redox conditions (Yusuf et al., 2011). Anthropogenic sources of Ni contamination include combustion of fossil fuels, incineration of waste and mining. Pentlandite [$(Fe,Ni)_9S_8$], is a Ni-containing sulfide mineral, which is usually associated with pyrrhotite ($Fe_{(1-x)}S$ [$x = 0$–0.2]). Tailings generated from the mining of pentlandite and other Ni-containing ores may generate

AMD containing high concentrations of metals. Dust generated during metallurgical operations can travel long distances, contaminating land over a radius of 4,000 km^2 (Barcan & Sylina, 1996).

3.7.2. Microbial Interactions With Nickel

3.7.2.1. Uptake Mechanisms and Mode of Toxicity

Nickel can enter the cell via several protein systems by binding to Ni-specific proteins, via permeases and via non-specific routes (Li & Zamble, 2009). There are two mechanisms of active Ni uptake in bacteria: ATP-binding cassette (ABC)-type transporters and Ni-specific permeases. The ABC transport system used by bacteria and archaea involves several proteins, the NikABCDE systems is the most widespread, while the NiCoT systems is found in bacteria and in eukaryotes (Zhang et al., 2009). The NikABCDE transporter is constituted of two transmembrane proteins, NikB and NikC that form a pore, NikD and NikE that bind and hydrolyze ATP and NikA which is a periplasmic protein that binds to Ni with a metallophore. The system is regulated by the fumarate-nitrate regulator (FNR; Rowe et al., 2005). The high-affinity nickel permeases, the NiCoT family, are divided in those that can transport Ni^{2+}, those that can transport Co or those that can transport both Ni and Co (Macomber & Hausinger, 2011). Non-specific Ni transport may occur via the CorA and other channels in the presence of high Ni concentrations (Macomber & Hausinger, 2011; Niegowski & Eshaghi, 2007). Macomber and Hausinger (2011) propose four mechanisms by which Ni causes toxicity: (a) by replacing other metals in metalloproteins; (b) by binding to active site residues; (c) by binding at a secondary site causing allosteric inhibition; and (d) by causing oxidative stress. For examples refer to Macomber & Hausinger (2011).

3.7.2.2. Direct Resistance Mechanisms

There are several efflux systems that microorganisms use to pump Ni outside the cell. The resistance nodulation division is a family of proteins driven by proton gradient that are believed to pump metals across the outer membrane (Li & Zamble, 2009; Macomber & Hausinger, 2011). Other proteins involved in detoxification are the NreB protein which pumps Ni out of the cytoplasm using proton motive force, and the DmeF efflux pump, which is a protein that provide resistance to several metals (i.e., Fe, Zn, Co, Cd, and Ni; Li & Zamble, 2009; Macomber & Hausinger, 2011). The RcnA efflux pump found in Proteobacteria, Cyanobacteria and archaea exports Ni and Co out of the cytoplasm (Rodrigue et al., 2005), other exporters include a putative metal efflux ATPase (Campbell et al., 2007) and a putative metal efflux pump (Cavet et al., 2002). In fungi, Ni direct resistance mechanisms involve the modification of a Mg transport system that also transports Ni (Joho et al., 1995).

3.7.2.3. Indirect Resistance Mechanisms

Sequestration of Ni by a mutant strain of *S. cerevisae* occurred by augmenting the production of histidine, which bound Ni to sequester it in a vacuole (Pearce & Sherman, 1999). *Thiocapsa roseopersicina* and *Pseudomonas* strain MBR can reduce Ni(II) to elemental Ni using H_2 as an electron donor, which is considered as a resistance mechanism as elemental Ni is less toxic (Zadvornyy et al., 2010; Zhan et al., 2012). The *Microbacterium* strain MRS-1 was able to produce NiO nanoparticles from soluble $NiSO_4$ (Sathyavathi et al., 2014).

3.7.2.4. Impact on Soil Microbial Processes and Microbial Communities

High concentrations of Ni in contaminated soils showed shifts in long-term bacterial community composition but results did not show a clear trend in diversity or abundance (J. Li et al., 2015). Analysis of industrial city soils showed that bacterial and fungal communities declined as metal concentrations (Ni and Cd) increased (Ansari & Malik, 2010). The decrease in certain enzymatic activities (e.g., dehydrogenase, urease, and phosphatase) is another effect of Ni contamination in soils (Kucharski et al., 2009; Moreno et al., 2003). In a batch reactor experiment, dehydrogenase activity was stable when Ni^{2+} was <5 mg L^{-1}, but it decreased at higher concentrations (≥10 mg L^{-1}), as did the enzymatic activity of denitrifying bacteria, and nitrate reduction was also inhibited (R. Liu, et al., 2020; B. Ma, et al., 2019). The addition of Ni to soils in a pot-culture experiment increased the enzymatic activity (dehydrogenase, triphenylformazan, acid phosphatase, and alkaline phosphatase) of soils spiked with Pb although the mechanism of this was not identified (Dotaniya & Pipalde, 2018). Long-term exposure to Ni has been shown to increase the abundance of antibiotic resistant

microorganisms in two long-term experimental stations (Hu et al., 2017). These studies demonstrate that Ni has implications beyond toxic effects

3.7.2.5. *Impact of Biogeochemical Cycling*

Ni is typically found in Fe/Mn (hydr)oxides in soils (Rinklebe & Shaheen, 2017). Changes in pH and redox potential conditions affect its solubility (Soares et al., 2011); at higher pH values Ni adsorbs to compounds such as silicates, organic matter or Fe/Mn oxides (Kabata-Pendias, 1993) while at low pH values Ni solubility increases. When reducing conditions prevail, the dissolution of poorly crystalline Fe/Mn (hydr)oxides by metal-reducing microorganisms will release Ni to solution. However, Ni associated with crystalline Fe minerals such as goethite is more recalcitrant; Ni speciation did not change in metal-reducing sediment microcosms despite redox transformations of Co and Mn being observed (Newsome et al., 2020). Should conditions become sulfidic, the precipitation of nickel sulfides would decrease aqueous Ni concentrations (Agency for Toxic Substances & Disease Registry, 2005a). The H_2S produced by sulfate-reducing bacteria will remove Ni from solution as NiS (Rinklebe & Shaheen, 2017). This was observed in a study by Joo et al. (2015) where *D. desulfuricans* was used to remove Ni, Cd and Cr from contaminated artificial sea-water. However when the dynamics of metals in floodplain soils were investigated in microcosm experiments, no evidence of NiS formation was observed (Weber et al., 2009).

3.7.3. Implications for Mine Waste Containing Nickel

Nickel contamination perhaps poses less of a challenge to planetary health compared to some of the other metals described here, due to its relatively low toxicity to humans and other organisms, and limited environmental mobility. Redox potential and pH seem to control the mobility of Ni in mine wastes and soils. Oxidising acidic conditions in sulfide mineral mine wastes increase Ni dissolution, but if the pH is high enough Ni will co-precipitate with Fe (hydr)oxides. Creating an anoxic layer when storing mine waste favors the immobilization of metals, including Ni, as pH and redox potential are kept at values where sulfate reduction occurs. Constructed wetlands could also be used to achieve the same objectives favoring the conditions for the proliferation of sulfidogenesis. The benefits of NiS formation can be seen by its application in the mining industry to recover Ni from multi-metal leaching solutions (Saari & Riekkola-Vanhanen, 2012). However, this sulfide was not biologically produced; instead the process bubbled Ni-rich solutions with H_2S. The formation of NiS generates acidity and addition of alkalinity is necessary for neutralization (Karbanee et al., 2008). Using microbial reduction of Ni^{2+} to Ni^0 to produce nanoparticles (NiO) could be a strategy for producing high value pure Ni products, although this is unlikely to be applicable as a bioremediation technology on a large scale.

3.8. Zinc

Zn is an essential trace element that is required for the functioning of many metalloenzymes in all domains of life, but it can be toxic at high concentrations, as well as deficient at low concentrations. As such, intracellular concentrations of Zn are carefully balanced by homeostasis; the regulation of acquisition, sequestration and efflux mechanisms. However if in excess, Zn can inhibit cellular activities and cause toxicity.

3.8.1. Zinc Geochemistry

Concentrations of Zn in the Earth's crust are typically 20–200 mg kg^{-1}; sphalerite (ZnS) is the most important Zn ore mineral, and Zn is also commonly found as Zn oxide, with Zn carbonates and silicates also present in the environment (Agency for Toxic Substances & Disease Registry, 2005b). Zinc is predominantly present as Zn(II) under almost all environmental conditions. It is relatively immobile in soils as it sorbs to soil particles such as clays, silts, Fe and Mn oxides and organic matter. The solubility of Zn in waters is limited by the formation of carbonate and hydroxides, but at low pH it is mobile as Zn^{2+}. It can form complexes with organic and inorganic ligands such as humic acids; the stability of these complexes is determined by pH (Agency for Toxic Substances & Disease Registry, 2005b). At near-neutral and high pH, Zn can precipitate as Zn sulfide under reducing conditions and under oxidising conditions it may co-precipitate with iron and manganese oxides. Zinc speciation does not change with redox.

3.8.2. Microbial Interactions With Zinc

3.8.2.1. Uptake Mechanisms and Mode of Toxicity

Given its physiological importance, there are a number of excellent reviews of Zn metabolism in prokaryotes. Zn enters prokaryotic cells either by non-specific movement across diffusion gradients or via energy-dependent active uptake systems, primarily ABC (ATP-binding cassette) transport proteins (Blencowe & Morby, 2003). Active uptake of Zn is regulated by the Zur (zinc uptake regulator) sensor protein, which is part of the Fur (ferric uptake regulator) family of proteins that sense and respond to low concentrations of metals and ensure homeostasis is maintained (Mikhaylina et al., 2018). Zur binds with Zn and represses further uptake, but when Zn is deficient Zur undergoes a conformational change to allow the expression of Zn uptake genes (Blindauer, 2015). Fungi use high-affinity Zn importers (ZRT-IRT-like proteins (ZIP) and cation diffusion facilitators) to ensure an adequate Zn supply (Gerwien et al., 2018) and can also secrete extracellular Zn scavengers called zincophores to aid Zn acquisition (Citiulo et al., 2012). Zn toxicity occurs either when the homeostasis mechanisms are overwhelmed by excess Zn, or when enzymes on the cell surface are poisoned (Chandrangsu et al., 2017). In both prokaryotes and fungi excess Zn competes with other metals for binding sites, causing toxic effects. For example, Zn outcompetes Mn(II) transport and uptake, and without Mn, cell growth and survival is impaired (McDevitt et al., 2011). Zinc can inactivate the electron transport chain required for aerobic respiration (Alhasawi et al., 2014; Beard et al., 1995), inhibit glucose metabolism and decrease capsule biosynthesis (Ong et al., 2015). Excess Zn also affects cellular metal homeostasis for example, down-regulating Cu uptake leading to Cu starvation (Hassan et al., 2017; Xu et al., 2019) and causes oxidative stress via stimulating intracellular heme accumulation and toxicity (Chandrangsu & Helmann, 2016).

3.8.2.2. Direct Resistance Mechanisms

Mechanisms for Zn export are essential for maintaining cellular homeostasis, and these efflux mechanisms can be employed to deal with excess Zn. In prokaryotes Zn efflux is mediated by sensor proteins, and can involve three mechanisms. Note these are energy dependent so require ATP, meaning there is a fitness cost to exporting excess Zn. First energy-dependent P-type ATPases translocate metal cations beyond the cell membrane; as well as Zn(II) these can also translocate Cd(II) and Pb(II) (Blencowe & Morby, 2003). Second, the CDF (cation diffusion facilitator) family of proteins include Zn(II) efflux systems in certain bacteria (Blencowe & Morby, 2003); this process requires energy in the form of an electrochemical potential to transport Zn^{2+} outside the cell (Blindauer, 2015). Finally, RND (resistance, nodulation and cell division) driven transporter proteins actively promote the extracellular efflux of Zn (Blindauer, 2015). Alternatively excess Zn can trigger the expression of Zn sequestration proteins such as metallothioneins that chelate metals intracellularly, and metallochaperones, which traffic metals within cell compartments and facilitate transfer to acceptor proteins (Blindauer, 2015; Z. Ma et al., 2009). In fungi, excess Zn can be sequestered in the vacuole and bound to polyphosphates, or by the use of metallothioneins (Gerwien et al., 2018).

3.8.2.3. Indirect Resistance Mechanisms

Few studies report indirect resistance mechanisms for Zn, perhaps unsurprising given the availability of multiple direct mechanisms. One study of organic amended soils showed that Zn addition led to increased production of extracellular polymeric substances and soluble microbial products (uronic acid), suggesting these were used by the native microbial community as metal tolerance mechanisms (Redmile-Gordon & Chen, 2016). Sulfate-reducing activity can remove completely Zn from acid mine drainage waters by precipitation as ZnS (Le Pape et al., 2017).

3.8.2.4. Impact on Soil Microbial Processes and Microbial Communities

Investigating the amendment of soils with Zn salts has been undertaken in the context of Zn acting as a soil fertilizer. One 9 year field study applied a range of Zn concentrations to soils and found slight differences in the bacterial (but not fungal) community composition compared to the no Zn control (Y.-M. Liu et al., 2020). No differences in microbial community (alpha) diversity were observed. Soil enzyme activities (urease, invertase, phosphatase, and catalase) increased at "optimal" Zn addition (~80 mg kg^{-1} Zn in soils), but significantly decreased with "excess" Zn (~200 mg kg^{-1} Zn in soils). A shorter-term study showed that adding 300 mg kg^{-1} of Zn to soils generally had non-significant effects on biomass specific respiration or

microbial biomass after 49 days incubation, but did somewhat decrease cumulative respiration in grassland soils (but not in arable soils; Renella et al., 2002). Another study spiked 15 soils with up to 191 mg kg^{-1} of Zn and observed soil microbial processes (nitrification rate and respiration) decreased significantly, but in contrast there were no significant negative effects observed in highly contaminated field samples (up to 3,700 mg kg^{-1}), suggesting soil functioning is sustained at much higher metal concentrations than is predicted from soil spiking studies (Smolders et al., 2004). Exposure of basidiomycete, ascomycete and zygomycete saprotrophic fungi to Cu or Zn found that all fungi were more sensitive to Cu than Zn (Hartikainen et al., 2012). Zn at 100 mg kg^{-1} decreased the growth of most ascomycetes, but one strain actually increased, as did six of the eight basidiomycetes. For all strains, concentrations of 400 mg kg^{-1} Zn led to much lower growth.

In relation to mining environments, six strains of fungi were grown with 0.5% Zn ore minerals for 10 days, and the results showed the growth rate on Zn sulfide was 89%–118% and biomass yield was 63%–84% compared to controls, while on Zn silicate the growth rate was 58%–94%, and the biomass yield was 62%–95% (Wei et al., 2013). A field study of soils at varying distances from a Pb/Zn mine (as described above for Pb) found a gradient in the number of culturable bacteria, bacterial community diversity, and soil enzyme activities (dehydrogenase, phosphatase, and urease), with a considerable decrease in these parameters observed when concentrations exceeded 877–995 mg kg^{-1} Zn (Qu et al., 2011).

A number of studies have looked into the long-term land application of sewage sludge containing metals, including Zn. The diversity of soils amended with Zn-rich sewage sludge (400 mg kg^{-1}) was lower than soils amended with sludge containing no Zn (57 mg kg^{-1}) 15 years after the experiment was set up (Moffett et al., 2003). Zn sludge was applied to land over a 4 year period (generating 300 mg kg^{-1} Zn in soils) and then 5 years later the increased metal concentrations (Zn, Cd, Cu) were shown to have little effect on fungal diversity and community composition (Anderson et al., 2008). At seven field sites Zn-rich sludge was applied to generate up to 450 mg kg^{-1} Zn in soils and sampled 11 years later (Macdonald et al., 2011). The results showed significant differences in bacterial community structure at all sites between soils amended with Zn-rich sludge, with a weaker trend between Zn and archaeal and fungal community structures; these dose-related effects were said to imply selection against metal-sensitive species and for metal-tolerant microorganisms.

3.8.2.5. Impact of Biogeochemical Cycling

The same column study described for Cd (Section 3.2.2) and Pb (Section 3.5.2) also contained Zn (23.5 g kg^{-1}), initially present as silicate phases (Karna et al., 2018). After 252 days of amendment with organic carbon and sodium sulfate the column sediment comprised 31% Zn-sulfide, and far less Zn was released to the aqueous phase compared to the unamended control (Karna et al., 2016). Again this demonstrates that reducing conditions and the activity of sulfate-reducing bacteria may be considered beneficial for the immobilization of toxic metals.

Fungi can weather recalcitrant Zn silicate and sulfide minerals by excreting organic acids, but instead of mobilizing Zn, secondary Zn (and Ca) oxalate minerals were produced (Wei et al., 2013). Another study used a ureolytic bacterium, *Enterobacter cloacae* EMB19 to remove Zn from solution by co-precipitating Zn with calcite (Bhattacharya et al., 2019).

3.8.3. Implications for Mine Waste Containing Zinc

Zinc is a reasonably common contaminant in mine wastes, but compared to some of the other metals mentioned here it does not pose such a significant risk to planetary health due to its relatively low toxicity and fewer environmental impacts. The effect of Zn on soils and soil microorganisms is well studied, with a number of long-term field studies available. It appears that Zn is less toxic to soils and soil microorganisms compared to other metals, which is unsurprising given that Zn is an essential micronutrient, and as such microorganisms maintain its intracellular concentration by regulating uptake and efflux pathways. In non-adapted soil microbial communities it appears that adding Zn in the low hundreds of mg kg^{-1} may affect soil enzyme activities, and with changes in the bacterial community more significant than fungi. However, soil functioning is maintained in contaminated field samples demonstrating that it is possible for soil microbial communities to adapt to high concentrations of Zn in the environment. Should remediation be required, it appears that stimulating the development of metal-reducing and sulfate-reducing conditions

by adding organic carbon to sediment microbial communities may stabilize Zn in the solid phase, and/or precipitate it from the aqueous phase, via the formation of sulfide minerals. Therefore the formation of anoxic conditions is likely to limit Zn bioavailability in the environment and could be used to remediate Zn-containing mine waste, as could stimulating the formation of calcite.

4. Bioremediation of Mine Wastes: Case Studies

Pollution of the environment by metal-rich mine wastes poses serious risks to human health, agriculture, soil functioning, wildlife and as such, planetary health. Bioremediation, that is using microbial activity to mitigate the impact of contaminants, has the potential to reduce these risks in a cost-effect and sustainable way. Metals cannot be destroyed, they can only be transformed into forms that are less mobile in the environment, and consequently are less likely to be available for uptake into living organisms. In this section we aimed to identify one excellent well-characterized study conducted at field scale to treat metal-impacted mine wastes and waters, in order to to highlight how microbial activity can be stimulated, augmented or controlled to remediate metal contamination in wastes that are acidic (pH −1–5), circumneutral (pH 5–8) and alkaline (pH 8–12). However, this was challenging due to a paucity of published information, therefore a more varied approach had to be taken to summarize the available information for each type of metal-impacted mine wastes.

4.1. Acid Mine Waste Field Studies

Metal mining produces wastes with high concentrations of sulfidic minerals which produce AMD when in contact with oxidising conditions (Section 2.2). The acidity and concentration of metals vary depending on the host rock composition and the presence of carbonates. There are numerous cases around the world where AMD is formed and not controlled, for example, the Iberian Pyrite Belt, Spain (Grande et al., 2018). In some places, the government has taken the responsibility of remediating and rehabilitating the contaminated sites, for example, the Lusatia mining district, Germany (Geller, 2013).

There are two strategies to deal with AMD, (1) prevent its formation and (2) remediation (Moodley, 2018). Johnson and Hallberg (2005) divide the remediation approaches in two categories: (a) abiotic systems where a chemical agent is used to neutralize the AMD and (b) biological systems where the use of microorganisms favors the neutralization of AMD and immobilization of metals. There are plenty of results from laboratory studies that focus on remediation of AMD, however, it was difficult to find examples of field based applications. An example of a biotic treatment system is the BioteQ BioSulphide® technology, which involves the production of sulfide by sulfate-reducing microorganisms in bioreactors to treat Cu cyanide solutions for Cu recovery and cyanide regeneration (Adams et al., 2008). After the cyanide is recovered from solution, this solution is bubbled with H_2S produced by the microbial reduction of sulfur coupled to the use of acetic acid as the electron donor.

In general, the bioremediation of AMD focuses on stimulating sulfate-reducing activity to promote the removal of sulfate and the precipitation of metals as metal sulfides, for example, Sánchez-Andrea et al. (2012), Santos and Johnson (2017), Wu et al. (2010). Providing a carbon source promotes the development of reducing conditions by acting as an electron donor for sulfate-reducing microorganisms. To minimize the cost of these systems, alternative sources of organic matter have been used during laboratory-scale studies. Sánchez-Andrea et al. (2012) used domestic wastewater to remediate AMD, achieving removals of >99% metals (except Mn), >88% sulfate and >75% Fe. Wu et al. (2010) tested woodchip and rice straw as sources of organic matter. Their results showed higher sulfate and Cu removal in the experiments where rice straw was used. In both studies the bacterial communities were dominated by fermentative bacteria, and sulfate-reducing bacteria, as well as cellulolytic bacteria in Wu et al. (2010).

Passive mine water treatment systems such as constructed wetlands provide surface area for oxidation to occur. Fe oxide precipitates have been shown to scavenge arsenic from AMD in passive treatment systems (Elbaz-Poulichet et al., 2006; Fernandez-Rojo et al., 2019; Valente et al., 2011). Analysis of the oxide precipitates identified that Fe(II) oxidising bacteria dominated and known arsenite oxidizers were also present, therefore microbes were likely contributing to As removal from solution (Laroche et al., 2018). The release of 25,000–50,000 m^3 of acidic mine water from the Wheal Jane mine to the Fal River estuary (Cornwall,

England) over 24 h in 1992 induced the UK Government to investigate remediation options (pumping 90–300 L $s^{-1;}$ Younger et al., 2005). One of the options trialled was a passive remediation pilot plant, designed to treat 2% of the discharge, with different system components to remove the metals. The first treatment promoted iron oxidation and the precipitation of Fe and As, the second promoted sulfate reduction to precipitate metals as metal sulfides, and the third, rock filters to promote algal blooms to increase pH and precipitate Mn (Hamilton et al., 1999). However, the pilot passive treatment system was ineffective for multiple reasons, and lessons have been learned from this experimental trial (Johnson & Hallberg, 2002). For example, understanding the kinetics of microbial Fe(II) oxidation can be used to optimize the design of engineered systems (Larson et al., 2014).

Three field-based examples are summarized in the following sections, including application of permeable reactive barriers, a passive treatment system and an iron oxidising lagoon.

4.1.1. Permeable Reactive Barrier

There are not many examples in the literature where *in situ* remediation systems have been successfully applied. Gibert et al. (2011) studied the performance of a permeable reactive barrier (PRB) for remediating AMD that was contaminating the Agrio aquifer after the dam failure that took place in the Aznalcollar mine in 1998 when acidic waters and pyritic tailings flooded the Agrio and Guadiamar river valleys. The location of the PRB and description of the geological settings can be found in Salvany et al. (2004). The PRB was 1.4 m thick, 3.0–4.5 m high, and 110 m long to cover the full width of the river Agrio floodplain, and was divided into three modules separated for non-reactive sections (Gibert et al., 2011). The PRB was filled with limestone, sewage sludge, vegetable compost and zero-valent iron. The limestone raised the pH which favored the formation of Fe (oxy)hydroxides and metal precipitation. Organic substrates (sewage sludge and compost) were supplied as electron donors for sulfate-reducing bacteria. The zero-valent iron was added to help develop reducing conditions and also because it produces H_2 by corrosion, which serves as an electron donor for some sulfate-reducing bacteria. The pH increased from 3.9–4.0 to 7.0–8.0 by the neutralizing effect of the limestone added into the PRB (Gibert et al., 2011). Metal removal was related to pH. The concentrations of Zn, Al and Cu entering the PRB were 20, 15, and 1.2 mg L^{-1}, although decreased metal concentrations were observed after 3 years, the average removal rates were 80%, 47%, and 76%, respectively (Gibert et al., 2011). Study of the solid fractions from the PRB showed that the metals co-precipitated with Fe (oxy)hydroxides in response to the pH increasing, instead of being caused by the sulfate-reducing activity. The authors stated that the system performance could be improved by increasing the residence times to remove sulfate through sulfate reducing activity. Overall, this system shows potential for dealing with AMD impacted waters.

4.1.2. Reducing Alkalinity Producing System

The Tan-y-Garn site in South Wales incorporates a passive water treatment scheme (Figure 5) combining a thick layer of compost and limestone gravel (Reducing Alkalinity Producing System, RAPS) where alkalinity is produced, followed by three settlement ponds and an aerobic wetland (Taylor et al., 2016). The treatment site was built in 2006 to improve the mine water quality that was contaminating a nearby river, treating 7–10 L s^{-1} (Smail & Thorn, 2016). At the time of construction, the average pH of the mine water was slightly acidic (~5.5) but over the years, the mine water pH had increased to ~6.5 due to the effect of rainfall in the shallow mine workings. Similarly, metal concentrations had also decreased over time, for example the total Fe concentration decreased from ~50 mg L^{-1} in 2006 to ~30 mg L^{-1} in 2015 (Smail & Thorn, 2016). This was suggested to be caused by the alkalinity in the passive treatment system generated by the dissolution of the limestone and by microbial activity (Smail & Thorn, 2016). The alkalinity generated in the oxic part of the RAPS system favored the formation of Fe-hydroxides and co-precipitation of metals (Fe, Al, Zn, Mn, and Ni) and the reducing conditions generated in the anoxic part of the RAPS favored the removal of metals due to the formation of metal sulfides. After passing through the RAPS, Al concentrations decreased from 0.12 mg L^{-1} to 0.03 mg L^{-1}, and Zn and Ni were removed from 0.02 mg L^{-1} and 0.03 mg L^{-1}, respectively, to <0.01 mg L^{-1} (Smail & Thorn, 2016). Mn concentrations only decreased by 7%, this may have been due to its higher mobility in anoxic conditions (Smail & Thorn, 2016).

During the monitoring of the site, the authors observed an increase in Fe coming out of the RAPS, which may have been caused by the reducing conditions diminishing over time. The settlement lagoons increased

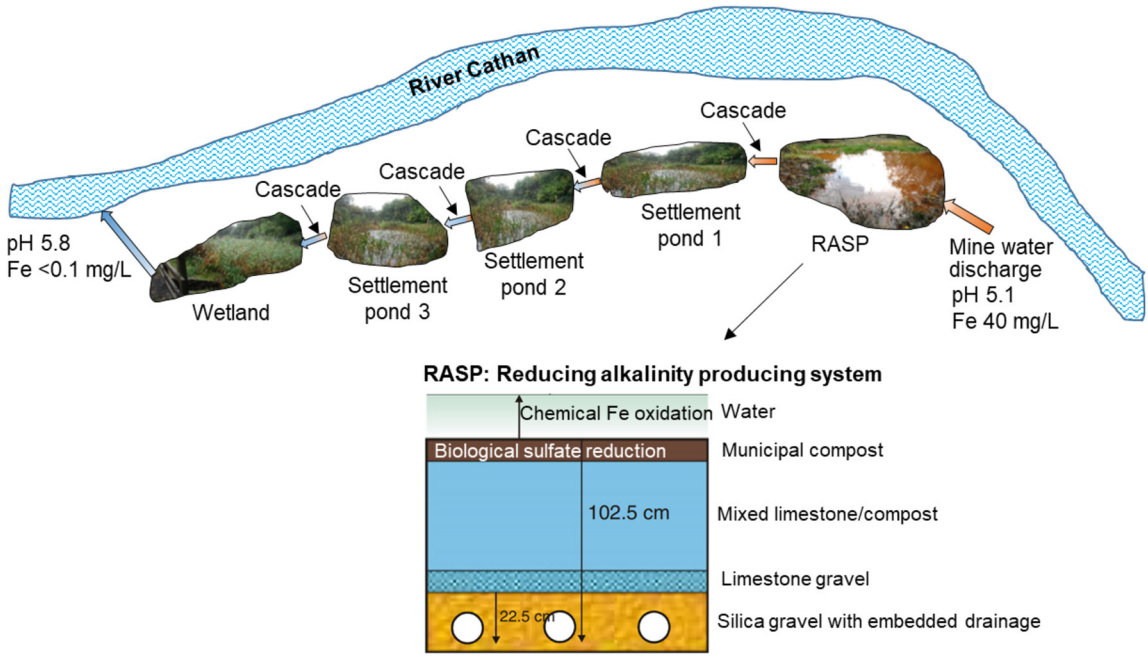

Figure 5. Remediation of contaminated mine waters at field scale: The Tan-y-Garn site in South Wales treating acidic mine waters. Image modified from Taylor et al., 2016. Photographs, pH and Fe data from Falagán et al., 2016.

metal removal, probably by co-precipitation with Fe-hydroxides due to the aeration of the waters. However, laboratory experiments showed that when provided with the adequate substrate, the presence of iron-reducing microorganisms favored the release of metals due to the reduction of Fe-hydroxides (Falagán et al., 2016), although this phenomenon was not detected *in situ*. Overall, the combination of the RAPS and settlement lagoons removed 100% of Fe, Mn, Zn, and Co from contaminated waters (Falagán et al., 2016) with little maintenance over 10 years (Smail & Thorn, 2016) hence, demonstrating the efficiency of this system. This type of alkalinity producing systems could be potentially applied to other mine waste impacted sites, although careful design and maintenance are required for the optimisation of the system. For example, heavy rain, flooding, and decreasing sulfate-reducing activity due to depleting organic carbon are some of the issues encountered in an alkalinity producing system constructed in South Korea (Bhattacharya et al., 2008).

4.1.3. Natural Fe-Oxidising Lagoon

Although most AMD remediation strategies are based on enhancing the activity of sulfate-reducing bacteria, there are other microbial metabolic activities that may be applied for remediating AMD effectively. A pre-treatment pond was constructed to favor biological Fe-oxidation and provoke Fe removal before neutralization with limestone (Macías et al., 2012) at the Monte Romero abandoned mine (Iberian Pyrite Belt, Southwest Spain). Iron was present in the AMD predominantly as Fe(II), this was oxidized in the lagoon, precipitating Fe(III) from solution as schwertmannite. Although the authors did not assess the contribution of the microbial community to the oxidation process, it is well known that microorganisms are able to accelerate Fe(II) oxidation by orders of magnitude (Nordstrom et al., 2015; Singer & Stumm, 1970). The schwertmannite not only removed Fe and sulfate from the mine water, it also contained high concentrations of As (38% of Fe and 80% of As were removed at this stage). After passing through the natural Fe(II)-oxidising lagoon, the water was treated downstream with limestone achieving a complete removal of Fe, Al, Cu, As, and Pb. Given only 6% of Zn was removed in this pilot operation, the authors suggested that a further increase of pH may be used to increase Zn removal. A combination of Fe-oxidation followed by sulfate reduction may also be a suitable option to achieve the complete removal of metals such as Zn.

4.2. Bioremediation of Neutral Metal Mine Waste

Surprisingly few field studies of treating neutral pH mine wastes (e.g., Figure 4) by bioremediation could be identified; the majority of field-scale remediation appears to have been undertaken to treat acid mine waters. In the United Kingdom, many mine waters are circumneutral (due to buffering by carbonates in bedrock) and it is estimated that 6% of rivers in England and Wales are impacted by metal-rich waters draining from abandoned mines (Jones et al., 2013). Some mines were worked from Roman times, and the majority were abandoned before 2000. Discharges from these abandoned mines contribute about half of the Cd, Zn, Pb, and Cu found in English and Welsh rivers, and therefore the associated flux to seas (Mayes et al., 2013).

Two field studies applying passive bioremediation to treat circumneutral Zn-contaminated mine waters are described below. Both rely on microbial sulfate reduction to remove Zn and other metals from waters by precipitating them as sulfide minerals. Both studies were conducted in the northwest region of the United Kingdom; the first a pilot scale treatment system at the Rampgill Mine, Nenthead, UK, and the second a full-scale passive mine water treatment system at the Force Crag Mine, Lake District National Park, UK.

4.2.1. Pilot Study of Mine Water Bioremediation at Rampgill, UK

Details of the pilot scale treatment system at Rampgill were reported by Gandy et al. (2016) and are summarized here. The Rampgill Mine was exploited for Pb and Zn, mine water discharge from the abandoned mine is at pH 7.7 and contained Zn (2.2 mg L^{-1}) and sulfate (134 mg L^{-1}). A 3.75 m^2 pilot scale vertical flow wetland was constructed in 2010, comprising limestone gravel (to provide permeability), and a layer of organic substrate comprising 45% compost (as a medium to long term source of carbon), 45% woodchips (to improve permeability) and 10% dried activated sewage sludge (to provide the initial source of carbon to stimulate the growth of sulfate-reducing bacteria). The composition of this organic substrate was selected based on previous laboratory experiments (Gandy & Jarvis, 2012).

Mine water was pumped into the wetland with a hydraulic residence time of 7.5–14.5 h. The mean total Zn removal efficiency was 68%, sulfate concentrations also decreased and analysis of the solid phase indicated that ZnS had been precipitated, with up to 12,000 mg kg^{-1} Zn in the solid phase. Adding an additional source of organic carbon in the form of brewery waste did not enhance Zn removal, demonstrating the effectiveness of the compost substrate used. A positive trend was observed between effluent temperature and Zn removal rate, potentially linked to decreased activity of sulfate-reducing bacteria at lower temperatures (Gandy & Jarvis, 2012). A later investigation found that metals from the Rampgill passive treatment system wastes could be leached using acidic waters containing active sulfur-oxidising microorganisms collected from drainage from a nearby mine, either to recover the metals or to decrease the costs of solid waste disposal (Bailey, 2018).

4.2.2. Full Scale Mine Water Bioremediation at Force Crag, UK

Details of the mine water treatment system were reported by Jarvis et al. (2015) and are described here. The Force Crag Mine was worked for galena, sphalerite and barite ($BaSO_4$) from 1835 until 1991. The drainage from the abandoned mine is circumneutral (pH 5.6–7.7) and contains Zn (1.7–4.6 mg L^{-1}), Pb (0.025–0.088 mg L^{-1}), and Cd (0.005–0.020 mg L^{-1}). This flowed into a nutrient sensitive upland river (the Coledale Beck), and into a Special Area of Conservation within one of the UK's most popular National Parks. A passive treatment system was designed to remove Zn by bacterial sulfate reduction and was constructed in 2014 (Jarvis et al., 2015). Drainage was diverted into two 760 m^2 vertical flow ponds that act as downwards flow bioreactors. Again these contained a layer of limestone overlain by a layer of organic substrate (as above), the hydraulic residence time was estimated to be 15–20 h. Following treatment the waters were then passed through a wetland to become oxygenated and to filter any remaining solids, before entering the Coledale Beck (Moorhouse et al., 2015).

The first three months of operation showed that 97% of Zn was removed from the mine waters (from 3.7 mg L^{-1} to 0.12 mg L^{-1}; Jarvis et al., 2015). Sulfate concentrations also decreased (from 32 mg L^{-1} to <10 mg L^{-1}). During the first 10 days of commissioning the water leaving the treatment system had high levels of ammonium, biochemical and chemical oxygen demand, likely due to flushing from the compost substrate, and this contaminated the nutrient-sensitive Coledale Beck. However within 4 months the river had returned to acceptable levels of organics. Detailed solid phase characterization and microbiological analyses are yet

to be published. It was calculated that over 10 years of operation, with 95%–99% Zn removal, the treatment system sludge would contain 21,500 mg kg^{-1} Zn which would cost €850k to dispose of Bailey et al. (2016). Longer term monitoring of the Force Crag mine water has shown that Zn concentrations are considerably diluted by rainfall; understanding the efficacy of the treatment system while accounting for this variability is the subject of ongoing study.

4.2.3. Summary and Future Outlook

Stimulating microbial sulfate reduction in constructed bioreactors and wetlands is effective at removing Zn from circumneutral mine waters. However, there are substantial gaps in the literature regarding this process for treating neutral mine waters, particularly around the microbial communities responsible, the mechanisms for metal removal and the composition of and metal speciation within the sludges that are formed. Operation of the passive mine water treatment system has highlighted the interesting aspect of considering what to do with the metal-rich and sulfide-rich sludges formed, whether they can be considered a resource or a liability that is expensive to dispose of. All water treatment systems will generate wastes, and this should be taken into account when designing a mine water bioremediation system.

4.3. Bioremediation of Alkaline Metal Mine Waste

The wastes generated from extracting alumina from bauxite (a mixture of hydrated aluminum oxides) are highly alkaline and saline; billions of tonnes of these 'red mud' wastes are stored at mine sites and more waste continues to be generated every year (Power et al., 2011). Remediation of bauxite residues aims to decrease the pH from above 11 to below 9, lower the conductivity and salinity, and increase the cation exchange capacity and availability of nutrients (Santini & Fey, 2018). In the absence of a well-characterized field trial where bioremediation has been applied to alkaline mine wastes, instead, the role of microorganisms in bauxite remediation in field and laboratory studies is provided here, together with details of the natural colonization and restoration of bauxite residues by microbial communities.

4.3.1. Field and Laboratory Studies of Bauxite Waste Remediation

Focusing on the contribution of microorganisms to bauxite waste remediation, laboratory experiments have shown that biostimulation (of indigenous microorganisms) and bioaugmentation (adding microorganisms) can be used to remediate leachates from bauxite waste storage ponds. In one study the best results were obtained by adding both a source of organic carbon and a soil inoculum containing microorganisms, and as well as decreasing the pH, the concentrations of As, Mo, V, and Al in solution also decreased, likely via sorption and precipitation (Santini & Peng, 2017). Solid bauxite tailings amended with glucose and microorganisms again demonstrated that stimulating the development of anaerobic and fermentative conditions was an effective remediation strategy (Santini et al., 2016). These results were replicated in scaled up 30 L experiments (Santini et al., 2019). Another laboratory study compared amending bauxite residue with a soil inoculum plus different types of organic matter and/or gypsum, again these organic amendments were effective at decreasing the pH and stimulated the formation of organic acids (You et al., 2019). The potential of applying fertilisers to successfully restore bauxite waste has also been assessed in laboratory experiments by measuring nitrogen cycling, the abundance of N-cycling prokaryotes and N-cycling genes (Goloran et al., 2015a, 2015b).

Constructed wetlands have been proposed as a mechanism to treat bauxite residue leachates and have been tested at the laboratory and field scale. Initial laboratory data showed that wetlands could lower the pH via precipitating sodium carbonate from solution (Buckley et al., 2016). Microbial respiration in wetlands contributes to this process by producing high levels of CO_2, which decreases the pH and aids carbonate mineral formation. At pilot field scale, a constructed wetland lowered the pH of bauxite residue leachate from an average of 10.3 to an average of 8.1 and substantially decreased the concentrations of aqueous Al, As, Cr, and V, although the conductivity and Na, Ca, and Mg concentrations were only slightly lowered (Higgins et al., 2017). Increases in carbonate-bound Ca and Na in the solid phase were observed, together with no significant increase in trace element bioavailability. Subsequent work confirmed that calcite and dawsonite ($NaAlCO_3[OH]0_2$) were precipitated via carbonation in the presence and absence of Ca respectively (Higgins et al., 2018). After 4 years this constructed wetland was still effective, and the effluent did not cause observable ecotoxicological effects (O'Connor & Courtney, 2020).

Other than constructed wetlands, most field (and column-based) studies of bauxite waste remediation have focussed on applying different amendments to tailings and then assessing their ability to support plant growth and form soils (Gräfe & Klauber, 2011). These include: organic amendments such as sewage sludge to stimulate soil formation (Santini & Fey, 2018); gypsum to neutralise bicarbonates as the source of alkalinity (Woodard et al., 2008); gypsum combined with organics (Courtney & Timpson, 2005; Courtney et al., 2009; Di Carlo et al., 2019; Harris, 2009; Tian et al., 2020; Wong & Ho, 1991); seawater to neutralise alkalinity, remove Na and replace Ca, Mg, and K (Menzies et al., 2004); or a combination of all three (Y. Li et al., 2019). Most (but not all) of these studies demonstrated that remediation was effective, although maintaining the long-term availability of plant nutrients appears to be required.

Most studies did not consider how microbial activity may have contributed to remediating the alkaline mine wastes, but one long-term field study of bauxite waste remediation including microbial community analysis was reported by Bray et al., (2018). The pilot site comprised three plots of bauxite residue; one unamended, one fully treated by adding process sand, organic matter, gypsum and seeded, and the third partially treated with process sand, organic matter and seeded. These were sampled 16 years after treatment to depths of 50 cm and the efficacy of remediation assessed in terms of decreased pH, lower salinity (Na), higher nutrients, and lower toxic metal content (Al, V, and As). The remediation was most successful in the fully treated plot and the surface soils of the partially treated plot; reflected by vegetation cover observed compared to the bare surface of the unamended control plot. The quantity of extracted DNA was used as an indication of microbial abundance. Concentrations were below 2.5 $\mu g\ g^{-1}$ in the unamended plot, in the partially treated plot ranged from 9.3 to 14 $\mu g\ g^{-1}$ and in the fully treated plot from 0.65 to 14 $\mu g\ g^{-1}$. The bacterial community diversity and composition at the phylum level in the fully treated plot and the partially treated plot were similar. The authors highlighted the presence of halotolerant Planctomycetes and high pH tolerating Acidobacteria, and suggest that overall this shows a bacterial community in transition between being adapted to alkaline mine waste and supporting plant growth.

4.3.2. Microbial Communities Present in Bauxite Wastes

Bauxite residues collected from a mine waste lake deposit were shown to contain bacterial communities but that exhibited little metabolic activity (Hamdy & Williams, 2001). After incubation in a medium containing glucose and nutrients, the colony forming units increased, and more than 150 bacteria were isolated. Of the isolates that could be identified, the *Bacillus, Lactobacillus* and *Leuconostoc* genera were predominant, with the *Micrococcus, Staphylococcus, Pseudomonas, Flavobacterium, Enterobacter*, and *Proteus* genera also present. Other prokaryotes isolated from bauxite wastes include alkaliphilic *Bacillus* spp. (G.-H. Liu, et al., 2020; Nogueira et al., 2017) and a *Kocuria* sp. belonging to the actinomycetes (Krishna et al., 2008). An acid-producing fungal isolate identified as *Penicillium oxalicum* was shown to decrease the pH of the waste when incubated under optimal growth conditions (Liao et al., 2018).

Two studies have characterized the bacterial community composition of environmental bauxite residue waste, both in China. The first study of a site in Henan province compared unweathered waste and 10, 25, and 25 year old waste that had become covered with grass (Wu, Chen, et al., 2020). Chemical measurements showed the pH decreased over time, from pH 11 in the unweathered waste to pH 10 in the 25 year old waste, and the amount of organic carbon, nitrogen and phosphorus increased with age and vegetation cover. Microbial community diversity (assessed as the number of operational taxonomic units and Shannon index) also increased with age, with the highest bacterial diversity observed in the 25 year old waste covered in grass. Linear correlations were observed between increasing Shannon indices and decreasing pH, increasing organic C, N, and P. At the phylum level the unweathered waste predominantly comprised Firmicutes (46%, mostly *Lactococcus* [20%] and *Bacillus* [14%] spp.) and Actinobacteria (34%, predominantly uncultured bacteria assigned to the Euzebyaceae family [17%]), but in the 25 year old waste these phyla formed only 13% and 12% of the bacterial communities respectively. The proportion of Chloroflexi, Proteobacteria, Acidobacteria and Planctomycetes increased with age. Although the mechanisms for these shifts in microbial community were not identified, the authors noted that Firmicutes and Actinobacteria have previously been found in highly alkaline and saline environments, and that increases in the abundance of Acidobacteria and Proteobacteria were also observed in long term ecological restoration of other wastes.

The second study, also by the same research group but from a site in Shandong province (Wu, Tang, et al., 2020) compared a 1 year old unrestored bauxite residue to a 50 year old residue that had naturally

become "well restored" or "poorly restored" in terms of plant coverage, and "natural" soil. As well as characterizing the bacterial community, they also measured microbial biomass, respiration and enzyme activities. Again the chemical parameters had improved in the aged wastes and linear correlations were observed with the Shannon diversity indices. The "well restored" bauxite waste was not significantly different to the "natural" soil in terms of microbial biomass, respiration rate and most enzyme activities and all these parameters were significantly higher than in the unrestored waste. Similar to the other site studied, the unrestored waste was dominated by the Firmicutes (34%) and Actinobacteria (32%) phyla, while the 50 year old "well restored" waste had a much higher proportion of Chloroflexi (25%), Acidobacteria (13%), and Planctomycetes (9.6%). It is not clear why certain areas of the same waste storage facility naturally became colonized by plants and better restored, a topic which warrants further investigation.

4.3.3. Summary and Future Outlook

In some instances, over periods of decades, alkaline bauxite waste ages and weathers to become more benign, the diversity of the microbial community increases to become more similar to adjacent soils, and it becomes successfully colonized by plants. However, even after 50 years some materials remained poorly restored, therefore understanding the factors that contribute to the successful natural colonization and restoration of bauxite residue is key and should be the focus of future investigation. For example, a study of gold tailings found that it took at least 6 months to become colonized by microorganisms via dust-borne dispersal (Santini et al., 2018); similar approaches could be applied to bauxite residues to determine whether dispersal is responsible for this heterogeneity in ecological succession or if there are other factors involved.

It is evident from both field and laboratory studies that anaerobic microbial metabolisms are beneficial for alkaline bauxite residues, and that stimulating these for example, via constructed wetlands may be applied as a bioremediation strategy. It would be interesting to characterize the dynamic microbial community response during application of constructed wetlands to treat bauxite residues. Identifying the key microorganisms that are the main contributors to carbonation could help determine the best way to maximize this effect and enhance the overall waste bioremediation. Alkaliphilic microorganisms can be isolated from bauxite residues and some have beneficial metabolisms that can lower the waste pH, but it is yet to be determined whether these could be applied as a bioaugmentation technology in the environment.

5. Conclusions

Metal contamination from mining causes serious environmental impacts and risks to human health on a global scale. Microorganisms inhabit mine wastes and microbial activity can both mobilize metals from mine wastes, and sequester metals from contaminated waters. Microbes have a range of resistance mechanisms to deal with metal toxicity, and can also indirectly change metal speciation. These microbial processes influence the environmental fate of metals, transferring them between the terrestrial and aquatic environments, and consequently their mobility and likelihood to cause adverse impacts on planetary health.

Metal contamination can cause decreased efficiency in soil functioning as microbes need to expend energy to maintain and repair cells when challenged with toxic metals. But perhaps the effect of this is less than would be expected, particularly observed in analyses of long-term field studies rather than laboratory experiments where soils were spiked with metal salts. This may be due to microbial metal tolerance, resistance and community adaption. It appears that the impact of metals that are essential elements and subject to homeostasis (e.g., Zn and Cu), or metals that have a close biochemical analog (e.g., As), have less of an impact on soil function compared to those which are neither (e.g., Cd, Cr, and Pb). This is rather simplistic though, as microbial metal and mineral transformations will also have an effect, as will mixtures of metals that are commonly encountered in mine wastes, plus geochemical factors like pH and organic carbon availability.

While there are many laboratory studies that investigate the addition of metal salts to soils, more studies using metal-impacted mine wastes are required to fully understand the combination of the waste mineralogy, geochemistry, and multiple metal contaminants. Ideally these should investigate long-term metal exposure to allow for the adaption of microbial communities. As well as this, more long-term field studies are required, especially that consider the geomicrobiological processes that influence metal speciation and microbial community dynamics. It is important that fungi as well as prokaryotes are considered in these systems. It would be exciting to see more molecular biology approaches applied to understand how microbial

communities respond and adapt to metal contamination in the field, to show which resistance mechanisms are most significant and if this response that can explain the observed (bio)geochemistry.

Stimulating beneficial microbial activity to remediate metal-impacted mine wastes has had some successes, particularly the application of constructed wetlands or passive bioreactors to generate (microbially mediated) anoxic and sulfidic conditions. The combination of different remediation strategies (oxic and anoxic) may confer advantages against the use of a single system. Optimisation of remediation strategies needs to be addressed in order to provide low-cost approaches for governments and companies to address metal contamination in water and soils, which affects almost every country in the world. Further research is required to allow bioremediation to be applied in future at large scale, particularly around engineering, costs, challenges with consistency, acceptable rate of reaction, and disposal of wastes. Alternative approaches could be also be assessed such as the potential for microbial formation of metal phosphate minerals and metal sequestration in association with manganese oxides; it would be interesting to see whether these processes can be stimulated at large-scale to remediate mine wastes. Fungi in particular grow quickly, make large amounts of biomass under aerobic conditions and can form phosphate and manganese oxides; more study of their potential is required. Finally, we have described microbial metal resistance mechanisms at the genetic level for single species, but can these be applied to develop new and novel treatment strategies, or even to optimise field based bioremediation?

Understanding microbe-metal interactions may hold the key to limiting metal toxicity in mine wastes, by informing remediation strategies to prevent the formation of acid mine waters, to recover metals from mine wastes and to remediate metal-impacted mine waters, therefore improving environmental outcomes and planetary health.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

Data were not used, nor created for this research.

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