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Antimony mobility in soils: current understanding and future research directions

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Antimony (Sb) has gained increased attention over the past few decades due to its possible detrimental effects on biota and its potential to leach and disperse from contaminated soils. The fate of Sb in the environment is largely controlled by its chemical speciation, as well as the speciation of solid phases (e.g. Mn/Fe-oxyhydroxides) that interact with Sb in soils. Microbes have the capacity to facilitate a multitude of oxidation and reduction reactions in soils. Therefore, they exert control over the reactivity of Sb in the environment, either directly and/or indirectly, by changing Sb speciation and/or affecting the redox state of soil solid phases. Here, we outline processes that determine the behaviour of Sb in soils. We conclude that based on laboratory studies there is a good theoretical understanding of pure soil components interacting with Sb species. However, comparatively little is known concerning the contribution of these interactions in complex natural systems that are dynamic in terms of biogeochemical conditions and that can hardly be simulated using laboratory incubations. We note that important biochemical foundations of microbially driven Sb conversions (*i.e.* molecular constraints on organisms, genes and enzymes involved) have emerged recently. Again, these are based on laboratory incubations and investigations in environments high in Sb. In this regard, an important remaining question is which microorganisms actively impact Sb speciation under real-world conditions, in particular where Sb concentrations are low. Multiple dissolved Sb species have been described in the literature. We note that more analytical development is needed to identify and quantify possible key Sb species in natural systems, as well as anthropogenically impacted environments with only moderate Sb concentrations. With these research needs addressed, we believe that the Sb fate in the environment can be more accurately assessed, and remediation options can be developed.

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Environmental significance

Sb has gained significant attention due to its potential to cause harm to ecosystems and human health, especially in contaminated soils. Sb, both naturally occurring and introduced through anthropogenic activities such as mining, industrial processes, and military operations, can migrate through the environment, posing risks to water quality and biodiversity. Its mobility and toxicity are largely controlled by its chemical speciation and interactions with various soil components, including microbial communities. However, much of the existing research has been based on simplified laboratory conditions, and there remains a gap of Sb behavior under dynamic, real-world environmental conditions. This review highlights the current state of knowledge on Sb biogeochemistry and identifies key research areas essential for enhancing environmental management and remediation efforts.

1. Introduction

Antimony (Sb) is a naturally occurring element with metallic and non-metallic characteristics. In its elemental form, it is a white, brittle, crystalline metalloid positioned within group 15

of the periodic table, with an atomic number of 51 and an atomic mass of 122.¹ Sb is relatively rare in the Earth's crust, with concentrations ranging from 0.2 $\mu\text{g g}^{-1}$ to 0.3 $\mu\text{g g}^{-1}$.² In the natural environment, Sb is often associated with sulphur (e.g. Sb_2S_3 , stibnite) or oxygen (e.g. Sb_2O_3 , valentinite).² Sb can be found at elevated concentrations in anthropogenically impacted soils and sediments because of metal mining, military training, smelting and pharmaceutical and pesticide manufacturing.² The world's Sb reserves amount to 1.8 million tonnes, and are concentrated in China (48%), Russia (18%) and Bolivia (16%).³ Due to its economic importance and potential risks and vulnerabilities related to future supply, the European Commission included Sb in its latest critical raw material list.⁴

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the processes underlying the mobilisation and immobilisation of Sb in the environment. In this review, we present the fundamental biogeochemical mechanisms that underlie the possible transformation of Sb in the environment. We review existing knowledge of possible redox reactions with common soil phases [Fe/Mn oxyhydroxides, clay minerals, soil organic matter and dissolved sulphide]. We elucidate the complex interplay between these phases, Sb and soil microbiota, as well as the interactive effects involving plants. With this, we identify knowledge gaps that need to be addressed to transfer our solid fundamental understanding of simplified, static laboratory systems to complex, dynamic natural environments. Addressing them will lay the basis for successful remediation measures in Sb-contaminated ecosystems in the future.

1.1. Detrimental effects of antimony

Despite beneficial uses (e.g. treatment of parasitic disease leishmaniasis), there are several adverse health effects documented following exposure due to oral ingestion, inhalation or dermal contact with Sb. These include respiratory, myocardial, gastrointestinal, developmental and metabolic (impact on blood glucose levels) effects²⁵ as well as genotoxicity²⁶ which has been the focus of several reviews (e.g. ref. 27 and 28). Besides the negative impact on human health, wildlife toxicity of antimony has been documented.²⁹ Due to its possible adverse effects and widespread occurrence, Sb has been classified as a priority pollutant by the US Environmental Protection Agency (USEPA);³⁰ that is, it belongs to the group of substances that are identified as being particularly harmful to human health and the environment, and that require careful monitoring and management to mitigate their detrimental effects. According to the USEPA, both the maximum contamination level goal and the maximum contaminant level are set at 0.006 mg L⁻¹.³¹ The European Union established a threshold of 0.01 mg L⁻¹ Sb in drinking water.^{32,33} According to the World Health Organization, the guideline value for Sb in drinking water is 0.02 mg L⁻¹.³⁴

Several geogenic sources contribute to global Sb emissions in the order of wind-borne dust < volcanic activity < sea salt spray < biogenic sources < forest fires.³⁵ A distinct rise of Sb in arctic ice cores starting approximately 900 years ago suggests that anthropogenic sources were contributing to atmospheric Sb emissions already in pre-industrial times.³⁶ Nowadays, anthropogenic activities result in locally and/or regionally elevated Sb concentrations in freshwaters, soils and sediments. For instance, Sb contamination in China has been related to mining activities, smelting and coal burning.^{37,38} In other countries that do not mine or refine primary Sb, the possible origins of locally elevated Sb concentrations include shooting activities. In Switzerland, for instance, up to ~25 tons of Sb enter the pedosphere each year because of shooting activities.^{39,40} As a result, target areas of shooting ranges are often heavily contaminated with high concentrations Sb and thus require remediation. In “moderately” contaminated soils (*i.e.*, those with increased Sb concentrations compared to the background), studying the fate of Sb is particularly relevant, as such soils may not require remediation under current laws. Various

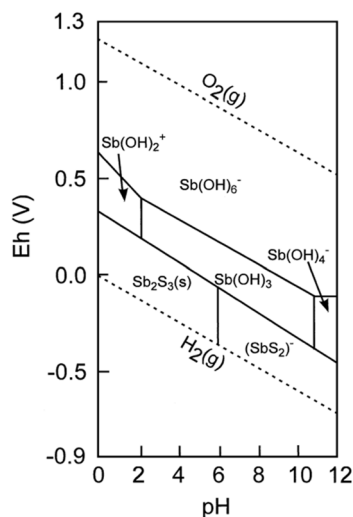


Fig. 1 Eh–pH diagram of antimony in the Sb–S–H₂O system at a dissolved antimony concentration of 10^{−8} mol L^{−1} and a dissolved sulfur concentration of 10^{−3} mol L^{−1} (reproduced from Filella *et al.*, 2002; with permission from Elsevier).¹⁰

mechanisms exist that act to mobilise Sb, increasing the likelihood of dispersal in the environment. This can pose severe threats to ecosystems, potentially affecting humans through food chain exposure.⁴¹

1.2. Geochemistry of antimony

As is also the case for other elements, the ‘chemical speciation’ determines the fate of Sb. Speciation refers to the specific forms of an element defined by its isotopic composition, electronic or oxidation state and/or complex or molecular structure.⁴² Temperature, pH, redox potential (Eh) and Sb concentrations are the key factors that determine the ‘expected’ (*i.e.* thermodynamically favoured) Sb speciation and thus its solubility and mobility in soils. In the environment, thermodynamic equilibrium is often not reached; thus, several Sb species are found at once.¹⁰ Sb exhibits a complex chemistry in the environment, which has been reviewed in several publications^{43,44} and is only briefly presented here.

In general, geochemical processes that control Sb mobility in soils or sediments are sorption–desorption reactions, Sb-mineral phase formation and dissolution and redox transformations. Furthermore, chelation by biogenic compounds, as well as biologically mediated alkylation reactions, can occur. In nature, Sb may be associated with oxygen and hydroxide, resulting in oxides, hydroxides or oxyanions, either in the pentavalent oxidation state or in the trivalent oxidation state under more reduced conditions. Solid $\text{Sb}(\text{OH})_3$ is not known to occur naturally, and the common convention is to represent the hydrolytic species of $\text{Sb}(\text{III})$ as hydroxide complexes, while the representation as oxyanions is also common.⁴⁵ Pentavalent antimony is presented as $\text{Sb}(\text{OH})_6^-$ and is the predominant form of Sb in the aqueous phases under oxidising conditions (Fig. 1).¹⁰ Furthermore, Sb associates with sulphur, forming either insoluble (*e.g.* stibnite, Sb_2S_3) or soluble sulphides (mostly anionic Sb–S complexes⁴⁶) (Fig. 2). Sb can also undergo biologically catalysed alkylation, leading to the formation of volatile Sb species, such as monomethyl Sb, dimethyl Sb and trimethyl Sb, in the environment.¹⁹ Biomethylation has long been suggested as a mechanism for the detoxification of different elements.¹⁹ Sb methylation appears to be a ubiquitous process in terms of organisms involved (fungi, archaea and bacteria), as well as environments, where methylated Sb compounds were detected (*e.g.* soil, sediment, sewage, freshwater, seawater and landfill gas).¹⁹

The environmental interactions between Sb and mineral phases and/or organic matter particles have been intensively

researched and are briefly summarised below. Notably, Fe and Mn (hydr)oxides are well-known sorbents, as well as redox-catalysts, for Sb,^{48–51} and soil organic matter (SOM) is recognised as an important complexing agent for Sb.^{16,46,52,53} Possible interactions with other mineral phases, such as clay minerals or sulphides, have been acknowledged but have received much less attention in previous studies.^{54,55}

1.2.1. Reaction with iron (hydr)-oxides. In natural soils and sediments, both crystalline minerals and amorphous iron (hydr)oxide minerals can exist as *e.g.* hematite (Fe_2O_3), ferrihydrite [$[\text{Fe}_{10}\text{O}_{14}(\text{OH})_2]$], goethite ($\alpha\text{-FeOOH}$) and magnetite (Fe_3O_4), which all represent possible sorbents for Sb.^{56–58} Many studies have quantitatively and mechanistically studied the interaction of Sb species with such phases.^{59–62} Fe (hydr)oxides have amphoteric properties and can steadily form complexes with cations and anions. Accordingly, one may expect that pentavalent Sb [being present as anionic $\text{Sb}(\text{OH})_6^-$ across the entire pH range; [see Fig. 1] will exhibit some sorption at pH values below the point of zero charge (PZC) of the respective iron (hydr)-oxide. Indeed, nearly complete $\text{Sb}(\text{V})$ sorption was observed, for example, on goethite at $\text{pH} < 7$ (average reported $\text{PZC} = \sim 8$; ⁶³). However, assessing the mobility of Sb is not simply a question of the ionic sorption of Sb species on pure mineral phases. For instance, in the natural environment, neither $\text{Sb}(\text{III})$ nor $\text{Sb}(\text{V})$ will occur as the only dissolved species but will be present together with other ions; hence, competition for sorption sites on Fe oxyhydroxides is likely (*e.g.* competition with the arsenite oxyanion⁶⁴). Furthermore, in simultaneous adsorption experiments with ferrihydrite, $\text{Sb}(\text{III})$ adsorption was not affected by the presence of $\text{Sb}(\text{V})$, while $\text{Sb}(\text{III})$ had an inhibitory effect on the adsorption of $\text{Sb}(\text{V})$.⁶⁵ This study points to another complication in the context of assessing Sb mobility: Sb species are prone to undergo redox reactions upon contact with certain solid surfaces. Ferrihydrite, for instance, can catalyse the oxidation of $\text{Sb}(\text{III})$ to $\text{Sb}(\text{V})$, which, in turn, influences Sb adsorption.⁶⁵ The oxidation of $\text{Sb}(\text{III})$ has also been shown, for instance, on goethite⁴⁹ and hydrous ferric oxide.⁶⁶ On the other hand, the reduction of $\text{Sb}(\text{V})$ has been demonstrated, for example, on mackinawite and magnetite (Kirsch *et al.* 2008),⁶⁰ as well as “green rust” [various redox active $\text{Fe}(\text{II})/\text{Fe}(\text{III})$ hydroxides].^{44,67} Recently, Peiffer *et al.* emphasised the universal importance of such redox-active mineral phases for the fate of contaminants.⁶⁸ Metastable mineral phases – including those of Fe (*e.g.* ferrihydrite or goethite; eventually transforming to haematite or magnetite) – are considered highly reactive surfaces, delivering or consuming electrons in redox reactions.



Fig. 2 Thioantimony transformation cycle in the environment. Adapted from (Ye & Jing, 2021).⁴⁷



Redox-active mineral phases obtain their specific redox-catalytic properties upon interaction with other redox-active constituents in solution and require activation by fluctuating redox conditions to maintain their high reactivity (Peiffer *et al.* 2021). The corresponding redox reactions of Sb often occur fast (*i.e.* from hours to a few days),^{48,65} thus controlling Sb mobility on diurnal or weekly time scales (*e.g.* upon periodic flooding and waterlogging after rain). This is certainly a challenge in understanding the mobility of Sb (and other redox-active elements such as As, Se and Te) in the environment. Moreover, the reaction with the Fe phases represents just one of the many possible reactions that Sb can undergo in the environment. Nevertheless, it is crucial to understand the reactivity of pure Fe phases with Sb, considering that such phases may be applied in natural environments for *in situ* remediation to decrease metal mobility in general (*e.g.* ref. 69), and specifically for Sb(v) and Pb from shooting range activities.^{70,71}

1.2.2. Reaction with manganese (hydr)oxides. Many Mn oxide/hydroxide phases are known to exist near the Earth's surface⁷² yet birnessite, pyrolusite, manganite and amorphous Mn oxides represent some of the most common solid Mn(III/IV) phases in soils. Sorption of Sb(III) and Sb(V) has been studied using several of such pure Mn phases. Sb(V) sorption on birnessite,⁷³ pyrolusite and manganite⁷⁴ showed the typical behaviour of an anionic species, with increased sorption with decreasing pH. The high adsorptive capacity of Mn oxides has been exploited in several functional materials (*e.g.* nanofibers of α -MnO₂, biogenic manganese oxides or Fe-doped birnessite) for Sb removal from waters.⁷⁵ When Sb(III) is brought into contact with solid manganese oxides, it gets oxidised due to the high oxidative power of these mineral phases. Reduced Mn(II)/(III) is either incorporated into the remaining solid or released as dissolved Mn²⁺, as shown for several phases^{76,77}.⁴⁸ showed a more efficient oxidation of Sb(III) by Mn oxides compared to Fe oxides, with the oxidation completed within a few days. Even faster oxidation of Sb(III) was observed on birnessite on a time-scale of minutes by.⁷⁸ The oxidation capacity of Mn oxides seems to be positively correlated with the Mn(III) content and surface-adsorbed oxygen but appears to be negatively correlated with its level of crystallinity.^{76,79} More precisely, it was demonstrated that the edge sites of birnessite represent key loci of Sb(III) oxidation and that, in turn, poorly crystalline birnessite exhibits higher oxidation and sorption capacities when compared with crystalline birnessite due to the availability of these edge sites.⁷⁶

During periods of waterlogging, soils can become anoxic, and solid Mn(IV) oxides can undergo reductive dissolution reactions, either through abiotic interactions with reducing compounds or microbial dissimilatory Mn reduction.⁸⁰ When such reduced soil solutions become oxidised again, solid Mn phases form upon dissolved Mn²⁺ oxidation. The products can be either amorphous or, to some degree, crystalline (mostly in the form of birnessite, rhodochrosite or bixbyite⁸¹), which impacts their sorption capacity.⁸² During redox transition periods, dissolved reduced Mn²⁺ and solid oxidised Mn may coexist (*i.e.* during the transition from reducing to oxidising conditions, and *vice versa*). The interaction with Mn²⁺ affects

Mn-oxide phase transformations and thus impacts Sb mobility indirectly. For instance, Sb(V)-bearing birnessite can undergo rapid (<1 day) transformation at circumneutral pH to manganite and hausmannite in the presence of Mn²⁺, effectively sequestering Sb.⁸³ In contrast, the absence of Mn²⁺ did not result in phase transformation but in the release of Sb(V) to the aqueous phase.⁸³

In the environment, the oxidation of dissolved Mn to form particulate Mn phases is mainly microbially driven (*e.g.* see the review by ref. 84 and 85), and the products are thus of a 'biogenic' nature. Biogenic Mn oxides appear to display a considerably (sometimes orders of magnitude) higher sorption potential than their 'synthetic' counterparts. For instance,⁸⁶ demonstrated that commercially available crystalline MnO₂ minerals showed a Pb sorption capacity between ~0.01 and 1 mmol Pb per mol Mn, whereas MnO₂ that was produced through microbial Mn²⁺ oxidation by *Leptothrix* displayed a much higher sorption capacity of around 550 mmol of Pb per mol Mn. This effect also seems to be pertinent to Sb sorption.⁸⁷ In addition,⁸⁶ demonstrated that sorption capacity is not constant over time. For example, as fresh synthetic Mn oxide phases age, their sorption capacity decreases.⁸⁶ Therefore, studies that rely solely on experiments with commercially chemically synthesised Mn phases that have possibly undergone ageing may not fully capture the true potential of these phase sorbents for Sb in natural environments. In soils and sediments prone to waterlogging and/or fluctuating redox conditions, complex redox reactions involving Mn and Sb will determine the mobility and speciation of Sb to a large extent. The impact of the biogenic origin and ageing of MnO₂ phases on the sorption of Sb remains to be systematically studied.

1.2.3. Association with clay minerals. Clay minerals play important roles in soil structure and function. They directly influence the availability of plant nutrients, control water retention/storage and contribute to the structural stability of soils.^{88,89} Sb mobility can be affected by the clay mineral content in soils, primarily due to their high surface area with abundant sorption sites. Certain phyllosilicates (for instance smectite- and montmorillonite-type clays) are well known for their capacity to sorb cations. This is because isomorphic substitution can occur,⁹⁰ which gives these minerals a permanent negative charge under most soil pH conditions. Therefore, next to sorption on the external plane, cations can sorb as interlayer complexes as well.⁹¹ Considering that dissolved Sb(V) occurs mostly as a charged anion, one can expect repulsion, and thus little retention on such phyllosilicates. Indeed, montmorillonite shows the lowest sorption affinity for Sb(V) in the sequence of montmorillonite < δ -MnO₂ < ferrihydrite at pH 5.5.⁹² Not all phyllosilicates undergo extensive isomorphic substitution. Kaolinite, for instance, a common variable-charge clay mineral, has a low capacity to adsorb cations, both because of little isomorphic substitution and due to its comparatively low surface area.⁸⁹ Indeed, Sb(V) sorption on kaolinite is high at a low pH.⁹³ Unlike anionic Sb(V), trivalent Sb(III) remains neutral over a broad pH range (Fig. 1) and should therefore be less susceptible to ion exchange reactions on positively charged minerals. However, only a handful of studies actually



investigated Sb(III) sorption on clay minerals and other Al-rich phases. An early study by⁹⁴ investigated Sb(III) sorption on different synthetic hydrous oxides, showing that trace concentrations of Sb(III) can effectively be sorbed by the synthesised $\text{Al}(\text{OH})_3$ gel at a pH of 6–7. Later,⁹⁵ compared the sorption of Sb(III) and Sb(V) by bentonite.⁹⁴ The bentonite used had a low PZC of 2.6 due to isomorphic substitution, confirming the greater adsorption of neutral Sb(III) compared to anionic Sb(V) at pH 6. Similarly,⁹⁶ observed greater sorption of Sb(III) compared to Sb(V) on kaolinite at a similar pH (pH = 5.5). Additionally, they found that Sb(V) sorption was enhanced at pH 5.5 compared to pH 8.0. Besides this expected general behaviour of Sb, further interesting observations could be made:⁹⁵ noted some desorption of Sb following Sb(III) adsorption, and they assigned this to the oxidation of Sb(III) on the bentonite surface and subsequent desorption of Sb(V).⁹⁶ used oxidised and reduced nontronite, an Fe-containing phyllosilicate, and found that for nontronite in the reduced state, sorption capacity towards Sb(III) was slightly decreased, whereas Sb(V) uptake was dramatically increased compared to oxidised nontronite. A certain Fe content in natural clay minerals is very common (as structural Fe in the lattice of clays, in the interlayer space and/or adsorbed on the external surface), and this Fe can cycle between its Fe(II) and Fe(III) oxidation states.⁹⁷ Therefore, one may speculate that Fe-containing clays can also act as redox catalysts similar to Fe oxyhydroxides (see above in Section 1.2.3). Despite this possible role, it is fair to say that, in contrast to the Fe and Mn solid phases, these reactions have remained almost entirely unstudied thus far.

1.2.4. Interaction of Sb with soil organic matter. Soil organic matter (SOM) comprises components from the breakdown of plant materials, faunal remains and microbial biomass, consisting of humic acids (HA), fulvic acids (FA) and humins.⁹⁸ In addition to its generally important role in the context of nutrient supply, soil structure, water storage and carbon sequestration, SOM also influences the biogeochemical cycle of Sb in different ways. SOM promotes electron flow and can serve as an electron donor and/or electron shuttle for microbial respiration in anaerobic environments, either reducing Sb(V) to Sb(III)⁹⁹ or reducing Sb-bearing solid phases of *e.g.* $\text{Fe}^{100,101}$ and Mn.¹⁰² SOM may also interact with Sb through complexation and binding. In general, Sb reactivity with natural organic matter will depend on the type of organic matter (HA, FA or humins) and the type of reactive functional groups present. It has been shown that the decreased availability of Sb upon the ‘ageing’ of soils may be largely determined by Sb binding to organic matter.¹⁰³ The interaction between SOM and Sb will depend on both Sb speciation and the presence of certain functional groups: cationic species (such as Sb(III) in the form of SbOH_2^+ , Fig. 1) may interact with carboxylate functional groups.¹⁰⁴ Anionic Sb species [such as Sb(V) in the form of $\text{Sb}(\text{OH})_6^-$] might involve amine-type functional groups.¹⁰⁵ For neutral species [such as Sb(III) in the form of $\text{Sb}(\text{OH})_3$], the presence of thiol moieties appears to impact Sb retention. In peatlands, Sb(III) may complex with carboxylic or phenol groups when the thiol content is low. However, under high-thiol conditions, Sb(III) sorption to SOM and thiol groups tends to

increase.^{10,46} Under highly acidic conditions (pH < 2), there is notable binding between both Sb species and SOM, with Sb(V) displaying a stronger preference over Sb(III) (present in cationic form, whereas Sb(V) is partially present as an anion).^{105,106} In contrast, under near-neutral conditions (pH > 4), the affinity to complex Sb(V) is reduced, which can be attributed to the negative charge of Sb(V) and SOM at neutral pH.^{105,106} In soil solutions, the disposition and availability of dissolved organic matter (DOM) determines the fate of Sb.^{46,99} In this regard, complexation of Sb with DOM has been shown to increase Sb mobility.⁹⁹ Fan *et al.* evaluated the effects of DOM on the sorption of Sb(V) in soils, and demonstrated that the sorption of Sb(V) can be considerably reduced in soil regions where DOM has been removed experimentally (by extraction with CaCl_2 solution; see ref. 107). The ability of Sb to form complexes with smaller carboxylic organic acids, potentially from biogenic sources in soils, is well established (*e.g.* in the form of citric acid;¹⁰⁸) and may increase Sb mobility as well.

In summary, a plethora of possible interactions between Sb and SOM exist, and a generally valid statement about whether SOM increases or decreases Sb mobility and bioavailability in soils seems almost impossible. Several fundamental reactions between SOM and Sb species have been quantitatively and spectroscopically examined. However, considering that SOM in healthy soils is continuously synthesised and decomposed,¹⁰⁹ it is crucial to deepen our understanding of these dynamic interactions.

1.2.5. Formation of dissolved thioantimony compounds.

Recently, particularly in sulphide-rich environments, such as geothermal systems, the natural formation of thioantimony (Sb–S) species has been noted. As a chalcophile element, the geochemistry of Sb is often coupled with the cycling of sulphur (S). A good example in this context is the formation of stibnite (Sb_2S_3), the primary Sb ore on Earth.^{43,110} Dissolved inorganic thioantimony compounds are formed by formally replacing the hydroxyl groups in Sb(III) and Sb(V) oxyanions with sulphhydryl groups, thus generating thioantimonates and/or thioantimonites (Fig. 2).^{111,112} The natural occurrence of Sb(V)–S species was reported for geothermal waters, hot springs and sulphidic landfills.^{55,113–115} Sb(III)–S species were, for instance, formed during the dissolution of Sb_2S_3 in a sulphide solution.^{116,117} This may occur in the environment, when the sulphide solution is of biogenic nature.¹¹⁸ However, in natural systems Sb(III)–S species are hard to detect due to inherent challenges linked to their analysis in real matrices. On the one hand, Sb(III)–S species are redox labile^{55,119} rendering sample preparation/conservation problematic. On the other hand, when using hyphenated techniques such as Liquid Chromatography Inductively Coupled Plasma Mass Spectrometry (LC-ICP-MS) for quantifying individual species, the chromatographic separation of multiple co-existing Sb–S species is difficult.

In terms of mobility, the repulsion of typically negatively charged thioantimonates and thioantimonites by negatively charged mineral (hydr)oxides of Fe and Mn may generally enhance overall Sb mobility in sulphide-rich natural environments.¹²⁰ Limited information, however, is available on the



occurrence of thioantimony in natural waters outside of geothermal and hot springs (see ref. 47 for more details). Future research should therefore focus on exploring the potential existence and fate of thioantimonates and/or thioantimonites in other ecosystems containing reduced sulphur. Considering the widespread presence and activity of sulphate-reducing bacteria that produce biogenic sulphide,¹²¹ one can expect that such Sb-S species will be discovered in Sb contaminated anoxic environments once the analytical challenges associated with the conservation of their speciation and quantification of individual species during analysis are addressed.

1.3. Role of microbial dissimilatory iron reduction in Sb mobility

The reduction of Fe(III) in the environment is to a large degree catalysed by Fe(III)-reducing microorganisms. This trait is phylogenetically widespread among bacteria and archaea and can occur by two different metabolic mechanisms: dissimilatory Fe-reducing microorganisms are strict or facultative anaerobes that conserve energy from the electron transfer to Fe(III) at their respiratory chain. Others, mostly fermenting bacteria, can dump electrons onto Fe(III) independently of a respiratory chain and improve thereby their growth yield.^{100,122} When soils become anoxic due to water saturation Fe minerals may undergo reductive dissolution promoted by the activity of Fe(III)-reducing microorganisms, potentially releasing previously adsorbed metals and metalloids.⁵³ In this regard, some studies have used pure strains of Fe-reducing bacteria to demonstrate the mobilisation of Sb to the aqueous phase (e.g. ref. 123). Other studies involving natural soils and sediments and their associated microbial consortia have observed that the release of dissolved Fe and Sb is closely linked. For instance,¹²⁴ could relate the release of Sb and Fe from different paddy soils of the Xikuangshan Sb mine (China) in simulated flooding conditions.¹²⁵ showed that Sb(III) formed as a result of the microbial reduction of Sb, which was first sorbed on iron (hydr)oxides before it was released as a result of reductive Fe dissolution in a shooting range soil.

While there seems to be some potential for increased Sb mobility under Fe-reducing conditions, evidence exists that the opposite may also be true. Microbial Fe(III) reduction can cause phase transformations and/or secondary mineral formation in/from metastable iron oxides. For instance, traces of Fe²⁺ can induce the rapid transformation of ferrihydrite into more stable forms such as goethite, lepidocrocite and magnetite.^{126–128} All these phases have a different metal-sorption capacity and a differential tendency to incorporate elements in their mineral structure compared to ferrihydrite. Thus, the transformation of metastable Fe phases into more stable phases can influence the mobility of the elements originally associated. For instance, using *Shewanella putrefaciens*¹²³ showed that Fe(II) can catalyse the rapid transformation of Sb(v)-bearing ferrihydrite to ferrihydrite and goethite, incorporating Sb(v) *via* substitution for Fe(III). Moreover, a study on the microbial reduction of Sb(v)-bearing ferrihydrite by *Geobacter sulfurreducens*¹²⁹ demonstrated microbially induced phase Fe transformations immobilising

Sb. While, in general, microbial control over Fe cycling is very well understood (e.g. ref. 130), the information on the impact of microbial Fe reduction on Sb mobilisation is still limited. The question of whether microbial Fe reduction ultimately results in increased or decreased mobility of Sb in nature cannot be fully answered to date.

1.4. Role of dissimilatory manganese reduction in Sb mobilisation

The reduction of Mn(IV) and Mn(III) in soils and freshwater sediments is primarily catalysed by microorganisms. As for Fe(III), Mn(IV) reduction is linked to the anaerobic oxidation of organic carbon¹⁰⁰ and Mn(IV) can serve as the terminal electron acceptor for dissimilatory reduction. Various microorganisms possess the capacity to reduce Mn oxides to support their growth (see e.g. ref. 131–133), and many microbes that can reduce Fe(III) can also reduce Mn(IV), and *vice versa*. Since Mn phases represent potent sorbents for Sb (see Section 1.2.2), their reductive dissolution may result in Sb mobilisation. For instance, column experiments using moderately contaminated shooting range soils showed that Sb(v) and Mn²⁺ effluent concentrations were correlated, providing evidence that Sb(v) was associated with these phases and suggesting that Sb was released by reductive dissolution.⁵⁷ Similarly, using an experimental setup with controlled redox conditions that suppress Fe and sulphate reduction¹³⁴ showed that the reductive dissolution of Sb-hosting Mn phases conferred Sb release. A relatively large number of studies exist that exploit the potential of Mn phases as sorbents and/or oxidants for Sb(III) (see Section 1.2.2). Only a few fundamental studies, however, have investigated the interplay among Mn oxyhydroxides, Mn dissimilatory microbial activity, and its impact on Sb mobilisation, despite the evidence that this may control the Sb fate in soils and sediments to a large degree.

2. Microbially catalysed redox reactions of Sb compounds

Microbial transformations directly involving Sb compounds can be broadly classified into oxidative and reductive reactions including the reduction of Sb(v) as well as hydride generation and alkylation reactions, see ref. 19. Since the first isolations back in the 1970s¹³⁵ there are currently well over 70 Sb oxidisers known.¹³⁶ Sb oxidisers can be divided into chemoautotrophs and heterotrophs. Chemoautotrophic oxidisers conserve energy from the oxidation of Sb(III) to Sb(v) and use CO₂ as a carbon source for biomass formation. Some examples of isolated pure cultures include *Variovax paradoxus* IDSBO-4, *Sulfobacillus* sp., *Leptospirillum* sp., *Ferroplasma* sp., *Sulfobacillus thermotolerans* Sb-K, *Sulfobacillus sibiricus* Sb-F and *Sulfobacillus thermosulfidooxidans*.^{11,12,137} Heterotrophic Sb(III) oxidisers cannot conserve energy from this reaction and use organic compounds (e.g. tartrate;¹¹) as the carbon and energy source. Here, the oxidation of Sb(III) may represent a detoxification mechanism. Most isolated Sb oxidisers known so far use O₂ as a terminal electron



Phytoremediation is frequently proposed as a cost-efficient and socially acceptable remediation technique for metals (see recent review by *e.g.* ref. 170). Certainly, some promising progress has been made in phytoremediation (*e.g.* the development of hyperaccumulating plants through genetic engineering and bioaugmentation with specific microbial strains;¹⁷⁰). Nonetheless, several limitations remain to date and often render phytoremediation uneconomical and/or impractical. One of the most common limitations of phytoremediation is the insufficient uptake and concentration of metals in plant tissues. For instance,¹⁷¹ investigated the levels of Sb accumulation across >34 plant species in an area heavily polluted with Sb ($\sim 6000 \text{ mg kg}^{-1}$), observing tissue concentrations of max $\sim 143.7 \text{ mg kg}^{-1}$. So-called 'enhanced phytoremediation' tries to overcome this limitation by using complexing agents to increase dissolved Sb concentration in the soil pore water and with this metal uptake in plants.^{172–174} However, the application of complexation comes at the risk of increased leaching from soils.^{175–177} Furthermore, for effective phytoremediation, Sb should be transferred to above-ground harvestable parts of the plant, which is quantified by the 'translocation factor' (ratio of shoot *versus* root concentration).¹⁷² This renders many plants with a low translocation factor unsuitable for phytoremediation (*e.g.* *Arundo donax* in the study of ref. 171). Accumulation of Sb within roots might in fact be a good strategy for plants to prevent Sb accumulation and transport into reproductive tissues in highly Sb-contaminated environments. For instance, some plants in an Sb mining area in Southwest China showed high Sb concentrations in the root tissue ($>1000 \text{ mg kg}^{-1}$), but translocation factors were well below 1.¹⁷⁸ To extract a high total amount of metals from the soil, it is necessary to build up a large amount of harvestable biomass with increased metal concentrations within the above-ground biomass. Despite being cost-efficient and socially acceptable, it remains to be proven whether phytoremediation of Sb will ever prove to be an 'effective' method of remediation, allowing a high mass of Sb to be extracted in a relatively short period of time. A better understanding of the processes governing Sb mobilisation into soil pore water, as well as the molecular processes of uptake and translocation within the plant, will be imperative for effectively identifying appropriate plants for bioremediation.

The interaction between Sb and SOM involves complexation by either DOM or organic matter associated with solid soil phases. These reactions are well studied, but it is still unclear whether SOM complexation generally increases or decreases the mobility and bioavailability of Sb. To resolve this uncertainty, we propose the use of species-specific methods, such as

spectroscopic techniques (e.g. XAFS) and mass spectrometry (e.g. LC-ICP-MS), to quantify and identify Sb-SOM complexes and thus to provide more conclusive answers related to the impact of SOM on Sb mobility. Having species-specific methods at hand would also allow a better understanding of the toxicity of Sb, which is species-dependent. However, hyphenated methods such as LC-ICP-MS will face a particular challenge regarding proper sample preparation, preserving original Sb speciation and resolving various species with sufficient sensitivity.

Another important open research question that we identified here is whether the interaction of Sb with sulphide ultimately increases or decreases Sb solubility and mobility. In sulphide-rich environments, such as geothermal systems, dissolved thioantimony species form naturally. Several studies exist on Sb solubility and speciation in sulfidic solutions (e.g., ref. 179 and references therein). However, there is only limited information on the occurrence of thioantimony in natural waters beyond geothermal settings and hot springs. Biogenic sulphide, produced by sulphate-reducing bacteria, can also form these species, as demonstrated in laboratory experiments. Given the widespread presence and activity of these bacteria, thioantimony species are likely to be found in many environments. On the other hand, some studies suggest that under sulphide-rich conditions, stibnite (Sb_2S_3) may form as a product of dissimilatory Sb reduction, potentially replacing Sb trioxide (Sb_2O_3) precipitation when sulphide is present. Since Sb_2S_3 is practically insoluble in water, this reaction would result in significantly lower dissolved Sb concentrations in the environment.

Microbial reactions involving Sb compounds can be broadly classified into oxidative reactions and reductive reactions. The genes and enzymes, particularly those involved in Sb(V) reduction, were identified only recently. Before the identification of specific genes and enzymes conferring Sb oxidation and/or reduction, our understanding of microbial interactions with Sb was limited to high-level taxonomic classifications and correlations with the Sb species quantified. This provided only little insight into the actual metabolic activities of specific strains in the environment. With the identification of relevant genes and enzymes, we can now perform transcriptomic analyses and design specific probes (such as RT-PCR) to investigate which microbial strains are actively driving Sb redox reactions in complex consortia in the environment. We emphasize that laboratory incubations typically use high Sb concentrations to enrich pure microbial strains. Soils and sediments, however, are not necessarily heavily contaminated with Sb (but still pose a risk of Sb migration and uptake into the food chain). Therefore, it remains to be determined whether the pure strains isolated thus far are truly representative of communities in moderately contaminated areas. A deeper understanding of the microbial processes affecting Sb in such environments will hopefully enhance our ability to manage Sb-associated risks and to remediate Sb contamination effectively.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Conflicts of interest

There are no conflicts to declare.

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References

- 1 C. G. Anderson, The metallurgy of antimony, *Chem. Erde*, 2012, 72(SUPPL.4), 3–8, DOI: [10.1016/j.chemer.2012.04.001](https://doi.org/10.1016/j.chemer.2012.04.001).
- 2 W. Zhuang, X. Lai, Q. Wang, Y. Liu, Q. Chen and C. Liu, Distribution characteristics, sources and ecological risk of antimony in the surface sediments of Changjiang Estuary and the adjacent sea, East China, *Mar. Pollut. Bull.*, 2018, 137, 474–480.
- 3 U.S. Geological Survey, *Antimony*, 2023.
- 4 European Commission, *Study on the Critical Raw Materials for the EU 2023 Final Report*, 2023, <http://www.europa.eu>.
- 5 D. Dupont, S. Arnout, P. Tom, J. Koen and P. T. Jones, Antimony Recovery from End-of-Life Products and Industrial Process Residues : A Critical Review, *J. Sustain. Metall.*, 2016, 2(1), 79–103.
- 6 K. J. Schulz, J. H. DeYoung Jr, R. R. Seal II and D. Bradley, *Critical mineral resources of the United States—An introduction*, 2017, Professional Paper, Available from: <http://periodic.lanl.gov/images/periodictable.pdf>.
- 7 J. Lewis, J. Sjöström, U. Skjellberg and L. Hägglund, Distribution, Chemical Speciation, and Mobility of Lead and Antimony Originating from Small Arms Ammunition in a Coarse-Grained Unsaturated Surface Sand, *J. Environ. Qual.*, 2010, 39(3), 863–870, DOI: [10.2134/jeq2009.0211](https://doi.org/10.2134/jeq2009.0211).
- 8 Z. Jin, Z. Zhang, J. Xiu, H. Song, T. Gatti and Z. He, A critical review on bismuth and antimony halide based perovskites and their derivatives for photovoltaic applications: recent advances and challenges, *J. Mater. Chem. A*, 2020, 8(32), 16166–16188. Available from: <https://pubs.rsc.org/en/content/articlehtml/2020/ta/d0ta05433j>.
- 9 J. Li, B. H. Zheng, Y. He, Y. Zhou, X. Chen, S. Ruan, *et al.*, Antimony contamination, consequences and removal techniques: A review, *Ecotoxicol. Environ. Saf.*, 2018, 156, 125–134.
- 10 M. Filella, N. Belzile and Y. W. Chen, Antimony in the environment: A review focused on natural waters II. Relevant solution chemistry, *Earth Sci. Rev.*, 2002, 59(1–4), 265–285.
- 11 L. R. Terry, T. R. Kulp, H. Wiatrowski, L. G. Miller and R. S. Oremland, Microbiological oxidation of antimony(III) with oxygen or nitrate by bacteria isolated from contaminated mine sediments, *Appl. Environ. Microbiol.*, 2015, 81(24), 8478–8488.
- 12 I. A. Tsaplina, V. V. Sorokin, A. E. Zhuravleva, V. S. Melamud, T. I. Bogdanova and T. F. Kondrat'eva, Oxidation of gold-antimony ores by a thermoacidophilic



- microbial consortium, *Microbiology*, 2013, **82**(6), 680–689, DOI: [10.1134/S0026261713060118](https://doi.org/10.1134/S0026261713060118).
- 13 J. Li, Q. Wang, M. Li, B. Yang, M. Shi, W. Guo, *et al.*, Proteomics and genetics for identification of a bacterial antimonite oxidase in *Agrobacterium tumefaciens*, *Environ. Sci. Technol.*, 2015, **49**(10), 5980–5989, DOI: [10.1021/es506318b](https://doi.org/10.1021/es506318b).
 - 14 J. Li, B. Yang, M. Shi, K. Yuan, W. Guo, Q. Wang, *et al.*, Abiotic and biotic factors responsible for antimonite oxidation in *Agrobacterium tumefaciens* GW4, *Sci. Rep.*, 2017, **7**, 1–11.
 - 15 V. K. Nguyen, W. Choi, Y. Park, J. Yu and T. Lee, Characterization of diversified Sb(V)-reducing bacterial communities by various organic or inorganic electron donors, *Bioresour. Technol.*, 2018, **250**, 239–246.
 - 16 T. R. Kulp, L. G. Miller, F. Braiotta, S. M. Webb, B. D. Kocar, J. S. Blum, *et al.*, Microbiological reduction of Sb(V) in anoxic freshwater sediments, *Environ. Sci. Technol.*, 2014, **48**(1), 218–226.
 - 17 C. Y. Lai, L. L. Wen, Y. Zhang, S. S. Luo, Q. Y. Wang, Y. H. Luo, *et al.*, Autotrophic antimonite bio-reduction using hydrogen as the electron donor, *Water Res.*, 2016, **88**, 467–474.
 - 18 S. Yamamura, C. Iida, Y. Kobayashi, M. Watanabe and S. Amachi, Production of two morphologically different antimony trioxides by a novel antimonite-reducing bacterium, *Geobacter* sp. SVR, *J. Hazard. Mater.*, 2021, **411**, 125100.
 - 19 R. Bentley and T. G. Chasteen, Microbial Methylation of Metalloids: Arsenic, Antimony, and Bismuth, *Microbiol. Mol. Biol. Rev.*, 2002, **66**(2), 250–271, DOI: [10.1128/mmbr.66.2.250-271.2002](https://doi.org/10.1128/mmbr.66.2.250-271.2002).
 - 20 J. Meyer, A. Schmidt, K. Michalke and R. Hensel, Volatilisation of metals and metalloids by the microbial population of an alluvial soil, *Syst. Appl. Microbiol.*, 2007, **30**(3), 229–238.
 - 21 M. C. Kasemodel, I. K. Sakamoto, M. B. A. Varesche and V. G. S. Rodrigues, Potentially toxic metal contamination and microbial community analysis in an abandoned Pb and Zn mining waste deposit, *Sci. Total Environ.*, 2019, **675**, 367–379.
 - 22 X. Pan, S. Zhang, Q. Zhong, G. Gong, G. Wang, X. Guo, *et al.*, Effects of soil chemical properties and fractions of Pb, Cd, and Zn on bacterial and fungal communities, *Sci. Total Environ.*, 2020, **715**, 136904.
 - 23 P. G. S. A. Jeyasundar, A. Ali, M. Azeem, Y. Li, D. Guo, A. Sikdar, *et al.*, Green remediation of toxic metals contaminated mining soil using bacterial consortium and *Brassica juncea*, *Environ. Pollut.*, 2021, 277. Available from: <https://pubmed.ncbi.nlm.nih.gov/33640810/>.
 - 24 I. Sazykin, L. Khmelevtsova, T. Azhogina and M. Sazykina, Heavy Metals Influence on the Bacterial Community of Soils: A Review, *Agriculture*, 2023, **13**(3), 653. Available from: <https://www.mdpi.com/2077-0472/13/3/653/html>.
 - 25 S. Sundar and J. Chakravarty, Antimony Toxicity, *Int. Res. J. Publ. Environ. Health*, 2010, **7**(12), 4267–4277. Available from: <https://www.mdpi.com/1660-4601/7/12/4267/html>.
 - 26 R. Wysocki, J. I. Rodrigues, I. Litwin and M. J. Tamás, Mechanisms of genotoxicity and proteotoxicity induced by the metalloids arsenic and antimony, *Cell. Mol. Life Sci.*, 2023, **80**(11), 1–30, DOI: [10.1007/s00018-023-04992-5](https://doi.org/10.1007/s00018-023-04992-5).
 - 27 Natasha, M. Shahid, S. Khalid, C. Dumat, A. Pierart and N. K. Niazi, Biogeochemistry of antimony in soil-plant system: Ecotoxicology and human health, *Appl. Geochem.*, 2019, **106**, 45–59.
 - 28 Z. Lai, M. He, C. Lin, W. Ouyang and X. Liu, Interactions of antimony with biomolecules and its effects on human health, *Ecotoxicol. Environ. Saf.*, 2022, **233**, 113317.
 - 29 B. E. Sample and C. A. Arenal, Wildlife Toxicity Assessment for Antimony, *Wildlife Toxicity Assessments for Chemicals of Military Concern*, 2015, pp. 325–348.
 - 30 USEPA. Priority Pollutant List [Internet]. 2014 [cited 2024 Nov 18]. Available from: <https://www.epa.gov/sites/default/files/2015-09/documents/priority-pollutant-list-epa.pdf>.
 - 31 USEPA. National Primary Drinking Water Regulations [Internet]. 2023 [cited 2023 Jul 30]. Available from: <https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations#Inorganic>.
 - 32 Official Journal of the European Union. DIRECTIVE (EU) 2020/2184 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 16 December 2020 on the quality of water intended for human consumption [Internet]. 2020 [cited 2024 Jun 27]. Available from: <https://eur-lex.europa.eu/eli/dir/2020/2184/oj>.
 - 33 European Union. European Union (Drinking Water) Regulations. 2023 [cited 2023 Aug 3]; Available from: <chrome-extension://efaidnbmnnnibpcajpcglclefindmkaj/https://www.irishstatutebook.ie/eli/2023/si/99/made/en/pdf>.
 - 34 World Health Organization, Guidelines for Drinking-Water Quality: Fourth Edition Incorporating the First Addendum, *Guidelines for Drinking-Water Quality: Fourth Edition Incorporating the First Addendum*, World Health Organization, 2017, p. 541, <https://www.ncbi.nlm.nih.gov/books/NBK442376/>.
 - 35 M. Filella, N. Belzile and Y. W. Chen, Antimony in the environment: A review focused on natural waters I. Occurrence, *Earth Sci. Rev.*, 2002, **57**(1–2), 125–176.
 - 36 M. Krachler, J. Zheng, D. Fisher and W. Shotyk, Atmospheric Sb in the Arctic during the past 16,000 years: Responses to climate change and human impacts, *Global Biogeochem. Cycles*, 2008, **22**(1), 1015, DOI: [10.1029/2007GB002998](https://doi.org/10.1029/2007GB002998).
 - 37 J. Chen, G. Liu, Y. Kang, B. Wu, R. Sun, C. Zhou, *et al.*, Atmospheric emissions of F, As, Se, Hg, and Sb from coal-fired power and heat generation in China, *Chemosphere*, 2013, **90**(6), 1925–1932.
 - 38 M. Adnan, B. Xiao, M. U. Ali, P. Xiao, P. Zhao, H. Wang, *et al.*, Heavy metals pollution from smelting activities: A threat to soil and groundwater, *Ecotoxicol. Environ. Saf.*, 2024, **274**, 116189.
 - 39 C. A. Johnson, H. Moench, P. Wersin, P. Kugler and C. Wenger, Solubility of Antimony and Other Elements in



- Samples Taken from Shooting Ranges, *J. Environ. Qual.*, 2005, **34**(1), 248–254, DOI: [10.2134/jeq2005.0248](https://doi.org/10.2134/jeq2005.0248).
- 40 B. H. Robinson, S. Bischofberger, A. Stoll, D. Schroer, G. Furrer, S. Roulier, *et al.*, Plant uptake of trace elements on a Swiss military shooting range: Uptake pathways and land management implications, *Environ. Pollut.*, 2008, **153**(3), 668–676.
 - 41 V. Antoniadis, E. E. Golia, Y. T. Liu, S. L. Wang, S. M. Shaheen and J. Rinklebe, Soil and maize contamination by trace elements and associated health risk assessment in the industrial area of Volos, Greece, *Environ. Int.*, 2019, **124**, 79–88.
 - 42 D. M. Templeton, F. Ariese, R. Cornelis, L. G. Danielsson, H. Muntau, H. P. Van Leeuwen, *et al.*, Guidelines for terms related to chemical speciation and fractionation of elements. Definitions, structural aspects, and methodological approaches (IUPAC recommendations 2000), *Pure Appl. Chem.*, 2000, **72**(8), 1453–1470, DOI: [10.1351/pac200072081453/html](https://doi.org/10.1351/pac200072081453/html).
 - 43 I. Herath, M. Vithanage and J. Bundschuh, Antimony as a global dilemma: Geochemistry, mobility, fate and transport, *Environ. Pollut.*, 2017, **223**, 545–559. Available from: <https://pubmed.ncbi.nlm.nih.gov/28190688/>.
 - 44 Y. Zhang, E. J. O'Loughlin and M. J. Kwon, Antimony redox processes in the environment: A critical review of associated oxidants and reductants, *J. Hazard. Mater.*, 2022, **431**, 128607.
 - 45 M. Filella, P. A. Williams and N. Belzile, Antimony in the environment: Knowns and unknowns, *Environ. Chem.*, 2009, **6**(2), 95–105.
 - 46 J. Besold, N. Kumar, A. C. Scheinost, J. Lezama Pacheco, S. Fendorf and B. Planer-Friedrich, Antimonite Complexation with Thiol and Carboxyl/Phenol Groups of Peat Organic Matter, *Environ. Sci. Technol.*, 2019, **53**(9), 5005–5015.
 - 47 L. Ye and C. Jing, Environmental geochemistry of thioantimony: formation, structure and transformation as compared with thioarsenic, *Environ. Sci.: Processes Impacts*, 2021, **23**(12), 1863–1872. Available from: <https://pubs.rsc.org/en/content/articlehtml/2021/em/d1em00261a>.
 - 48 N. Belzile, Y. W. Chen and Z. Wang, Oxidation of antimony (III) by amorphous iron and Manganese oxyhydroxides, *Chem. Geol.*, 2001, **174**(4), 379–387.
 - 49 A. K. Leuz, H. Mönch and C. A. Johnson, Sorption of Sb(III) and Sb(V) to goethite: Influence on Sb(III) oxidation and mobilization, *Environ. Sci. Technol.*, 2006, **40**(23), 7277–7282.
 - 50 S. Mitsunobu, Y. Takahashi, Y. Terada and M. Sakata, Antimony(V) incorporation into synthetic ferrihydrite, goethite, and natural iron oxyhydroxides, *Environ. Sci. Technol.*, 2010, **44**(10), 3712–3718, DOI: [10.1021/es903901e](https://doi.org/10.1021/es903901e).
 - 51 S. Rakshit, D. Sarkar, P. Punamiya and R. Datta, Antimony sorption at gibbsite–water interface, *Chemosphere*, 2011, **84**(4), 480–483.
 - 52 D. T. Scott, D. M. Mcknight, E. L. Blunt-Harris, S. E. Kolesar and D. R. Lovley, Quinone moieties act as electron acceptors in the reduction of humic substances by humics-reducing microorganisms, *Environ. Sci. Technol.*, 1998, **32**(19), 2984–2989, DOI: [10.1021/es980272q](https://doi.org/10.1021/es980272q).
 - 53 A. Kappler and P. V. Cappellen, Biogeochemical Redox Processes and their Impact on Contaminant Dynamics, *Environ. Sci. Technol.*, 2010, **44**(1), 15–23.
 - 54 J. Xi, M. He and C. Lin, Adsorption of antimony(V) on kaolinite as a function of pH, ionic strength and humic acid, *Environ. Earth Sci.*, 2010, **60**(4), 715–722, DOI: [10.1007/s12665-009-0209-z](https://doi.org/10.1007/s12665-009-0209-z).
 - 55 B. Planer-Friedrich and A. C. Scheinost, Formation and structural characterization of thioantimony species and their natural occurrence in geothermal waters, *Environ. Sci. Technol.*, 2011, **45**(16), 6855–6863, DOI: [10.1021/es201003k](https://doi.org/10.1021/es201003k).
 - 56 S. Denys, K. Tack, J. Caboche and P. Delalain, Bioaccessibility, solid phase distribution, and speciation of Sb in soils and in digestive fluids, *Chemosphere*, 2009, **74**(5), 711–716.
 - 57 K. Hockmann, S. Tandy, M. Lenz and R. Schulin, Antimony leaching from contaminated soil under manganese- and iron-reducing conditions: column experiments, *Environ. Chem.*, 2014, **11**(6), 624–631. Available from: <https://www.publish.csiro.au/en/EN14123>.
 - 58 S. Tandy, K. Hockmann, M. Keller, B. Studer, A. Papritz and R. Schulin, Antimony mobility during prolonged waterlogging and reoxidation of shooting range soil: A field experiment, *Sci. Total Environ.*, 2018, **624**, 838–844.
 - 59 R. Watkins, D. Weiss, W. Dubbin, K. Peel, B. Coles and T. Arnold, Investigations into the kinetics and thermodynamics of Sb(III) adsorption on goethite (α -FeOOH), *J. Colloid Interface Sci.*, 2006, **303**(2), 639–646.
 - 60 R. Kirsch, A. C. Scheinost, A. Rossberg, D. Banerjee and L. Charlet, Reduction of antimony by nano-particulate magnetite and mackinawite, *Mineral. Mag.*, 2008, **72**(1), 185–189. Available from: <https://www.cambridge.org/core/journals/mineralogical-magazine/article/abs/reduction-of-antimony-by-nanoparticulate-magnetite-and-mackinawite/D2194571EF9AC9424DD48262BCE6FEA9>.
 - 61 P. Qi and T. Pichler, Competitive adsorption of As(III), As(V), Sb(III) and Sb(V) onto ferrihydrite in multi-component systems: Implications for mobility and distribution, *J. Hazard. Mater.*, 2017, **330**, 142–148, DOI: [10.1016/j.jhazmat.2017.02.016](https://doi.org/10.1016/j.jhazmat.2017.02.016).
 - 62 L. Yan, T. Chan and C. Jing, Mechanistic Study for Antimony Adsorption and Precipitation on Hematite Facets, *Environ. Sci. Technol.*, 2022, **56**(5), 3138–3146, DOI: [10.1021/acs.est.1c07801](https://doi.org/10.1021/acs.est.1c07801).
 - 63 M. Kosmulski, The pH dependent surface charging and points of zero charge. VIII. Update, *Adv. Colloid Interface Sci.*, 2020, **275**, 102064.
 - 64 Z. Wu, Y. Zhao, Y. Zheng, M. Yin, J. Wang, N. Bolan, *et al.*, The fate of Sb(V) and As(V) during the aging of ferrihydrite, *Chem. Eng. J.*, 2024, **479**, 147671.
 - 65 P. Qi and T. Pichler, Sequential and simultaneous adsorption of Sb(III) and Sb(V) on ferrihydrite: Implications for oxidation and competition, *Chemosphere*, 2016, **145**, 55–60.



- 66 X. Guo, Z. Wu, M. He, X. Meng, X. Jin, N. Qiu, *et al.*, Adsorption of antimony onto iron oxyhydroxides: Adsorption behavior and surface structure, *J. Hazard. Mater.*, 2014, **276**, 339–345.
- 67 S. Mitsunobu, Y. Takahashi and Y. Sakai, Abiotic reduction of antimony(V) by green rust (Fe(4)(II)Fe(2)(III)(OH)(12)SO(4).3H(2)O), *Chemosphere*, 2008, **70**(5), 942–947. Available from: <https://pubmed.ncbi.nlm.nih.gov/17761212/>.
- 68 S. Peiffer, A. Kappler, S. B. Haderlein, C. Schmidt, J. M. Byrne, S. Kleindienst, *et al.*, A biogeochemical–hydrological framework for the role of redox-active compounds in aquatic systems, *Nat. Geosci.*, 2021, **14**(5), 264–272. Available from: <https://www.nature.com/articles/s41561-021-00742-z>.
- 69 M. Komárek, A. Vaněk and V. Ettler, Chemical stabilization of metals and arsenic in contaminated soils using oxides – A review, *Environ. Pollut.*, 2013, **172**, 9–22.
- 70 F. Kolbe, H. Weiss, R. Wennrich, W. G. Lorenz and B. Daus, Remobilization of pentavalent antimony and vanadium from a granular iron hydroxide material – A comparative study of different leaching systems, *Talanta*, 2011, **85**(4), 2089–2093.
- 71 G. Okkenhaug, K. A. Grasshorn Gebhardt, K. Amstaetter, H. Lassen Bue, H. Herzel, E. Mariussen, *et al.*, Antimony (Sb) and lead (Pb) in contaminated shooting range soils: Sb and Pb mobility and immobilization by iron based sorbents, a field study, *J. Hazard. Mater.*, 2016, **307**, 336–343. Available from: <https://pubmed.ncbi.nlm.nih.gov/26799225/>.
- 72 J. E. Post, Manganese oxide minerals: Crystal structures and economic and environmental significance, *Proc. Natl. Acad. Sci. U. S. A.*, 1999, **96**(7), 3447.
- 73 M. E. Essington and K. A. Vergeer, Adsorption of Antimonate, Phosphate, and Sulfate by Manganese Dioxide: Competitive Effects and Surface Complexation Modeling, *Soil Sci. Soc. Am. J.*, 2015, **79**(3), 803–814, DOI: [10.2136/sssaj2014.12.0482](https://doi.org/10.2136/sssaj2014.12.0482).
- 74 X. Wang, Y. Yang, L. Tao and M. He, Antimonite oxidation and adsorption onto two tunnel-structured manganese oxides: Implications for antimony mobility, *Chem. Geol.*, 2021, **579**, 120336.
- 75 X. Zhang, N. Xie, Y. Guo, D. Niu, H. b. Sun and Y. Yang, Insights into adsorptive removal of antimony contaminants: Functional materials, evaluation and prospective, *J. Hazard. Mater.*, 2021, **418**, 126345.
- 76 Q. Sun, P. X. Cui, C. Liu, S. M. Peng, M. E. Alves, D. M. Zhou, *et al.*, Antimony oxidation and sorption behavior on birnessites with different properties (δ -MnO₂ and triclinic birnessite), *Environ. Pollut.*, 2019, **246**, 990–998.
- 77 J. Nie, Z. Yao, P. Shao, Y. Jing, L. Bai, D. Xing, *et al.*, Revisiting the adsorption of antimony on manganese dioxide: The overlooked dissolution of manganese, *Chem. Eng. J.*, 2022, **429**, 132468.
- 78 Z. Shi, S. Peng, P. Wang, Q. Sun, Y. Wang, G. Lu, *et al.*, Modeling coupled kinetics of antimony adsorption/desorption and oxidation on manganese oxides, *Environ. Sci.:Processes Impacts*, 2018, **20**(12), 1691–1696. Available from: <https://pubs.rsc.org/en/content/articlehtml/2018/em/c8em00323h>.
- 79 J. Liu, W. Chen, X. Hu, H. Wang, Y. Zou, Q. He, *et al.*, Effects of MnO₂ crystal structure on the sorption and oxidative reactivity toward thallium(I), *Chem. Eng. J.*, 2021, **416**, 127919.
- 80 H. Li, F. Santos, K. Butler and E. Herndon, A Critical Review on the Multiple Roles of Manganese in Stabilizing and Destabilizing Soil Organic Matter, *Environ. Sci. Technol.*, 2021, **55**(18), 12136–12152, DOI: [10.1021/acs.est.1c00299](https://doi.org/10.1021/acs.est.1c00299).
- 81 J. E. Johnson, P. Savalia, R. Davis, B. D. Kocar, S. M. Webb, K. H. Nealson, *et al.*, Real-Time Manganese Phase Dynamics during Biological and Abiotic Manganese Oxide Reduction, *Environ. Sci. Technol.*, 2016, **50**(8), 4248–4258.
- 82 L. Peng, N. Wang, T. Xiao, J. Wang, H. Quan, C. Fu, *et al.*, A critical review on adsorptive removal of antimony from waters: Adsorbent species, interface behavior and interaction mechanism, *Chemosphere*, 2023, **327**, 138529.
- 83 N. Karimian, S. G. Johnston and E. D. Burton, Reductive transformation of birnessite and the mobility of co-associated antimony, *J. Hazard. Mater.*, 2021, **404**, 124227.
- 84 H. Zhou and C. Fu, Manganese-oxidizing microbes and biogenic manganese oxides: characterization, Mn(II) oxidation mechanism and environmental relevance, *Rev. Environ. Sci. Biotechnol.*, 2020, **19**(3), 489–507, DOI: [10.1007/s11157-020-09541-1](https://doi.org/10.1007/s11157-020-09541-1).
- 85 Y. Cai, K. Yang, C. Qiu, Y. Bi, B. Tian and X. Bi, A Review of Manganese-Oxidizing Bacteria (MnOB): Applications, Future Concerns, and Challenges, *Int. Res. J. Publ. Environ. Health*, 2023, **20**(2), 1272.
- 86 Y. M. Nelson, L. W. Lion, W. C. Ghiorse and M. L. Shuler, Production of Biogenic Mn Oxides by Leptothrix discophora SS-1 in a Chemically Defined Growth Medium and Evaluation of Their Pb Adsorption Characteristics, *Appl. Environ. Microbiol.*, 1999, **65**(1), 175.
- 87 Q. Li, Y. He, A. Yang, X. Hu, F. Liu, J. Mu, *et al.*, Antimony(III) removal by biogenic manganese oxides formed by Pseudomonas aeruginosa PA-1: kinetics and mechanisms, *Environ. Sci. Pollut. Res.*, 2023, **30**(43), 97102–97114, DOI: [10.1007/s11356-023-29277-z](https://doi.org/10.1007/s11356-023-29277-z).
- 88 J. B. Dixon, Roles of clays in soils, *Appl. Clay Sci.*, 1991, **5**(5–6), 489–503.
- 89 I. Bibi, J. Icenhower, N. K. Niazi, T. Naz, M. Shahid and S. Bashir, Clay Minerals: Structure, Chemistry, and Significance in Contaminated Environments and Geological CO₂ Sequestration, *Environmental Materials and Waste: Resource Recovery and Pollution Prevention*, 2016, pp. 543–567.
- 90 X. Liang, Y. Zang, Y. Xu, X. Tan, W. Hou, L. Wang, *et al.*, Sorption of metal cations on layered double hydroxides, *Colloids Surf. A Physicochem. Eng. Asp.*, 2013, **433**, 122–131.
- 91 A. M. L. Kraepiel, K. Keller and F. M. M. Morel, A Model for Metal Adsorption on Montmorillonite, *J. Colloid Interface Sci.*, 1999, **210**(1), 43–54.
- 92 C. M. van Genuchten and J. Peña, Antimonate and arsenate speciation on reactive soil minerals studied by differential



- pair distribution function analysis, *Chem. Geol.*, 2016, **429**, 1–9.
- 93 S. Rakshit, D. Sarkar and R. Datta, Surface complexation of antimony on kaolinite, *Chemosphere*, 2015, **119**, 349–354.
 - 94 P. Thanabalasingam and W. F. Pickering, Specific sorption of antimony (III) by the hydrous oxides of Mn, Fe, and Al, *Water Air Soil Pollut.*, 1990, **49**(1–2), 175–185, DOI: [10.1007/BF00279519](https://doi.org/10.1007/BF00279519).
 - 95 J. Xi, M. He and C. Lin, Adsorption of antimony(III) and antimony(V) on bentonite: Kinetics, thermodynamics and anion competition, *Microchem. J.*, 2011, **97**(1), 85–91.
 - 96 A. G. Ilgen and T. P. Trainor, Sb(III) and Sb(V) sorption onto al-rich phases: Hydrous al oxide and the clay minerals kaolinite KGa-1b and oxidized and reduced nontronite NAu-1, *Environ. Sci. Technol.*, 2012, **46**(2), 843–851, DOI: [10.1021/es203027v](https://doi.org/10.1021/es203027v).
 - 97 Q. Fan, L. Wang, Y. Fu, Q. Li, Y. Liu, Z. Wang, *et al.*, Iron redox cycling in layered clay minerals and its impact on contaminant dynamics: A review, *Sci. Total Environ.*, 2023, **855**, 159003.
 - 98 G. Angst, K. E. Mueller, K. G. J. Nierop and M. J. Simpson, Plant- or microbial-derived? A review on the molecular composition of stabilized soil organic matter, *Soil Biol. Biochem.*, 2021, **156**, 108189.
 - 99 M. Verbeeck, Y. Thiry and E. Smolders, Soil organic matter affects arsenic and antimony sorption in anaerobic soils, *Environ. Pollut.*, 2020, **257**, 113566.
 - 100 D. R. Lovley and E. J. P. Phillips, Novel Mode of Microbial Energy Metabolism: Organic Carbon Oxidation Coupled to Dissimilatory Reduction of Iron or Manganese, *Appl. Environ. Microbiol.*, 1988, **54**(6), 1472.
 - 101 N. Stern, J. Mejia, S. He, Y. Yang, M. Ginder-Vogel and E. E. Roden, Dual Role of Humic Substances As Electron Donor and Shuttle for Dissimilatory Iron Reduction, *Environ. Sci. Technol.*, 2018, **52**(10), 5691–5699, DOI: [10.1021/acs.est.7b06574](https://doi.org/10.1021/acs.est.7b06574).
 - 102 M. Xie, X. Zhang, S. Li, N. Maulani, F. Cai, Y. Zheng, *et al.*, Humic substances as electron acceptor for anaerobic oxidation of methane (AOM) and electron shuttle in Mn (IV)-dependent AOM, *Sci. Total Environ.*, 2024, **912**, 169576.
 - 103 S. Diquattro, P. Castaldi, S. Ritch, A. L. Juhasz, G. Brunetti, K. G. Scheckel, *et al.*, Insights into the fate of antimony (Sb) in contaminated soils: Ageing influence on Sb mobility, bioavailability, bioaccessibility and speciation, *Sci. Total Environ.*, 2021, **770**, 145354.
 - 104 J. Buschmann and L. Sigg, Antimony(III) binding to humic substances: Influence of pH and type of humic acid, *Environ. Sci. Technol.*, 2004, **38**(17), 4535–4541.
 - 105 M. Tella and G. S. Pokrovski, Stability and structure of pentavalent antimony complexes with aqueous organic ligands, *Chem. Geol.*, 2012, **292–293**, 57–68.
 - 106 M. Filella and P. A. Williams, Antimony interactions with heterogeneous complexants in waters, sediments and soils: A review of binding data for homologous compounds, *Geochemistry*, 2012, **72**(SUPPL.4), 49–65.
 - 107 Y. Fan, C. Zheng, A. Huo, Q. Wang, Z. Shen, Z. Xue, *et al.*, Investigating the binding properties between antimony(V) and dissolved organic matter (DOM) under different pH conditions during the soil sorption process using fluorescence and FTIR spectroscopy, *Ecotoxicol. Environ. Saf.*, 2019, **181**, 34–42. Available from: <https://pubmed.ncbi.nlm.nih.gov/31158721/>.
 - 108 J. Zheng, A. Iijima and N. Furuta, Complexation effect of antimony compounds with citric acid and its application to the speciation of antimony(III) and antimony(V) using HPLC-ICP-MS, *J. Anal. At. Spectrom.*, 2001, **16**(8), 812–818. Available from: <https://pubs.rsc.org/en/content/articlehtml/2001/ja/b101943k>.
 - 109 H. Wu, H. Cui, C. Fu, R. Li, F. Qi, Z. Liu, *et al.*, Unveiling the crucial role of soil microorganisms in carbon cycling: A review, *Sci. Total Environ.*, 2024, **909**, 168627.
 - 110 C. L. Hollabaugh, Chapter 2 Modification of Goldschmidt's geochemical classification of the elements to include arsenic, mercury, and lead as biophile elements, *Dev. Toxicol. Environ. Sci.*, 2007, **5**, 9–31.
 - 111 J. F. W. Mosselmans, G. R. Helz, R. A. D. Patrick, J. M. Charnock and D. J. Vaughan, A study of speciation of Sb in bisulfide solutions by X-ray absorption spectroscopy, *Appl. Geochem.*, 2000, **15**(6), 879–889. Available from: <https://research.manchester.ac.uk/en/publications/a-study-of-speciation-of-sb-in-bisulfide-solutions-by-x-ray-absor>.
 - 112 W. W. Bennett, K. Hockmann, S. G. Johnston and E. D. Burton, Synchrotron X-ray absorption spectroscopy reveals antimony sequestration by reduced sulfur in a freshwater wetland sediment, *Environ. Chem.*, 2017, **14**(6), 345–349. Available from: <https://www.publish.csiro.au/en/EN16198>.
 - 113 B. Planer-Friedrich, J. London, R. B. McCleskey, D. K. Nordstrom and D. Wallschläger, Thioarsenates in geothermal waters of yellowstone National Park: Determination, preservation, and geochemical importance, *Environ. Sci. Technol.*, 2007, **41**(15), 5245–5251, DOI: [10.1021/es070273v](https://doi.org/10.1021/es070273v).
 - 114 B. Planer-Friedrich, J. Forberg, R. Lohmayer, C. F. Kerl, F. Boeing, H. Kaasalainen, *et al.*, Relative Abundance of Thiolated Species of As, Mo, W, and Sb in Hot Springs of Yellowstone National Park and Iceland, *Environ. Sci. Technol.*, 2020, **54**(7), 4295–4304, DOI: [10.1021/acs.est.0c00668](https://doi.org/10.1021/acs.est.0c00668).
 - 115 Q. Guo, B. Planer-Friedrich, L. Luo, M. Liu, G. Wu, Y. Li, *et al.*, Speciation of antimony in representative sulfidic hot springs in the YST Geothermal Province (China) and its immobilization by spring sediments, *Environ. Pollut.*, 2020, **266**(Pt 1), 115221. Available from: <https://pubmed.ncbi.nlm.nih.gov/32698057/>.
 - 116 N. J. Olsen, B. W. Mountain and T. M. Seward, Antimony(III) Speciation in Hydrosulfide Solutions from 70 to 400 °C and up to 300 bar, *ACS Earth Space Chem.*, 2019, **3**(6), 1058–1072. Available from: https://www.researchgate.net/publication/332337000_AntimonyIII_Speciation_in_Hydrosulfide_Solutions_from_70_to_400_C_and_up_to_300_bar.



- 117 L. Yan, T. Chan and C. Jing, Mechanistic study for stibnite oxidative dissolution and sequestration on pyrite, *Environ. Pollut.*, 2020, **262**, 114309.
- 118 L. Ye, W. Zhong, M. Zhang and C. Jing, New Mobilization Pathway of Antimonite: Thiolation and Oxidation by Dissimilatory Metal-Reducing Bacteria *via* Elemental Sulfur Respiration, *Environ. Sci. Technol.*, 2022, **56**(1), 652–659, DOI: [10.1021/acs.est.1c05206](https://doi.org/10.1021/acs.est.1c05206).
- 119 B. Planer-Friedrich and N. Wilson, The stability of tetrathioantimonate in the presence of oxygen, light, high temperature and arsenic, *Chem. Geol.*, 2012, **322–323**, 1–10.
- 120 L. Ye, X. Meng and C. Jing, Influence of sulfur on the mobility of arsenic and antimony during oxic-anoxic cycles: Differences and competition, *Geochim. Cosmochim. Acta*, 2020, **288**, 51–67.
- 121 G. Muyzer and A. J. M. Stams, The ecology and biotechnology of sulphate-reducing bacteria, *Nat. Rev. Microbiol.*, 2008, **6**(6), 441–454. Available from: <https://www.nature.com/articles/nrmicro1892>.
- 122 K. A. Weber, L. A. Achenbach and J. D. Coates, Microorganisms pumping iron: anaerobic microbial iron oxidation and reduction, *Nat. Rev. Microbiol.*, 2006, **4**(10), 752–764. Available from: <https://www.nature.com/articles/nrmicro1490>.
- 123 E. D. Burton, K. Hockmann, N. Karimian and S. G. Johnston, Antimony mobility in reducing environments: The effect of microbial iron(III)-reduction and associated secondary mineralization, *Geochim. Cosmochim. Acta*, 2019, **245**, 278–289.
- 124 J. Long, D. Zhou, Y. Huang, Z. Yi, D. Bin, Y. Luo, *et al.*, Iron reduction process and antimony behavior change in paddy soils under stationary flooding conditions, *Appl. Geochem.*, 2022, **142**, 105311.
- 125 K. Hockmann, M. Lenz, S. Tandy, M. Nachtegaal, M. Janousch and R. Schulin, Release of antimony from contaminated soil induced by redox changes, *J. Hazard. Mater.*, 2014, **275**, 215–221. Available from: <https://pubmed.ncbi.nlm.nih.gov/24862348/>.
- 126 C. M. Hansel, S. G. Benner, J. Neiss, A. Dohnalkova, R. K. Kukkadapu and S. Fendorf, Secondary mineralization pathways induced by dissimilatory iron reduction of ferrihydrite under advective flow, *Geochim. Cosmochim. Acta*, 2003, **67**(16), 2977–2992.
- 127 H. Liu, P. Li, M. Zhu, Y. Wei and Y. Sun, Fe(II)-induced transformation from ferrihydrite to lepidocrocite and goethite, *J. Solid State Chem.*, 2007, **180**(7), 2121–2128.
- 128 R. S. Cutting, V. S. Coker, J. W. Fellowes, J. R. Lloyd and D. J. Vaughan, Mineralogical and morphological constraints on the reduction of Fe(III) minerals by *Geobacter sulfurreducens*, *Geochim. Cosmochim. Acta*, 2009, **73**(14), 4004–4022.
- 129 J. Xie, V. S. Coker, B. O'Driscoll, R. Cai, S. J. Haigh and J. R. Lloyd, Microbial Reduction of Antimony(V)-Bearing Ferrihydrite by *Geobacter sulfurreducens*, *Appl. Environ. Microbiol.*, 2023, **89**(3), e0217522, DOI: [10.1128/aem.02175-22](https://doi.org/10.1128/aem.02175-22).
- 130 A. Kappler, C. Bryce, M. Mansor, U. Lueder, J. M. Byrne and E. D. Swanner, An evolving view on biogeochemical cycling of iron, *Nat. Rev. Microbiol.*, 2021, **19**(6), 360–374. Available from: <https://www.nature.com/articles/s41579-020-00502-7>.
- 131 J. F. Su, S. C. Shao, T. L. Huang, F. Ma, S. F. Yang, Z. M. Zhou, *et al.*, Anaerobic nitrate-dependent iron(II) oxidation by a novel autotrophic bacterium, *Pseudomonas* sp. SZF15, *J. Environ. Chem. Eng.*, 2015, **3**(3), 2187–2193.
- 132 X. Wang, G. J. Xie, N. Tian, C. C. Dang, C. Cai, J. Ding, *et al.*, Anaerobic microbial manganese oxidation and reduction: A critical review, *Sci. Total Environ.*, 2022, **822**, 153513.
- 133 L. Huang, X. Liu, C. Rensing, Y. Yuan, S. Zhou and K. H. Nealson, Light-independent anaerobic microbial oxidation of manganese driven by an electrosynthetic coculture, *ISME J.*, 2022, **17**(1), 163–171. Available from: <https://www.nature.com/articles/s41396-022-01335-3>.
- 134 L. Costa, M. Martinez, M. Suleiman, R. Keiser, M. Lehmann and M. Lenz, Manganese reductive dissolution coupled to Sb mobilization in contaminated shooting range soil, *Appl. Microbiol. Biotechnol.*, 2024, **108**(1), 295. Available from: <https://pubmed.ncbi.nlm.nih.gov/38598118/>.
- 135 N. N. Lialikova, [Stibiobacter senarmontii—a new microorganism oxidizing antimony], *Mikrobiologiya*, 1974, **43**(6), 941–948. Available from: <https://pubmed.ncbi.nlm.nih.gov/4449497/>.
- 136 R. Biswas and A. Sarkar, Microbes: Key Players of the Arsenic Biogeochemical Cycle, in *Microbial Metabolism of Metals and Metalloids, Advances in Environmental Microbiology*, ed. C. J. Hurst, Springer Nature Switzerland AG, Cham, 2022, vol. 10, pp. 197–223, <https://link.springer.com/10.1007/978-3-030-97185-4>.
- 137 R. Deng, Y. Chen, X. Deng, Z. Huang, S. Zhou, B. Ren, *et al.*, A Critical Review of Resistance and Oxidation Mechanisms of Sb-Oxidizing Bacteria for the Bioremediation of Sb(III) Pollution, *Front. Microbiol.*, 2021, **12**, 738596.
- 138 M. Zhang, Z. Li, M. M. Häggblom, F. Li, G. Lu and R. Xu, Bacteria Responsible for Nitrate-dependent Antimonite Oxidation in Antimony-contaminated Paddy Soil Revealed by the Combination of DNA-SIP and Metagenomics, *Soil Biol. Biochem.*, 2021, **156**, 108194.
- 139 D. Min and D. F. Liu, It Is Time to Explore Unique Mechanisms for Microbial Antimony Conversion Rather Than Relying on Analogies with Arsenic Bioconversion, *Environ. Sci. Technol.*, 2023, **57**(42), 15780–15781, DOI: [10.1021/acs.est.3c08029](https://doi.org/10.1021/acs.est.3c08029).
- 140 V. K. Nguyen and J. U. Lee, Antimony-Oxidizing Bacteria Isolated from Antimony-Contaminated Sediment – A Phylogenetic Study, *Geomicrobiol. J.*, 2015, **32**(1), 50–58, Available from: <https://www.tandfonline.com/doi/abs/10.1080/01490451.2014.925009>.
- 141 E. Hiller, B. Lalinská, M. Chovan, Ľ. Jurkovič, T. Klimko, M. Jankulár, *et al.*, Arsenic and antimony contamination of waters, stream sediments and soils in the vicinity of abandoned antimony mines in the Western Carpathians, Slovakia, *Appl. Geochem.*, 2012, **27**(3), 598–614.



- 142 W. Guo, Z. Zhang, H. Wang, H. Qin and Z. Fu, Exposure characteristics of antimony and coexisting arsenic from multi-path exposure in typical antimony mine area, *J. Environ. Manage.*, 2021, **289**, 112493.
- 143 C. A. Abin and J. T. Hollibaugh, Dissimilatory antimonate reduction and production of antimony trioxide microcrystals by a novel microorganism, *Environ. Sci. Technol.*, 2014, **48**(1), 681–688, DOI: [10.1021/es404098z](https://doi.org/10.1021/es404098z).
- 144 D. R. Lovley, Dissimilatory metal reduction, *Annu. Rev. Microbiol.*, 1993, **47**, 263–290. Available from: <https://pubmed.ncbi.nlm.nih.gov/8257100/>.
- 145 D. Lovley, Dissimilatory Fe(III)- and Mn(IV)-Reducing prokaryotes, *The Prokaryotes: Prokaryotic Physiology and Biochemistry*, 2013, pp. 287–308, https://link.springer.com/referenceworkentry/10.1007/978-3-642-30141-4_69.
- 146 G. M. Gadd, Metals, minerals and microbes: geomicrobiology and bioremediation, *Microbiology (Read.)*, 2010, **156**(Pt 3), 609–643. Available from: <https://pubmed.ncbi.nlm.nih.gov/20019082/>.
- 147 R. S. Oremland and J. F. Stolz, The Ecology of Arsenic, *Science*, 1979, **300**(5621), 939–944, DOI: [10.1126/science.1081903](https://doi.org/10.1126/science.1081903).
- 148 V. K. Nguyen and J. U. Lee, Isolation and Characterization of Antimony-Reducing Bacteria from Sediments Collected in the Vicinity of an Antimony Factory, *Geomicrobiol. J.*, 2014, **31**(10), 855–861, Available from: <https://www.tandfonline.com/doi/abs/10.1080/01490451.2014.901440>.
- 149 K. Oorts, E. Smolders, F. Degryse, J. Buekers, G. Gascó, G. Cornelis, *et al.*, Solubility and toxicity of antimony trioxide (Sb₂O₃) in soil, *Environ. Sci. Technol.*, 2008, **42**(12), 4378–4383, DOI: [10.1021/es703061t](https://doi.org/10.1021/es703061t).
- 150 N. Wang, S. Zhang and M. He, Springer #, Berlin V. Bacterial community profile of contaminated soils in a typical antimony mining site, *Environ. Sci. Pollut. Res.*, 2016, **25**(1), 141–152, DOI: [10.1007/s11356-016-8159-y](https://doi.org/10.1007/s11356-016-8159-y).
- 151 H. Zhang and X. Hu, Bioadsorption and microbe-mediated reduction of Sb(V) by a marine bacterium in the presence of sulfite/thiosulfate and the mechanism study, *Chem. Eng. J.*, 2019, **359**, 755–764.
- 152 J. Ramírez-Patiño, J. Pérez-Trevilla, F. J. Cervantes and I. Moreno-Andrade, Removal of antimony by dissimilatory and sulfate-reducing pathways in anaerobic packed bed bioreactors, *J. Chem. Technol. Biotechnol.*, 2023, **98**(4), 932–939, DOI: [10.1002/jctb.7296](https://doi.org/10.1002/jctb.7296).
- 153 A. V. Zotov, N. D. Shikina and N. N. Akinfiev, Thermodynamic properties of the Sb(III) hydroxide complex Sb(OH)₃(aq) at hydrothermal conditions, *Geochim. Cosmochim. Acta*, 2003, **67**(10), 1821–1836.
- 154 L. Ye, H. Chen and C. Jing, Sulfate-Reducing Bacteria Mobilize Adsorbed Antimonate by Thioantimonate Formation, *Environ. Sci. Technol. Lett.*, 2019, **6**(7), 418–422, DOI: [10.1021/acs.estlett.9b00353](https://doi.org/10.1021/acs.estlett.9b00353).
- 155 J. Chen, G. Zhang, C. Ma and D. Li, Antimony removal from wastewater by sulfate-reducing bacteria in a bench-scale upflow anaerobic packed-bed reactor, *Acta Geochem.*, 2020, **39**(2), 203–215, DOI: [10.1007/s11631-019-00382-6](https://doi.org/10.1007/s11631-019-00382-6).
- 156 W. Sun, X. Sun, M. M. Häggblom, M. Kolton, L. Lan, B. Li, *et al.*, Identification of Antimonate Reducing Bacteria and Their Potential Metabolic Traits by the Combination of Stable Isotope Probing and Metagenomic-Pangenomic Analysis, *Environ. Sci. Technol.*, 2021, **55**(20), 13902–13912, DOI: [10.1021/acs.est.1c03967](https://doi.org/10.1021/acs.est.1c03967).
- 157 H. Liu, W. Sun and M. M. Häggblom, Microbial Transformations of Antimony, in *Advances in Environmental Microbiology*, 2022, vol. 10, pp. 223–54, Available from: https://link.springer.com/chapter/10.1007/978-3-030-97185-4_9.
- 158 J. Pratas, M. N. V. Prasad, H. Freitas and L. Conde, Plants growing in abandoned mines of Portugal are useful for biogeochemical exploration of arsenic, antimony, tungsten and mine reclamation, *J. Geochem. Explor.*, 2005, **85**(3), 99–107.
- 159 M. Tschan, B. H. Robinson and R. Schulin, Antimony in the soil - Plant system - A review, *Environ. Chem.*, 2009, **6**(2), 106–115.
- 160 R. W. Feng, L. Lei, J. M. Su, R. R. Zhang, Y. M. Zhu, W. X. Chen, *et al.*, Toxicity of different forms of antimony to rice plant: Effects on root exudates, cell wall components, endogenous hormones and antioxidant system, *Sci. Total Environ.*, 2020, **711**, 134589.
- 161 F. Cai, J. Ren, S. Tao and X. Wang, Uptake, translocation and transformation of antimony in rice (*Oryza sativa* L.) seedlings, *Environ. Pollut.*, 2016, **209**, 169–176.
- 162 J. Bech, I. Corrales, P. Tume, J. Barceló, P. Duran, N. Roca, *et al.*, Accumulation of antimony and other potentially toxic elements in plants around a former antimony mine located in the Ribes Valley (Eastern Pyrenees), *J. Geochem. Explor.*, 2012, **113**, 100–105.
- 163 X. Pan, D. Zhang, X. Chen, A. Bao and L. Li, Antimony accumulation, growth performance, antioxidant defense system and photosynthesis of zeas in response to antimony pollution in soil, *Water Air Soil Pollut.*, 2011, **215**(1–4), 517–523, DOI: [10.1007/s11270-010-0496-8](https://doi.org/10.1007/s11270-010-0496-8).
- 164 C. S. N. Vidya, R. Shetty, M. Vaculíková and M. Vaculík, Antimony toxicity in soils and plants, and mechanisms of its alleviation, *Environ. Exp. Bot.*, 2022, **202**, 104996.
- 165 A. Ortega, I. Garrido, I. Casimiro and F. Espinosa, Effects of antimony on redox activities and antioxidant defence systems in sunflower (*Helianthus annuus* L.) plants, *PLoS One*, 2017, **12**(9), e0183991, DOI: [10.1371/journal.pone.0183991](https://doi.org/10.1371/journal.pone.0183991).
- 166 T. Kamiya and T. Fujiwara, Arabidopsis NIP1;1 Transports Antimonite and Determines Antimonite Sensitivity, *Plant Cell Physiol.*, 2009, **50**(11), 1977–1981. Available from: <https://academic.oup.com/pcp/article/50/11/1977/1846008>.
- 167 R. W. Feng, L. Lei, B. X. Liu, W. X. Chen, R. R. Zhang, L. Z. Wang, *et al.*, Effects of different inhibitors such as malonic acid, Na₃PO₄ and HgCl₂ on uptake of different forms of antimony in rice plant, *Plant Soil*, 2019, **445**(1–2), 259–271, DOI: [10.1007/s11104-019-04296-3](https://doi.org/10.1007/s11104-019-04296-3).
- 168 R. Feng, C. Wei, S. Tu, Y. Ding, R. Wang and J. Guo, The uptake and detoxification of antimony by plants: A review, *Environ. Exp. Bot.*, 2013, **96**, 28–34.



- 169 R. Tisarum, Y. Chen, X. Dong, J. T. Lessl and L. Q. Ma, Uptake of antimonite and antimonate by arsenic hyperaccumulator *Pteris vittata*: Effects of chemical analogs and transporter inhibitor, *Environ. Pollut.*, 2015, **206**, 49–55.
- 170 H. Tang, M. U. Hassan, M. Nawaz, W. Yang, Y. Liu and B. Yang, A review on sources of soil antimony pollution and recent progress on remediation of antimony polluted soils, *Ecotoxicol. Environ. Saf.*, 2023, **266**, 115583.
- 171 C. Qi, F. Wu, Q. Deng, G. Liu, C. Mo, B. Liu, *et al.*, Distribution and accumulation of antimony in plants in the super-large Sb deposit areas, China, *Microchem. J.*, 2011, **97**(1), 44–51.
- 172 V. Antoniadis, S. M. Shaheen, H. J. Stärk, R. Wennrich, E. Levizou, I. Merbach, *et al.*, Phytoremediation potential of twelve wild plant species for toxic elements in a contaminated soil, *Environ. Int.*, 2021, **146**, 106233.
- 173 M. Gavrilescu, Enhancing phytoremediation of soils polluted with heavy metals, *Curr. Opin. Biotechnol.*, 2022, **74**, 21–31.
- 174 P. Seridou, K. Fyntrilakis, E. Syranidou and N. Kalogerakis, Hydroponic phytoremediation of antimony by *Tamarix smyrnensis* and *Nerium oleander*, *J. Chem. Technol. Biotechnol.*, 2023, **98**(9), 2214–2223, DOI: [10.1002/jctb.7434](https://doi.org/10.1002/jctb.7434).
- 175 L. H. Wu, Y. M. Luo, X. R. Xing and P. Christie, EDTA-enhanced phytoremediation of heavy metal contaminated soil with Indian mustard and associated potential leaching risk, *Agric. Ecosyst. Environ.*, 2004, **102**(3), 307–318.
- 176 A. Yano, A. Yano, K. Iwasaki, Y. Kang, K. Sakurai and S. Tanaka, Influence of Chelating Agent Addition on Copper Distribution and Microbial Activity in Soil and Copper Uptake by Brown Mustard (*Brassica juncea*), *Soil Sci. Plant Nutr.*, 2005, **51**(2), 193–202, DOI: [10.1111/j.1747-0765.2005.tb00023.x](https://doi.org/10.1111/j.1747-0765.2005.tb00023.x).
- 177 Z. Wu, Q. Jiang, T. Yan, S. Xu, H. Shi, L. Peng, *et al.*, Antimony symplastic and apoplastic absorption, compartmentation, and xylem translocation in *Brassica parachinensis* L. under antimonate and antimonite, *Ecotoxicol. Environ. Saf.*, 2020, **197**, 110621.
- 178 Z. Ning, T. Xiao and E. Xiao, Antimony in the Soil-Plant System in an Sb Mining/Smelting Area of Southwest China, *Int. J. Phytorem.*, 2015, **17**(11), 1081–1089, Available from: <https://www.tandfonline.com/doi/abs/10.1080/15226514.2015.1021955>.
- 179 N. J. Olsen, B. W. Mountain and T. M. Seward, Antimony(III) sulfide complexes in aqueous solutions at 30 °C: A solubility and XAS study, *Chem. Geol.*, 2018, **476**, 233–247.

