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Review

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Antimony in the soil–plant system – a review

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Environmental context. Soil contamination by antimony (Sb) has become an environmental problem of much concern in recent years, because increasing mining and industrial use has led to widespread soil contamination by this biologically unessential, but potentially carcinogenic element. We reviewed the available literature and found that Sb is generally taken up by terrestrial plants in proportion to the concentration of soluble Sb in soil over a concentration range covering five or more orders of magnitude, a finding that is relevant in particular for the assessment of environmental and health risks arising from Sb-contaminated soils. But very little is known about the mechanisms of Sb uptake by plants.

Abstract. Soil contamination by antimony (Sb) due to human activities has considerably increased in the recent past. We reviewed the available literature on Sb uptake by plants and toxicity risks arising from soil contamination by Sb and found that Sb is generally taken up by terrestrial plants in proportion to the concentration of soluble Sb in soil over a concentration range covering five or more orders of magnitude. However, very little is known about the mechanisms of Sb uptake by plants. Also the deposition of resuspended soil particles on the surfaces of aerial plant surfaces can result in high plant Sb concentration in the vicinity of Sb-contaminated sites. Although soil pollution by Sb may be rarely so severe as to cause toxicity problems to humans or animals consuming plants or food derived from plants grown on Sb-contaminated sites, such risks may arise under worst-case conditions.

Introduction

Natural concentrations of antimony (Sb) in the environment are low. Its abundance in the earth's crust is in the order of 0.2–0.3 mg kg^{-1}.[1] In topsoils, Sb tends to be slightly enriched. Background concentrations of antimony in soils range between 0.3 and 8.6 mg kg^{-1} (Table 1).[2,3] In general, they are below 1 mg kg^{-1}.[4] Higher concentrations are usually related to anthropogenic sources. Antimony has many uses, and these are still increasing.[5,6] In its metallic form, its major use is as a hardener for lead, e.g. in lead–acid batteries, cable sheathings and ammunition, and it is also an important component in semiconductors. Antimony trioxide (Sb_2O_3) is widely used as a flame-retardant, e.g. in textiles, papers, plastics and adhesives. Therefore, textiles and plastics are major sources of Sb in municipal waste.[7] Furthermore, antimony trioxide is used as a paint pigment, ceramic opacifier, catalyst, mordant and glass decolouriser. Antimony tetroxide (Sb_4O_8) is used as an oxidation catalyst, particularly for the oxidative dehydrogenation of olefins. The wide use of Sb has led to considerable inputs of this element into the environment (Fig. 1). Important anthropogenic sources of antimony in the environment are emissions from vehicles (where it is used as a fire-retardant in brake linings), waste disposal and incineration, fuel combustion, metal smelters, and shooting activities.[8,9]

Particularly high Sb concentrations in soils have resulted from mining and shooting activities. For example, Sb concentrations up to 15 g kg^{-1} were found in an area in southern Tuscany where Sb ores have been mined and smelted until recently.[10] Reuse of material from mining dumps has also been identified as a cause of severe Sb contamination of agricultural land and residential areas.[11,12] Recently, shooting ranges were also found to not only be hotspots of soil pollution by lead (Pb), but also by Sb.[3] Antimony is used in bullets to harden them. Next to Pb, Sb generally is their second-most important component, with a content ranging between 1 and 7% by mass.[13] Johnson et al. found up to 13.8 g kg^{-1} Sb in the topsoils of Swiss shooting ranges.[3] Although such pollution is usually restricted to very small areas, it constitutes a major environmental problem because of the abundance of shooting ranges. Switzerland alone has more than 2000 shooting ranges that are still in use.

Antimony has no known essential biological function. Similar to other trace elements, it can be toxic at elevated concentrations, and some Sb compounds are even considered potentially carcinogenic.[14] A potentially important Sb exposure pathway of humans and animals to antimony in areas with contaminated soils is through food and feed plants.[11,15] However, owing to the fact that Sb mostly occurs as a co-contaminant of more toxic elements such as Pb or As, research into its biogeochemistry and ecotoxicity has been neglected in the past. Thus, little is still known also about the factors determining the phytoavailability of Sb in soils and its uptake by crop plants. The objective of the present study was to review the available literature on the transfer of Sb from soil into plants and on the toxicity risks associated with soil pollution by this element.

Toxicity of antimony to plants and soil organisms

In general, inorganic Sb compounds were found to be more toxic than organic ones, and Sb^{III} more than Sb^{V} species.[5]

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Table 1. Published values of Sb concentrations in the environment

Medium	Source of pollution	Concentration (mg kg^{-1}, unless given otherwise)	Reference
Igneous rocks	–	0.1–1	[57]
Sedimentary rocks	–	0.05–1.5	[55]
Soil background	–	0.3–2.3	[2]
Seawater	–	0.0002	[5]
Water near mine	Mercury mine	418	[58]
Soils near mine	Mercury mine	0.5–52	[58]
Emissions waste deposit	Waste deposit	10 μg m^{-3}	[59]
Roadside highway (100 m distance)	Traffic pollution	0.53	[8]
Needles of trees	Residential area	2.4	[27]
Orchard soil	Pesticide	0.4–1.5	[60]
Grass	Antimony smelter	400	[48]
Garden soil near disused mine	Past mining activities	500	[11]
Detritivore invertebrates	Smelter	290	[15]
Ectomycorrhizal fungi	Lead smelter	100–1400	[43]
Aquatic plants	Mine tailing pond	19	[51]
Garden and crop plants	Spiked pots	399	[11]
Shooting range	Bullets	13 800	[3]

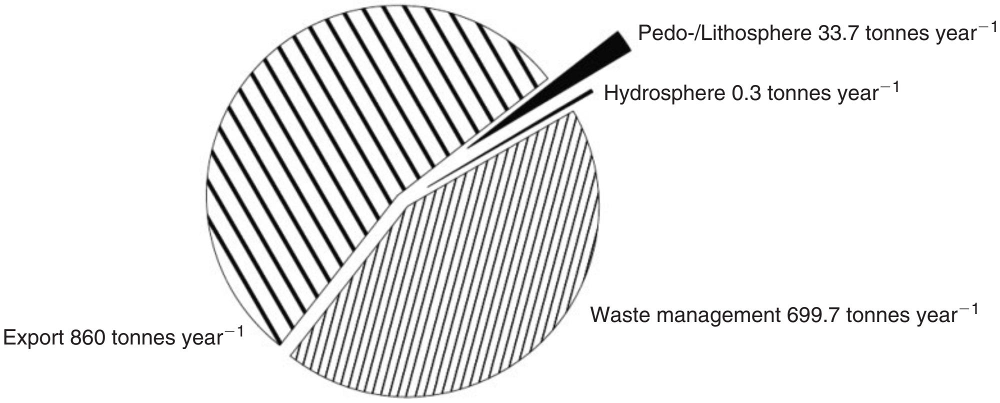

Fig. 1. Fate of Sb consumed in Switzerland. Adapted from Mathys et al.[6]

In its trivalent form, Sb may have a level of genotoxicity similar to trivalent As.[16] Flynn et al. found that the bioluminescence of As and Sb-specific biosensors (*Escherichia coli* strain CM1166 pC200) was suppressed at Sb^{III} concentrations in solution exceeding 1 mg L^{-1}.[12] Although sodium stibogluconate has been used for more than 75 years to treat leishmaniasis, a disease caused by the protozoan parasite *Leishmania* sp. and affecting 12 million people in 88 countries (in 2007),[17] little is known about the toxicity of elemental and methylated Sb.

Only a few toxicity tests have been performed with plants or other organisms exposed to Sb-contaminated soil. Table 2 summarises half maximal effective concentration (EC$_{50}$) values for various soil organisms and terrestrial plants. According to the data given in Table 2, plants were generally found to be more tolerant to soil Sb than soil fauna.

Hammel et al. found that aqueous extracts of a Luvisol and a Chernozem that had been spiked with 1000 mg kg^{-1} dry weight (DW) Sb_2S_3 and Sb_2S_5 and aged for 6 months were more toxic to the soil alga *Chlorococcum infusionum* than similar extracts from a Cambisol.[18] Oorts et al. found a 50% reduction of root elongation in barley and a 50% reduction of shoot growth in lettuce at ~40 mg L^{-1} Sb in centrifuged soil solution after spiking the soil used in their study with ~7 g kg^{-1} Sb in the form of Sb_2O_3.[19] At the time of sampling, ~70% of the Sb in solution was present as Sb^{V}. He and Yang found no significant difference in the toxicity of Sb^{III} and Sb^{V} on root and shoot growth of rice grown in pots.[20]

Davis et al. showed that phytotoxicity of Sb does not necessarily require Sb accumulation in the shoots. Growth of barley (*Hordeum vulgare*) was depressed in sand cultures at concentrations of 50–100 mg L^{-1} Sb in solution, although Sb was below the detection limit in the shoots (<2 mg kg^{-1}).[21]

Uptake of antimony by plants

Relationship between plant and soil Sb concentrations

Antimony uptake by plants has been found to vary widely among plant species and study sites (see Table A1 in the Accessory publication). Particularly high plant Sb concentrations occur in Sb mining areas. Baroni et al. found up to 1367 mg kg^{-1} Sb in the basal leaves of *Achillea ageratum* growing in southern Tuscany at a tailing pond in an abandoned Sb mining area where the soil contained ~9000 mg kg^{-1} Sb with an extractable concentration of 793 mg kg^{-1}. Foliar Sb concentrations exceeded 100 mg kg^{-1} also in other plant species on this site.[10]

Table 2. Published half maximal effective concentration (EC_{50}) values for Sb toxicity to plants and soil organisms

Organism		Soil type	Test variable	Sb compound	EC_{50} (mg kg^{-1}) (total Sb concentration in soil)	EC_{50} (mg L^{-1}) (soil solution concentration)	References
Common name	Latin name						
Earthworm	*Eisenia fetida*	Typic Haplodult	Reproduction	$Sb_2(SO_4)_3$	70		[61]
Potworm	*Enchytraeus crypticus*				316		
Collembola	*Folsomia candida*				169		
Soil algae	*Chlorococcum infusionum*	Cambisol	Chlorophyll density	$K(SbO)C_4H_4O_6$	>1000		
		Luvisol			>1000		[18]
		Chernozem			>1000		
		Cambisol		Sb_2S_3	>1000		
		Luvisol			257		
		Chernozem			125		
		Cambisol		Sb_2S_5	>1000		
		Luvisol			172		
		Chernozem			314		
Barley	*Hordeum vulgare* cv. Mauritia	Haplic Luvisol	Root elongation	Sb_2O_3	6819	39	[19]
Lettuce	*Lactuca sativa* cv. Pontiac		Shoot yield		7549	41.4	
Clover	*Trifolium pratense* cv. Milvus	Agar	Root elongation	$KSb(OH)_6$	1247		[28]
		Potting soil	Shoot yield	$KSb(OH)_6$	1111	10	
Maize	*Zea mays* cv. Magister	Agar	Root elongation	$KSb(OH)_6$	829		
		Potting soil	Shoot yield	$KSb(OH)_6$	1178	10.6	
Indian mustard	*Brassica juncea*	Agar	Root elongation	$KSb(OH)_6$	>2463		
Sunflower	*Helianthus annuus* cv. Iregi	Agar	Root elongation	$KSb(OH)_6$	829		
		Potting soil	Shoot yield	$KSb(OH)_6$	1122	10.1	
Wheat	*Triticum aestivum* cv. Galaxie	Agar	Root elongation	$KSb(OH)_6$	631		

In contrast to these high concentrations, there are also reports of low Sb uptake from plants growing on heavily contaminated soils. Pratas et al. reported maximum Sb concentrations of less than 5 mg kg^{-1} Sb in tree stems and herbaceous plants growing on mine spoils of abandoned mines in Portugal with an average soil Sb concentration of 663 mg kg^{-1}.[22] In comparison with the study of Baroni et al., Sb uptake was not only much less in absolute terms, but also relative to the soil Sb concentration in the Portuguese study. Relatively low soil-to-plant transfer or bioaccumulation coefficients were also reported by Dominguez et al.[23] from the Guadiamar valley of southern Spain, where soils had been covered by mine tailing sludges after a dam break at Aznalcóllar. Antimony concentrations of woody plant leaves ranged between 0.03 and 0.07 mg kg^{-1} on soil that contained between 4.5 and 37.7 mg kg^{-1} Sb, which corresponds to bioaccumulation coefficients of less than 0.03. Similar bioaccumuation rates were also obtained by Leduc and Gardou, who analysed plants growing on Sb-rich ore deposits near Brouzils in the Vendée department, France.[24] The Sb concentration of the sampled soil averaged 38 mg kg^{-1}. On soil with the maximum Sb concentration of 105 mg kg^{-1}, oak branches accumulated 0.23 mg kg^{-1} Sb in their tips and hawthorn branches 0.19 mg kg^{-1} Sb.

Rather low plant Sb concentrations were also reported in studies of roadside soils and residential areas where soil Sb concentrations were elevated to some, but not a high degree, presumably owing to atmospheric deposition. Lehndorff and Schwark measured Sb concentrations of ~0.5 mg kg^{-1} dry weight in the needles of pines (*Pinus nigra*) growing in a heavy traffic area in Cologne, Germany.[25] Krachler et al. found concentrations up to 0.15 mg kg^{-1} Sb dry weight in leaves of elder bushes in a residential area.[26] Also in a residential area, Pohl et al. measured up to 2.4 mg kg^{-1} Sb in the dry mass of thuja needles.[27]

These results indicate that plant Sb accumulation increases with the Sb concentration of soil over a very wide range of concentrations. In fact, combining available published data from field studies in which Sb concentrations have been analysed in plants as well as in the soils on which the sampled plants were growing produced a relationship with a significant correlation between plant and total soil Sb (Fig. 2). Despite considerable scatter, this relationship is described well by a linear log-log regression model. The fact that the slope of the regression line approximately equals 1 means that the two variables are on average almost proportional to each other. A large part of the scatter is due to the variation in Sb solubility among the soils included in the studies. Performing the same analysis with soluble instead of total soil Sb concentrations, a similar but much closer relationship was obtained, although a variety of different analytical methods were used and very different plants examined in the studies on which this analysis is based (Fig. 3). Again the slope of the log-log line was almost exactly equal to 1, indicating proportionality. The average proportionality factor (i.e. ratio between plant and soil concentration or bioaccumulation coefficient) was 0.02 (kg soil per kg plant dry matter) for total soil Sb and 2.57 for soluble soil Sb. Similar linear relationships were also found within individual studies,[11,20,24,28] indicating that proportionality between plant and soluble soil Sb indeed represents a common pattern. That fact that this proportionality is found to extend over at least five orders of magnitude of Sb concentrations suggests a very general and rather simple mechanism. A mechanism easily explaining it would be passive transport by convection with the stream of transpirational water into and through the plants. However, this hypothesis has to be reconciled with the existence of selective barriers in plant roots controlling the root-to-shoot transfer of water and solutes.

Mechanisms of Sb uptake and root-to-shoot transfer

Little is known about the mechanisms of Sb uptake by plants. In microorganisms, $Sb(OH)_3$ was found to be taken up through aquaglyceroporins like $As(OH)_3$, which can be attributed to the small size of these two neutral molecules and their similarity in conformation and charge distribution with glycerol.[29,30] Also, active membrane transport of arsenite and antimonite is known in microorganisms. This transport is mediated by ArsB proteins, which are ATP-dependent efflux transporters for arsenite. Cai et al. found that the same genes coding for the ArsB protein in *Pseudomonas aeruginosa* also contributed to Sb resistance when they were cloned and inserted into *E. coli*.[31]

No such analogy has been found between Sb and its sister element As with respect to their uptake in oxidation state V. Whereas arsenate is transferred through cell membranes by the same transporters as phosphate, resulting in mutual inhibition of uptake due to competition between these two anions for transporter binding sites,[32] plant uptake of antimonate was not found to be affected by phosphate, suggesting that it does not occur by the same pathway.[33] This difference may be due to structural factors. The structure of antimonate is octahedral, whereas that of phosphate and arsenate is tetrahedral, and together with the larger size and lower charge density set antimonate clearly apart from other oxyanions (Table 3).[33]

Also, antimonite and arsenite do not always show similar effects. The deletion of genes responsible for the production of phytochelatins in *Schizosaccharomyces pombe* reduced the tolerance to arsenite and arsenate, but not to antimonite.[34]

The presented evidence suggests that the mechanisms of cellular uptake and transport in plants are also probably not the same for antimonate and antimonite. Antimonite may cross cell membranes passively with water through aquaporins. Such transport would be consistent with the observed proportionality between plant and soluble soil Sb concentrations. Aquaporins, however, are not open for anions like antimonate, and cellular uptake of antimonate would require mediation by transporters. A linear rate law extending over a concentration range of several orders of magnitudes may be produced by a cascade of transporters with different kinetics, but is highly unlikely in the case of Sb, given that this element is not essential for organisms. However, as antimonate usually is the dominating Sb species in soil solution, a mechanism with a linear rate-dependence on concentration is also needed for this species in order to explain the observed linearity in the Sb uptake characteristics of plants. To understand how this may work, we have to consider the pathways along which solutes are transported from the soil solution into plant roots and shoots.

There are two parallel transport pathways for water and solutes through plant tissues: the apoplastic pathway through intercellular spaces including pores in the cell walls and the symplastic pathway from cell to cell (selective transport across membranes). The symplastic pathway is only accessible by crossing a cell membrane. The apoplast of the root cortex is directly accessible to solutes from the external solution, whereas the apoplast of the root stele is separated from the cortex by the Casparian bands, thickenings impregnated with hydrophobic materials, in particular suberin, in the radial and transverse walls of the endodermis.[35] The function of the Casparian bands is to force water and solutes to enter the symplastic pathway and pass

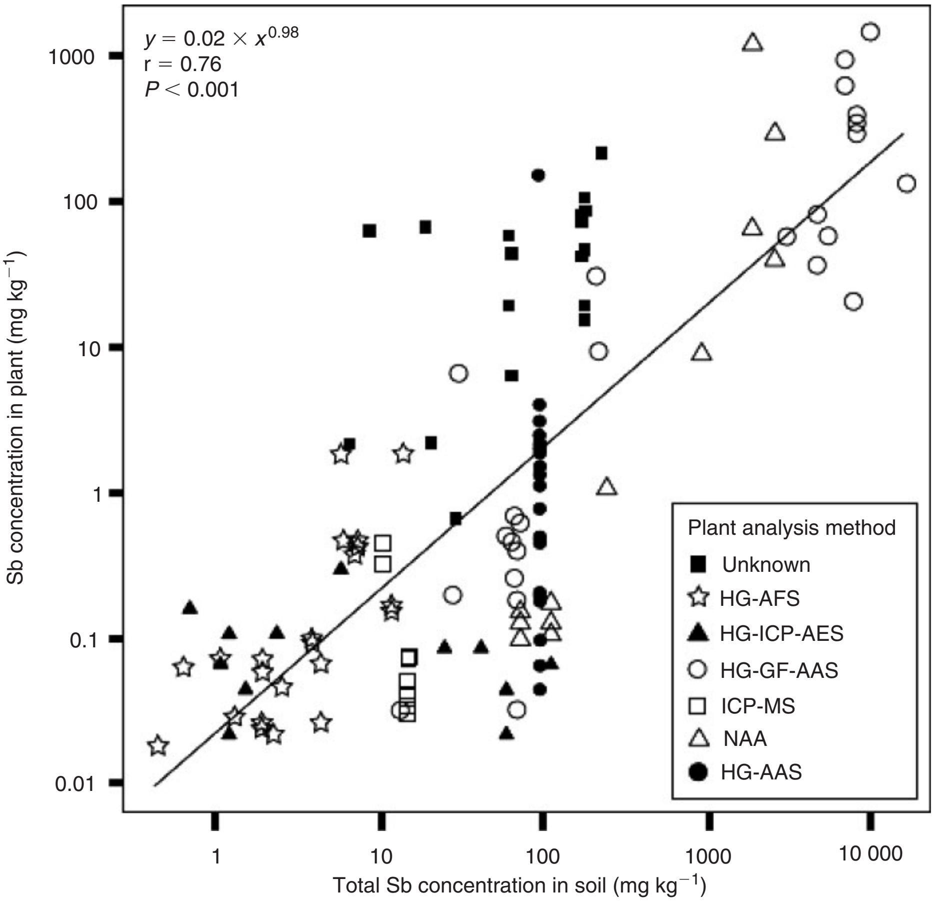

Fig. 2. Relationship between total Sb concentrations of field-contaminated soils and Sb in plants grown on these soils, based on published data.[10,11,22–24,39,41,53,56,70–74] The points represent averages of replicate samples or pot trials. Regression was performed on the log-transformed data. The slope of the log-log regression line is not significantly different from 1. Methods used for Sb analysis: HG-AFS, hydride generation atomic fluorescence spectrometry; HG-ICP-AES, hydride generation inductively coupled plasma atomic emission spectrometry; HG-GF-AAS, hydride generation graphite furnace atomic absorption spectrometry; ICP-MS, inductively coupled plasma mass spectrometry; NAA, neutron activation analysis; and HG-AAS, hydride generation atomic absorption spectrometry.

Table 3. Structure and other molecular properties of antimonate in comparison with other common oxyanions in soils

Volumes and charge densities are calculated on the basis of bond lengths and van der Waals radii

Molecular formula	Radius (Å)	Structure	Predominant species at pH 7	Volume (Å^3)	Charge density (e Å^{-3})	Reference for bond length
$Sb(OH)_6^-$	3.68	Octahedral	$Sb(OH)_6^-$	209.2	−0.0048	[62]
$B(OH)_4^-$	3.13	Tetrahedral	$B(OH)_4^-$	129.0	−0.0078	[63]
PO_4^{3-}	3.12	Tetrahedral	$H_2PO_4^-$	127.5	−0.0078	[64]
AsO_4^{3-}	3.36	Tetrahedral	$HAsO_4^{2-}$	158.3	−0.0126	[65]
MoO_4^{2-}	3.29	Tetrahedral	MoO_4^{2-}	149.3	−0.0134	[66]
SeO_4^{2-}	3.16	Tetrahedral	SeO_4^{2-}	132.0	−0.0151	[67]
CrO_4^{2-}	3.14	Tetrahedral	CrO_4^{2-}	129.7	−0.0154	[68]
SO_4^{2-}	2.99	Tetrahedral	SO_4^{2-}	112.0	−0.0179	[69]

through the endodermis cells in order to reach the inner cylinder of the root, which allows the plant to exert control on the uptake of solutes. The Casparian bands, however, are not a perfect barrier for apoplastic transport. Apart from 'leaks' at branching points where lateral roots emerge, they are not fully developed at the root tips,[36] and the endodermis may also be damaged by chemical or biological agents, such as herbicides, toxic metals or root pathogens.[37] Using this bypass, even big molecules such as ethylenediamine-*N*,*N*′-disuccinic acid (EDDS) can be taken up along the apoplastic pathway and translocated from the roots into the shoots without any membrane passage.[38] Transport along this pathway would plausibly explain why Sb accumulation by plants was found to be proportional to the concentration of Sb in the soil solution.

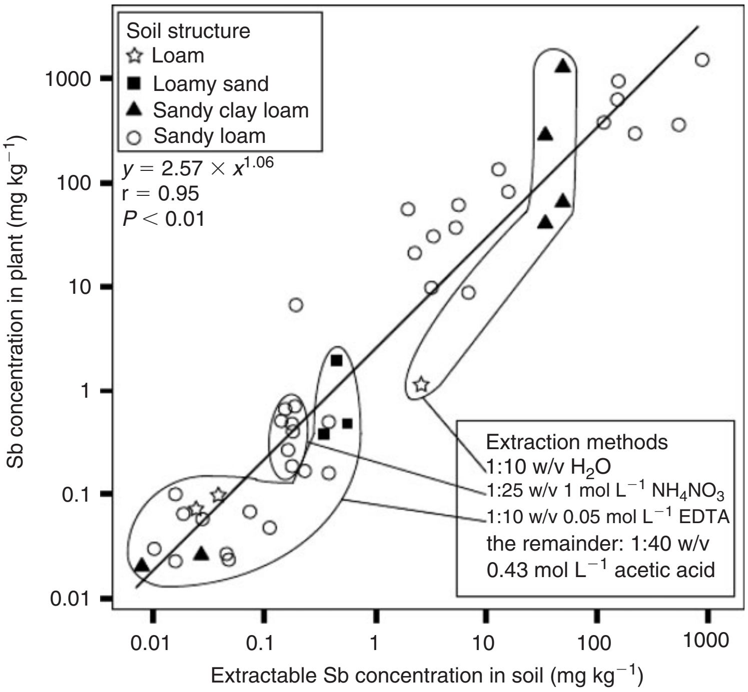

Fig. 3. Relationship between soluble Sb concentrations of field-contaminated soils and Sb in plants grown on these soils, based on published data.[10,11,22,23,41,56,71,73,74] The points represent averages of replicate samples or pot trials. Regression was performed on the log-transformed data. The slope of the log-log regression line is not significantly different from 1.

Passive apoplastic transport also explains the pattern of Sb allocation within plants. Jung et al., who investigated Sb accumulation and allocation in crop plants on soil polluted with Sb, As and Bi around a mining area in Korea, found the highest Sb concentrations in plant leaves and the lowest in grains and fruits.[39] Baroni et al. found that Sb was not deposited in the roots, but in the epigeal parts of *Achillea ageratum* and *Silene vulgaris* that died at the end of the growing season.[10]

Although most of the available evidence suggests that Sb is translocated within plants primarily along the apoplastic pathway through the xylem, this does not exclude that some symplastic transport may also occur. Studying the environmental distribution of the radioisotope ^{125}Sb emitted from a nuclear fuel processing plant, Ghuman et al. found that Sb deposited onto the leaves of *Agropyron dasystachyum*, *Artemisia tridentata* and *Chrysothamnus viscidiflorus* was transferred into the roots of these plants, indicating Sb transport through the phloem.[40]

Influence of other factors than soil Sb concentration on plant Sb uptake

If Sb uptake by plant roots were primarily a passive process of convection with root water uptake, a close relationship with the rate of transpiration would be expected. No studies on such a relationship have been published so far, however. Also, it has not been investigated to what extent water consumption may explain differences in Sb uptake or accumulation observed among different plants. Such differences can be large as shown by studies of plants growing under the same conditions. Rached-Mosbah et al.[41] found that some plant species in the area of the Djebel Hamimat, Algeria, seemed to exclude Sb, while others apparently accumulated it. An example for exclusion was *Lygeum spartum* L. Plants of this species growing on soil with 168 mg kg^{-1} Sb only had 17.5 mg kg^{-1} Sb in the leaves. Conversely, *Carduncellus pinnatus* (Desf.) DC accumulated up to 61 mg kg^{-1} Sb on a soil with only 17.5 mg kg^{-1} Sb.[41]

Temperature is another factor that has been found to influence Sb accumulation in plants. Baghour et al. investigated the effect of root-zone temperature on the accumulation of As, Ag, Cr and Sb in different organs of potato plants under field conditions by applying mulches. The soil was an alkaline 21 μg kg^{-1} extractable Sb, associated with As, Ag, and Cr. The temperature range tested was 16 to 30°C. The highest accumulation of Sb was 0.85 mg kg^{-1} in roots, 0.14 mg kg^{-1} in tubers and 1.64 mg kg^{-1} in stems at 30°C, and 2.70 mg kg^{-1} in leaves at 20°C.[42] Although the growth was maximal, the Sb concentration of tubers and leaves was minimal at 23°C, indicating that Sb was more 'diluted' in the larger biomass produced at this temperature. Also, at higher temperatures, increased diffusion and desorption rates of soil Sb may have contributed to enhanced Sb uptake.

The study performed by Hammel et al.[11] indicates that rates of short-range transport and phase transfer processes may be an important factor in limiting the transfer of Sb from soil into plants. These authors conducted a pot experiment with spinach using contaminated garden and agricultural soils, soils from a mining area and artificially Sb-contaminated arable soils (aged for 6 months after spiking) and compared the uptake of Sb from the potted soils with the Sb concentrations of plant samples collected at the field sites. Approximately linear relationships between soil and plant Sb concentrations were found in the pot experiment, with soil-to-plant transfer factors ranging between 4.5 and 12.9 for NH_4NO_3-extractable soil Sb and 0.17 and 0.54 for total soil Sb (depending primarily on the soil type), whereas the uptake under field conditions was two to three orders of magnitude lower (ranging from <0.02 to

2.2 mg Sb per kg dry weight) and did not show a significant dependence on the NH_4NO_3-extractable soil Sb concentration (ranging from <0.02 to 0.29 mg Sb per kg soil) owing to the relatively large scatter in the measurements in this concentration range.[11] These results suggest that the availability of Sb for plant uptake was highly increased by the structural disruption and physical homogenisation of the soils for the pot experiment.

In the context of bioaccessibility and bioavailability of Sb to uptake by plant roots, mycorrhyzal fungi may also play an important role. Borovicka et al.[43] analysed more than a hundred species of macrofungi, ectomycorrhizal fungi and terrestrial saprobes in the vicinity of a lead smelter. Several of the tested ectomycorrhizal species were found to have accumulated more than 100 mg kg^{-1} Sb, and specimens of *Chalciperus piperatus* were found with up to 1400 mg kg^{-1} Sb. However, whether Sb is transferred from mycorrhizal fungi to host plants is not known.

Antimony uptake by plants via surface deposition

Plants may take up contaminants into their aboveground parts not only through the roots, but also through deposition of aerosols from the atmosphere onto the surfaces or aerial plant parts, where part of the contamination then can become so tightly bound or incorporated that they cannot be removed even by vigorous washing.[44] Like lead and mercury, antimony can also be transported over long distances through the atmosphere, before it is deposited on plant, soil or water surfaces. Analysing samples of the two moss species *Hylocomium splendens* and *Pleurozium schreberi*, Berg and Steinnes showed that Sb is among the elements that are transported over long distances even to the remotest parts of northern Norway.[45] Cloy et al.[46] and Shotyk et al.[47] found that patterns of Sb and Pb concentrations in peat cores from remote areas of Switzerland and Scotland reflected the history of anthropogenic air pollution over the past two millennia. Sb was found to be immobile in peat like Pb and also similarly distributed. Current anthropogenic Sb fluxes in the atmosphere are $\sim$10 times greater than natural fluxes. Short-range atmospheric transport may be even more important, at least locally, than long-distance transport. In particular, on highly contaminated sites with reduced ground vegetation cover, resuspension of soil particles by wind erosion or rain splash can be an important pathway of contaminant transfer from soil to plants.

As the following evidence demonstrates, atmospheric deposition of Sb onto plant surfaces may in fact be a dominating pathway in the soil-to-plant transfer of Sb under field conditions. It may explain part of the variability in plant Sb concentrations shown in Figs 2 and 3 in addition to the factors discussed before. Ainsworth et al. measured $\sim$300 mg kg^{-1} Sb in leaf samples of various grasses near an Sb smelter in north-east England, where soil Sb concentrations reached 400 mg kg^{-1}.[48] A control experiment in which plants were grown under open-air conditions in pots with uncontaminated soil revealed that almost all this Sb uptake could be attributed to dust deposition onto the plant leaves. Robinson et al. obtained similar results at a highly polluted shooting range in Switzerland.[49] Using iron as a reference element to determine the rate of resuspended soil deposition, they concluded that almost all Sb found in leaf and shoot samples from the study site was attributable to this pathway.

Short-range transfer of resuspended soil particles from contaminated soil to aerial plant parts would not invalidate the general relationship between total concentrations of Sb in soil and Sb in the aboveground parts of plants shown in Fig. 2. However, it cannot be expected to produce a close relationship between plant Sb and soluble Sb in soil. In fact, it may be one of the major reasons for the scatter in this relationship shown in Fig. 3.

Direct transfer of contaminants to the aerial parts of plants by dust deposition and rain splash can be avoided under greenhouse conditions. Unfortunately, only few experiments have been performed on Sb uptake by plants under such controlled conditions so far. These experiments, however, show the same type of linear relationships between plant and soil Sb concentrations as those shown in Figs 2 and 3 with comparable bioaccumulation coefficients, showing that high uptake of Sb is possible via the root–shoot pathway and does not necessarily imply atmospheric deposition of resuspended contaminated soil particles.[11,28]

In aquatic environments, Sb may also be directly transferred to submerged shoot and leaf surfaces through the water phase. This phenomenon has been shown for arsenic in aquatic vegetation and may also be involved in the uptake of Sb by aquatic plants reported in some studies.[50] Hozhina et al. found that *Typha latifolia* and *Scirpus sylvaticus* growing around a mine tailing pond that contained up to 3.6 mg L^{-1} Sb, accumulated up to 19 mg kg^{-1} Sb.[51] Similarly, Kawamoto and Morisawa reported Sb concentrations of up to 7 mg kg^{-1} not only in green algae, but also in the roots and leaves of higher plants growing along a river in which the water contained 3.4 to 4.0 mg L^{-1} Sb due to discharges from a dye factory.[52]

Toxicity risks posed by consumption of plants grown on Sb-contaminated soil

If Sb is taken up by crop plants, it may enter the food chain and present a health risk for animals and humans, even if the plants themselves remain unaffected.

Li and Thornton investigated soil and pasture herbage contaminated by As, Sb and Bi. They came to the conclusion that very little of these elements is usually absorbed by grazing animals from the soil or herbage and that health problems in grazing livestock therefore are uncommon.[53] The chemical forms of these elements and other related metals in soil and herbage, and possible subclinical effects of long-term, low-level exposure require further study.

A possible danger is the low Sb toxicity to plants. As has been mentioned before, plants can take up high amounts of Sb while still being and looking healthy. Humans as well as animals consuming such plants over longer periods of time may thus become poisoned.

Gebel et al. studied Sb exposure by taking urine, blood and scalp hair sample from a population living in a contaminated area in northern Palatinate, Germany. No significant differences in Sb concentrations compared with the control group were found. Also, risk factors like consuming seafood or home-grown produce apparently did not affect Sb concentrations in urine, blood or scalp hair.[54]

Owing to the limited knowledge about Sb toxicity, it is difficult to assess the health risks of exposure to elevated concentrations of Sb. Acute Sb poisoning of humans or animals via ingestion of Sb-contaminated soil or consumption of plants grown on Sb-contaminated soil is extremely unlikely. Also, chronic effects are to be expected only under rare circumstances. Assuming an average Sb concentration in vegetables grown in a contaminated garden of 100 mg kg^{-1} dry weight (a value that has rarely been found exceeded under field conditions), then a person hypothetically would have to consume in average 1 kg dry matter of these plants per day in order to reach a dose of

Table 4. Estimates of the time necessary to reduce Sb concentrations in polluted topsoil (0–10 cm depth) to certain target levels by phytoextraction, based on model calculations (see text for further explanation)

Soil concentrations in the examples were taken from Table 1. For the calculations, an annual biomass yield of 10 t dry matter and a soil-to-plant accumulation coefficient of 0.022 was used, based on the data given in Fig. 2. Soil bulk density was assumed to be 1.3 kg L^{-1}

Site	Initial soil Sb concentration (mg kg^{-1})	Time necessary to halve concentration in soil (years)	Target concentration (mg kg^{-1})	Time required to reach a certain Sb concentration in the topsoil (years)
Mine spoil	26.3	4096	1	19 307
Shooting range	13 800	4096	100	29 113
Roadside along highway	0.53	4096	0.5	344
Garden soil near mine	500	4096	100	9510
Orchard	0.95	4096	0.5	3792

100 mg day^{-1} Sb, i.e. the threshold of Sb intake considered to be critical.[55]

Treatment of Sb-contaminated soil

In principle at least, phytoextraction would be the method of choice to remove Sb from a polluted soil without destroying it. Murciego Murciego et al. proposed to use *Dittrichia viscosa* for phytoextraction of Sb from mine waste.[56] The practical feasibility of this approach has not been demonstrated yet, however, and simple spreadsheet calculations reveal that this will not be easy. With a constant bioaccumulation coefficient of 0.022 (the average ratio between plant and total soil concentrations derived from the data presented in Fig. 2), an annual yield of 10 t plant dry mass per ha, a soil bulk density of 1.3 kg L^{-1}, and a contamination depth of 0.1 m, the time required to halve the Sb concentration of the soil by phytoextraction would be more than 4000 years. This value is independent of the initial Sb concentration because the assumption of a constant bioaccumulation coefficient means that the rate of Sb extraction decreases in proportion to the concentration of Sb in the soil. For other scenarios, estimates of the time required to reduce a given initial Sb contamination to a specified target concentration by phytoextraction are presented in Table 4. These example calculations demonstrate that phytoextraction is generally not a realistic option, unless high-biomass Sb hyperaccumulator plants are found that are much more efficient for this purpose.

Conclusions

The main findings of the present literature review are that Sb is generally taken up in proportion to the concentration of soluble Sb in the soil and that this proportionality holds over a concentration range of five or more orders of magnitude. Almost nothing is known about the mechanisms of Sb uptake by plants, but the general occurrence of proportionality suggests passive uptake by convection along the apoplastic pathway with the stream of transpiration water. Crossing of the endodermis could occur through leaks in the Casparian bands or, in the case of antimonite, also through aquaporins. Although soil pollution by Sb may be rarely so severe as to cause toxicity problems to humans or animals consuming plants or food derived from plants grown on Sb-contaminated sites, such risks also cannot be excluded in all cases. There is a general need for more controlled laboratory and greenhouse experiments to elucidate the mechanisms and processes that govern the fate of Sb in soil–plant systems, including the ecotoxicity of Sb and its transfer through the food chain.

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