Arsenic in Soils, Mine Tailings, and Former Industrial Sites

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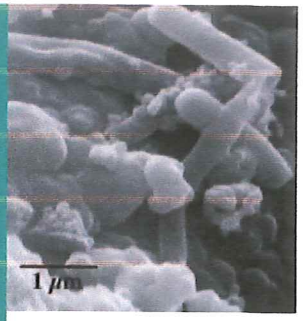

SEM micrograph of sediments from the Carnoulès (France) acid mine drainage site, showing amorphous As^{5+}–Fe^{3+} hydrous oxides associated with bacteria. MODIFIED FROM MORIN ET AL. (2003)

Much progress has recently been made on the relation between the crystal chemistry of arsenic and its speciation and distribution at the Earth's surface. The investigation of As-impacted soils and acid mine drainages, using synchrotron-based techniques, shows the importance of As adsorption on, or coprecipitation with, hydrous ferric oxides in delaying the long-term impact of As on the biosphere. Arsenic mobility often depends on bacterial activity, with accompanying major seasonal modifications of As speciation, even at extreme As concentrations. Remediation technologies use geochemical affinities between arsenic and specific low-temperature phases to reduce the bioavailability of arsenic.

KEYWORDS: arsenic, contamination, soils, acid mine drainage, speciation

INTRODUCTION

Although arsenic occurs naturally in soils, human activities have greatly increased arsenic contamination in the environment, e.g. through releases associated with mining, waste disposal, indiscriminate use of certain pesticides and herbicides, as well as the manufacture of As-bearing chemicals. Contaminated soils act as a source of arsenic, which can be further dispersed in the environment and may adversely affect the growth of plants and animals and, eventually, human health (Duker et al. 2005). A major source of contamination comes from the breakdown of insoluble As minerals, the arsenides and sulfides. Under the conditions prevailing at the Earth's surface, inorganic arsenic is progressively released as pentavalent arsenate (As^{5+}) or trivalent arsenite (As^{3+}) species, and these form a large variety of minerals (Anthony et al. 2000; O'Day this issue). However, most arsenate and arsenite minerals are not stable in soils over the long term. Arsenic may be encountered in a variety of other forms, such as poorly crystalline As-bearing solids, As-sorbed species, and organic forms of arsenic, mainly methylated compounds and carbohydrate derivatives. The difficulty in providing a robust assessment of As mobility at the Earth's surface comes from the complex interplay among the various forms of As and natural waters, together with the major role exerted by biotic processes (Lloyd and Oremland this issue). Depending on local conditions, As concentration and partitioning between solid phases and solutions may be further modified by changes in pH and redox conditions. For example, the dissolution of As may be counteracted by the precipitation of Fe-oxyhydroxides, which efficiently scavenge As^{3+} and As^{5+} at neutral pH. The commonly observed increase in solubility of As under reducing conditions is now attributed primarily to the reductive dissolution of Fe^{3+}-oxide phases and the subsequent release of adsorbed As. Aided by a rapidly expanding body of experimental data and by the information provided by modern analytical tools such as synchrotron radiation, a better picture of the control exerted by the crystal chemistry of arsenic on its biogeochemical properties is emerging. With this in mind, we will present some examples of studies of contaminated soils, former industrial sites, and mine tailings. These examples show the importance of oxidation and dissolution reactions, microbial activity, and water regime. The investigation of both natural high-arsenic geochemical anomalies and old mining and industrial sites contaminated by arsenic provides good data to establish what the most stable As-bearing phases are.

ARSENIC MINERALOGY AT FORMER INDUSTRIAL SITES

Industrial sites may be contaminated with by-products from the processing of As-bearing ores or by chemicals associated with the arsenic industry. These sites provide examples of major contamination, where arsenic has been mobilized from wastes by meteoric waters and has then reacted with mineral phases present in the environment. At most such sites, interaction of arsenic-rich waters with surrounding soils or bedrock may limit the contamination of the neighboring groundwaters and surface waters.

An example of the latter is provided by an old industrial site located on limestone in southern France (Juillot et al. 1999). For more than a century, sulfuric acid and various arsenic compounds were produced at this site, now under restoration. An integrated study of this contaminated area allowed identification of the source of the arsenic and of secondary As-bearing minerals formed at the site. The latter consist of secondary Ca- and Ca–Mg-arsenates, occurring either as surficial crusts or as transported particles. The arsenates formed as a result of the interaction of the runoff waters with As-bearing wastes and underlying limestone. Key geochemical parameters, such as pH and Ca, As, and sulfate concentrations, were monitored during several field campaigns, together with the proportions of various solid phases present, as determined from Rietveld refinement of X-ray diffraction patterns. It was found that the initially carbonate-buffered waters are strongly acidified (pH = 2.2) and enriched in sulfates as a result of the oxidation of

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wastes containing sulfide ores. The subsequent interaction with the underlying limestone causes the pH to shift back to neutrality, and the concentrations of Ca and Mg also progressively increase. The anhydrous arsenate weilite [$Ca(AsO_3OH)$] is the first phase formed during the neutralization of acidic As-bearing solutions, followed by pharmacolite ($CaHAsO_4 \cdot 2H_2O$). The high stability of these Ca-arsenates at this limestone site may be explained by a common ion effect, in which high Ca activity in the runoff waters inhibits the dissolution of Ca-arsenates. This explains an apparent As concentration three to four times lower in these waters than expected from the solubility product of weilite (Swash and Monhemius 1994). Arsenates such as scorodite ($FeAsO_4 \cdot 2H_2O$) are seldom encountered because of the scarcity of iron in the As-rich zones of the site. Field observations on the stability of Ca-arsenates may shed light on their long-term efficiency for remediation in soils, in which As may be rapidly immobilized by treatment with lime slurries, leading to the formation of Ca-hydroxyarsenates (Moon et al. 2004).

MINE SITES AND RELATED ENVIRONMENTS

Mining can release high concentrations of arsenic by means of the oxidation of sulfide minerals, either through the roasting of arsenical ores or through acid mine drainage (AMD) (Williams 2001). The latter results from the atmospheric exposure and weathering of sulfide-bearing rocks, such as the waste rock and mine tailings generated during mining and milling operations. Oxidation of sulfide minerals, often mediated by microbial activity, causes waters to become acidified and enriched in sulfate anions and heavy metals. During this process, an overall two-stage reaction governs the dissolution and further oxidation of As:

$$FeAsS\ (s) + 11/4\ O_2\ (aq) + 3/2\ H_2O\ (aq) \Leftrightarrow Fe^{2+}\ (aq) + SO_4^{2-}\ (aq) + H_3AsO_3\ (aq) \quad (1)$$

$$H_3AsO_3 + 1/2\ O_2\ (aq) \Leftrightarrow H_2AsO_4^- + H^+ \quad (2)$$

The oxidation of sulfide (reaction 1) can be catalyzed directly by bacterial activity and indirectly by the Fe^{3+} resulting from the oxidation of Fe^{2+} by bacteria such as *Acidithiobacillus ferrooxidans*. Bacterial oxidation of dissolved Fe^{2+} also leads to the formation of various iron oxides (Cornell and Schwertmann 2003) and hydroxysulfates (Bigham et al. 1996; Alpers et al. 2000). Arsenite oxidation (reaction 2) is slow, especially under acidic conditions, but may be catalyzed by the activity of bacteria such as *Thiomonas* sp. (Bruneel et al. 2003). Reaction (2) is important because As^{5+} is less toxic, less soluble, and adsorbs more efficiently than As^{3+} under acidic conditions.

Trapping of As by iron minerals is an efficient natural attenuation process, which reduces considerably the arsenic concentration in AMD waters. At pH lower than 2.5, As^{5+} may be incorporated in jarosite [$KFe_3(SO_4)_2(OH)_6$] (Savage et al. 2000; Foster et al. 1998). At higher pH, As^{5+} can sorb onto iron minerals with high specific surface areas (Fukushi et al. 2003; Courtin-Nomade et al. 2005), such as schwertmannite [$Fe_8O_8(OH)_6SO_4$] and ferrihydrite ($Fe_5HO_8 \cdot 4H_2O$) (for $2.5 \leq pH \leq 6$ and $6 \leq pH \leq 8$, respectively; Bigham et al. 1996). Arsenic speciation in mining environments provides an interesting picture of the complex interplay among the sources of the arsenic, the geochemical conditions, the dynamics of the system, and bacterial activity.

One of the first studies of arsenic speciation in mine tailings was that of the Mother Lode district, California, USA (Foster et al. 1998; Brown et al. 1999). A quantitative assessment of As speciation, based on XRD and extended X-ray absorption fine-structure (EXAFS) spectroscopy, was undertaken for three mine wastes: fully oxidized tailings (Ruth mine), partially oxidized tailings (Argonaut mine), and a roasted sulfide ore (Spenceville mine). As^{5+} was the predominant oxidation state in the Ruth and Spenceville mine samples, but mixed oxidation states were observed in the Argonaut mine wastes. These analyses suggested the presence of As^{5+} species similar to those found in scorodite and As^{5+} adsorbed on goethite (α-FeOOH) and gibbsite [α-$Al(OH)_3$]. Linear least-squares fits of mine waste EXAFS spectra indicated variable As speciation in each of the three mine wastes. Ferric oxyhydroxides and aluminosilicates (probably clay minerals) bind roughly equal proportions of As^{5+} in the Ruth mine. Tailings from the Argonaut mine contain ~20% reduced As bound in arsenopyrite (FeAsS) and arsenical pyrite ($FeS_{2-x}As_x$) and ~80% As^{5+} in a ferric arsenate precipitate similar to scorodite. Roasted sulfide ore from the Spenceville mine contains As^{5+}, both substituting for sulfate in the crystal structure of jarosite and sorbed to iron-oxide surfaces. These investigations show the importance of the mineralogical composition of the As source material and of sorbed As species.

Recent studies of arsenic-rich mine tailings (Paktunc et al. 2004) suggest that the stability of these mineral phases generally increases with increasing Fe/As ratio. For instance, leaching tests on tailings from the Ketza River mine, Canada, showed that As adsorbed in small quantities on Fe oxides appears to be less soluble than crystalline minerals such as arseniosiderite [$Ca_2Fe_3(AsO_4)_3O_2 \cdot 3H_2O$] (Paktunc et al. 2004). These findings agree with the few available solubility data on crystalline and amorphous As–Fe minerals.

An example of natural attenuation via the formation of As–Fe mineral phases is provided by an AMD at Carnoulès, Gard, France, with exceptionally high concentrations of dissolved arsenite. This AMD is generated by 1.5 million tons of mine tailings containing arsenical pyrite (Leblanc et al. 1996). Here, bacteria play an important role, and this biogeochemical coupling causes spatial and seasonal modifications in As speciation (Morin et al. 2003; Casiot et al. 2005). At or near the source of AMD, the anoxic and acid (pH = 2–3) waters are strongly enriched in Fe (0.5–1 g L^{-1}), As (50–350 mg L^{-1}), and sulfate (1–3 g L^{-1}). Under such conditions, arsenite is the predominant dissolved arsenic species. After 30 m of downflow, 20–60% of the As has been removed via the biogenic precipitation of rare mineral species, such as amorphous ferric arsenic hydroxysulfates and nanocrystalline tooeleite, a ferric arsenite (FIG. 1). This intense microbial activity results in an efficient detoxification of the AMD waters although the As-rich mineral phases formed in the upstream zone are fairly soluble. Further downstream, the progressive decrease of the dissolved arsenic concentration allows the precipitation of schwertmannite, which traps most of the remaining dissolved arsenic. The dissolved arsenic concentration thus decreases to about 1 mg L^{-1} before the confluence with the non-polluted river, 1.5 km downstream from the waste pile (Casiot et al. 2005). An important finding of the studies carried out on the Carnoulès AMD concerns the influence of bacterial activity on the nature of the minerals forming. In the field, seasonal variation of arsenic speciation has been observed over four years of study in the acidic upstream zone. In winter, only microbial oxidation of Fe^{2+} is efficient, leading to the formation of amorphous Fe^{3+}–As^{3+} precipitates together with nanocrystalline tooeleite [$Fe_6(AsO_3)_4SO_4(OH)_4 \cdot 4H_2O$] (FIG. 1).

In spring and summer, biotic oxidation of both As^{3+} and Fe^{2+} leads to the precipitation of mixed Fe^{3+}–As^{5+} hydrous oxides, similar to biominerals occurring at geothermal springs (Inskeep et al 2004). These distinct mineral phases have been replicated in the laboratory using single bacterial strains isolated from the site. Oxidation of Fe^{2+} by

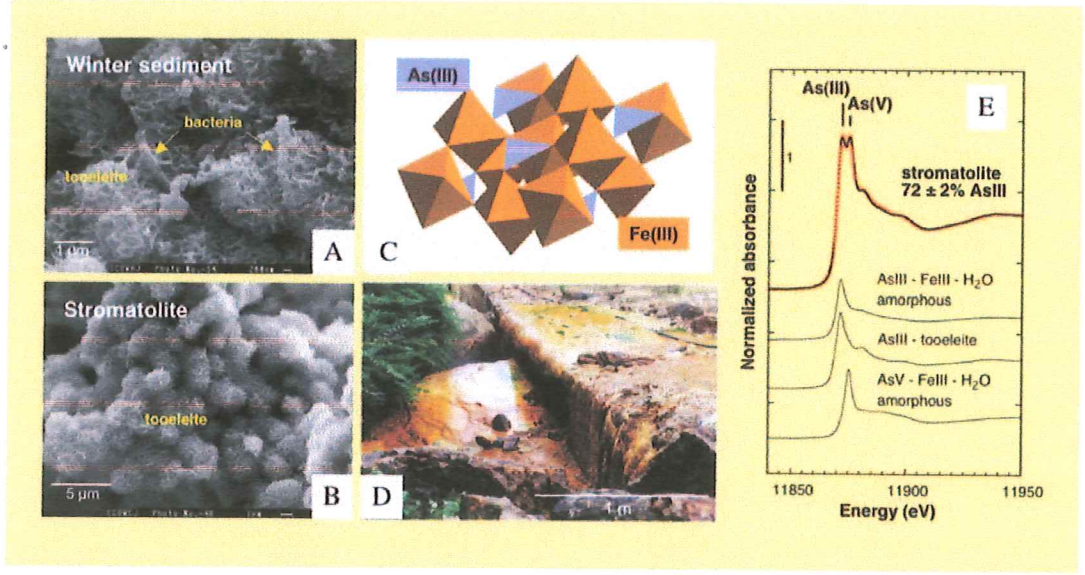

FIGURE 1 Massive bacterial oxidation of iron and arsenic leads to the formation of spectacular outcrops of arsenic-bearing (up to 20 wt% As) sediments and meter-wide stromatolites (bottom center) at the Carnoulès (France) acid mine drainage (**D**). The proportion of seasonally alternating As^{3+} and As^{5+} species associated with ferric oxides can be quantified by XANES spectroscopy (**E**). SEM micrograph of winter sediments (**A**) shows the close association between bacteria and a Fe^{3+}-arsenite mineral, tooeleite. This rare mineral, with a distinctive layer structure (**C**), is the main component of the stromatolite (**B**). Laboratory experiments showed that *Acidithiobacillus ferrooxydans* isolated from the site can form tooeleite by oxidizing Fe^{2+} but not As^{3+}. Modified from Morin et al. (2003)

Acidithiobacillus ferroxydans strains, which are unable to oxidize As^{3+}, leads to the formation of mixed Fe^{3+}–As^{3+} amorphous hydroxysulfates and nanocrystalline tooeleite (Morin et al. 2003), or As^{3+}-schwertmannite (Duquesne et al. 2003). *Thiomonas* strains, which oxidize both As^{3+} and Fe^{2+}, rapidly form Fe^{3+}–As^{5+} amorphous hydroxysulfates with As:Fe mole ratios up to 0.7 (Leblanc et al. 1996; Morin et al. 2003). This value approaches the upper limits observed for synthetic coprecipitates of As^{5+}–hydrous ferric oxides (Carlson et al. 2002). EXAFS analysis of these mineral phases confirms the similarity between the natural and *in vitro* mineral phases. In addition, spectroscopic evidence of the formation of stable arsenic complexes on the schwertmannite surface (Waychunas et al. 1995) explains the inhibiting role of As in the crystallization of schwertmannite, leading to the formation of amorphous As-rich ferric hydroxysulfates (Carlson et al. 2002).

Eventually, farther downstream in the AMD, the mixing of acid waters from former mining sites, with typical pH values of 2–3, with non-polluted neutral waters strongly modifies arsenic speciation (Gault et al 2003; Casiot et al. 2005). Neutralization at the confluence leads to a solubilization of arsenate and arsenite complexes and to the oxidation of any residual Fe^{2+}. Most of the remaining As is sorbed at the surface of the precipitated hydrous Fe- and Al- oxides, which settle out during the first hundreds of meters downstream. Traces of arsenic will be transported farther in colloidal form (Kimball et al. 1995; Casiot et al. 2005).

ARSENIC SPECIATION IN SOILS

Arsenic can accumulate in soils (Voigt et al. 1996), contaminate both surface waters and groundwaters, and be taken up by plants and animals, thus affecting the whole food chain. The arsenic may be derived from the parent rocks or introduced anthropogenically by industrial activities, such as the mining and processing of arsenic or the manufacture of arsenic chemicals, or by agriculture through various pesticides. The global average concentration of arsenic in uncontaminated soil is 5 to 6 mg kg^{-1}, with variations of more than an order of magnitude, depending on the kind of soil considered (Chen et al. 2002). Although the regulations governing As contamination in waters are well defined, the regulatory goals for remediation of contaminated soils vary greatly among countries and even locally, and are around 1 to 25 mg kg^{-1} for residential soils. Important issues centre on the bioavailability of the arsenic, which is related to its speciation, as well as the change of As mobility (and bioavailability) with time.

Iron oxides play a pivotal role in the biogeochemical behavior of As. They provide a ubiquitous As-trapping process in environments such as sediments (Belzile and Tessier 1990) and soils (Morin et al. 2002; Cancès et al. 2005). Hydrous ferric oxides (HFO), e.g. ferrihydrite, are the most reactive soil components as regards As sorption and can take up hundreds of mg kg^{-1} As, either as As^{3+} or As^{5+} (Goldberg 2002 and references therein). Acidic conditions favor the protonation of mineral surfaces and the adsorption of arsenate polyanions, $H_2AsO_4^-$ or $HAsO_4^-$, while As^{3+} remains soluble in such conditions, as arsenious acid, H_3AsO_3. Under alkaline conditions, As^{3+} adsorbs preferentially to As^{5+} on iron oxide surfaces. Near neutral pH, i.e. closer to the *pKa* of H_3AsO_3 (9.2), arsenate and arsenite both adsorb with the same efficiency at the surfaces of HFO and crystalline iron oxides via the formation of strong inner-sphere surface complexes. Similar bidentate binuclear sorption mechanisms have been found for As^{3+} (Manning et al. 1998; Farquhar et al. 2002; Ona-Nguema et al. 2005) and As^{5+} (Waychunas et al. 1996; Sherman and Randall 2003), although there is evidence for an additional bidentate mononuclear complex for As^{3+}, especially in the case of hematite and ferrihydrite (Ona-Nguema et al. 2005).

Anoxic conditions, e.g. in the saturated zone of hydromorphic soils or in groundwater, may favor the reduction of Fe^{3+} and As^{5+}, often assisted by bacterial activity involving dissimilatory iron-reducing bacteria (DIRB) and dissimilatory arsenic-reducing bacteria (DARB) (see Lloyd and Oremland this issue). In natural environments, iron reduction is generally accompanied by the reduction of As, which can lead to the release of soluble As^{3+}. However, the respective roles of the reduction of iron and arsenic in the mobilization of arsenic are still not clear (van Geen et al. 2004), and in this context, some specific characteristics of As^{3+}

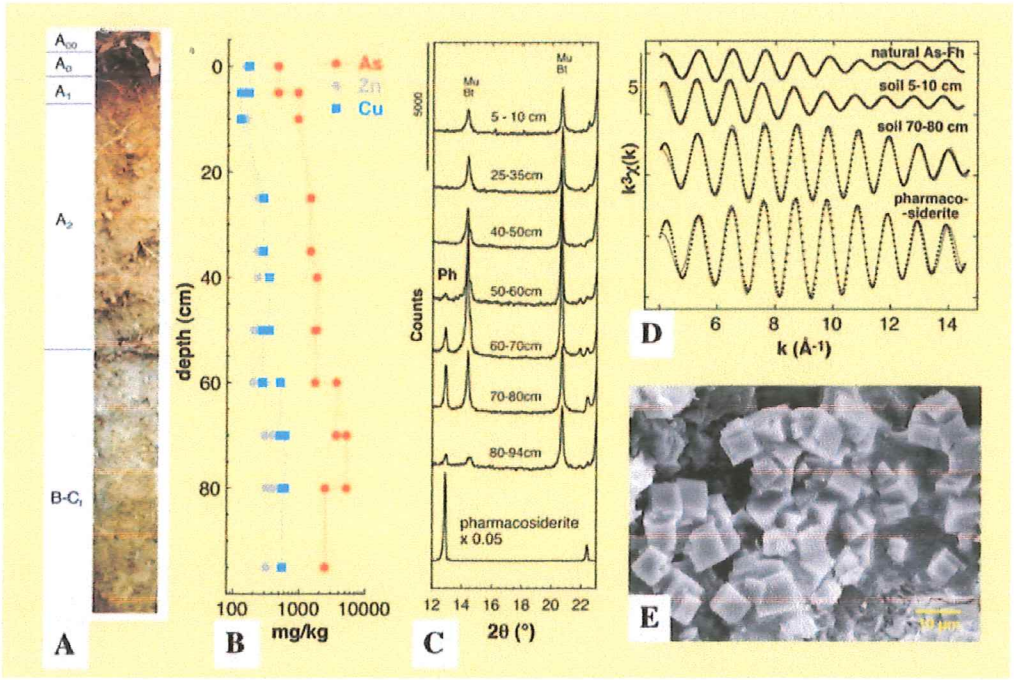

FIGURE 2 Changes in As speciation in a soil profile (**A**) developed on mineralized schists in the Echassières region, France. (**B**) As, Cu, and Zn concentrations indicate some enrichment relative to the bedrock in the upper part of the saprolite (B and C_1 horizons) and a progressive depletion towards surficial A_2–A_{00} horizons. (**C**) XRD patterns show the progressive disappearance of primary pharmacosiderite (Ph) towards the upper part of the saprolite; the main Bragg reflections of muscovite (Mu) and biotite (Bt) are also indicated. (**D**) Fourier filtered contributions of the second neighbor contributions to the EXAFS spectra at As *K*-edge indicating changes in As speciation between the saprolite and the upper horizons; the spectra are similar to those of pharmacosiderite and As adsorbed on HFO, respectively. (**E**) SEM photograph displaying the typical euhedral cubic crystals of pharmacosiderite formed after hydrothermal weathering of primary iron–arsenic sulfide minerals. Modified from Morin et al. (2002)

speciation need to be taken into account, especially its low sorption efficiency on clay and Al-hydroxide surfaces as compared to As^{5+} (Goldberg 2002).

We discuss here two contrasting examples of arsenic-rich soils, one a former industrial site and the other a natural "geochemical anomaly." Both emphasize the role of iron oxides in the immobilization of arsenic in soils. The first example is a former pesticide plant at Auzon (Haute-Loire, France). Here, industrial activities started at the beginning of the 20th century and lasted until 1949. The first activity at this site was the roasting of arsenic sulfides [arsenopyrite and realgar (AsS)] from the neighboring mines in order to produce arsenolite (As_2O_3). Subsequently, other As-containing chemical products were manufactured at the site, including arsenical pesticides. The high arsenic concentrations encountered at this site (up to 1.2 wt% in topsoils and 35 mg L^{-1} in groundwaters) have motivated research to understand the processes of contamination of the soils and underlying sediments (Cancès et al. 2005). The upper horizons contain arsenic minerals inherited from the contaminated site, such as arseniosiderite, formed by oxidation of sulfide ores, and schultenite ($PbHAsO_4$), manufactured for pesticides. However, detailed analysis of arsenic speciation throughout several soil profiles revealed that most of the arsenic was present as arsenate scavenged by Fe-oxyhydroxides. However, detailed analysis of arsenic speciation throughout several soil profiles revealed that most of the arsenic was present as arsenate scavenged by Fe-oxyhydroxides. This trapping process appeared to take place after the breakdown of source minerals such as schultenite.

Geochemical anomalies provide examples of regional, long-term environmental contamination. At Echassières (Allier, France) in the Massif Central (FIG. 2; Morin et al. 2002), soils have developed on schists enriched in As over tens of km^2. This has led to As concentrations of up to 5000 mg kg^{-1} in the lowermost weathered horizon (saprolite) and up to 900 mg kg^{-1} at the soil surface. The primary As-bearing minerals in the underlying rocks are arsenopyrite, löllingite ($FeAs_2$), and a pharmacosiderite solid solution close to the barium-pharmacosiderite end-member, $[BaFe_4(AsO_4)_3(OH)_5 \cdot 5H_2O]$. This pharmacosiderite formed during a late hydrothermal event at the expense of sulfides and arsenides and represents 70% of the total As in the saprolite. However, it accounts for only 20–30% of total As in the upper horizons, which display a progressive decrease in As concentration upwards through the soil profile. The rest of the arsenic in the soils occurs as arsenate adsorbed as inner-sphere complexes at the surfaces of poorly crystalline Fe-oxides. In this case, adsorption provides long-term trapping of the arsenic, given slightly acidic and oxidizing conditions, and delays potential release of As into the biosphere.

Finally, the release of arsenic through agricultural activities remains a great concern. Various approaches have been tried to reduce the leachability of arsenic from pesticides in order to protect surface water and groundwater from contamination and reduce the bioavailability of arsenic to human receptors. Adding Fe- and Mn-containing materials to cause adsorption and coprecipitation of the arsenic has been one remediation strategy. On the other hand, addition of phosphate-based components increases the leachability of arsenic, whereas mixed phosphate–iron additions reduce both the leachability and the bioaccessibility of arsenic relative to the unamended soils (Martin and Ruby 2003). Much remains to be done in order to develop a clear picture of the complex interplay among the impacts of As on the biosphere, on soil biogeochemistry, and on remediation technologies.

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