Antimony bioavailability: Knowledge and research perspectives for sustainable agricultures

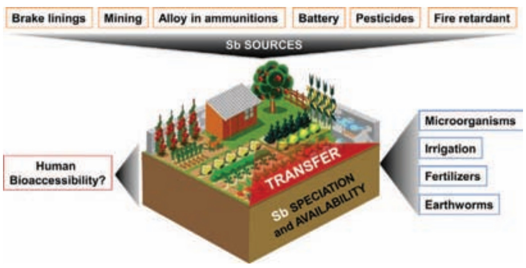
Antoine Pierart[a,b], Muhammad Shahid[c], Nathalie Séjalon-Delmas[a,b], Camille Dumat[d,*]

[a] Université de Toulouse, INP, UPS, EcoLab (Laboratoire d'écologie et environnement), ENSAT, Av. de l'Agrobiopôle, F-31326 Castanet-Tolosan, France
[b] UMR 5245 CNRS, EcoLab, F-31326 Castanet-Tolosan, France
[c] Department of Environmental Sciences, COMSATS Institute of Information Technology, 61100 Vehari, Pakistan
[d] CERTOP UMR5044 – CERTOP, Université Jean Jaurès, Toulouse, France

HIGHLIGHTS

- This paper reviews Sb in edible plants in relation to sanitary consequences.
- Sb contamination in urban areas has been increasing for 50 years.
- Sb values in edible plants are very scattered.
- A serious lack of data exists about Sb behavior with arbuscular mycorrhizal fungi.
- There is no legal threshold for Sb in edibles, but potential human risk can occur.

GRAPHICAL ABSTRACT



Keywords:
Antimony
Bioavailability
Edible crops
Arbuscular mycorrhizal fungi
Human health risk

ABSTRACT

The increasing interest in urban agriculture highlights the crucial question of crop quality. The main objectives for environmental sustainability are a decrease in chemical inputs, a reduction in the level of pollutants, and an improvement in the soil's biological activity. Among inorganic pollutants emitted by vehicle traffic and some industrial processes in urban areas, antimony (Sb) is observed on a global scale. While this metalloid is known to be potentially toxic, it can transfer from the soil or the atmosphere to plants, and accumulate in their edible parts. Urban agriculture is developing worldwide, and could therefore increasingly expose populations to Sb.

The objective of this review was in consequences to gather and interpret actual knowledge of Sb uptake and bioaccumulation by crops, to reveal investigative fields on which to focus. While there is still no legal maximal value for Sb in plants and soils, light has to be shed on its accumulation and the factors affecting it. A relative absence of data exists about the role of soil flora and fauna in the transfer, speciation and compartmentation of Sb in vegetables. Moreover, little information exists on Sb ecotoxicity for terrestrial ecosystems. A human risk assessment has finally been reviewed, with particular focus on Sb bioaccessibility.

Contents

* Corresponding author. Tel.: +33 5 62 19 39 03; fax: +33 5 62 19 39 00.
E-mail address: camille.dumat@ensat.fr (C. Dumat).

1. Introduction

Antimony (Sb) is a metalloid occurring naturally as a trace element in soils [1,2]. Its deposits are scattered worldwide, but differ greatly in terms of concentration. According to Krachler et al. [3], for the last 30 years Arctic snow and ice have recorded a 50% increase in Sb accumulation, mainly from anthropogenic sources [4]. Actually, it has been estimated that the total remaining world pool of Sb is equivalent to about 12 years of consumption at the current anthropogenic rhythm [5]. Antimony is used in numerous human activities, including smelting and mining, but its use as a fire retardant is the most important [6]. In addition, Sb contamination comes from shooting ranges (because of Pb–Sb alloys used in munitions) [7]. It has been reported that 5.56 mm bullets are comprised of almost 0.7 wt.% antimony [8], while 9 mm rounds contain up to 1.8 wt.% [9,10]. Antimony compounds are also used to treat Leishmaniasis, AIDS, and cancer [11,12]. Moreover, in the past, agricultural lands have faced large-scale Sb inputs, with the presence of this persistent element in the manufacture of pesticides and/or herbicides, and applications of sewage sludge [13,14].

Today, agricultural and urban lands with farms and gardens are facing new Sb contamination sources. In recent decades, the increased use of Sb in old batteries, and as a lubricant and alloy in brake linings, has been causing contamination through manufactures recycling battery and road traffic dust [15,16]. Airborne particles enriched with metal(loid)s can pollute soils [17,18], and metal(loid)s can accumulate in plants, both through root [19] and foliar uptake [20–23]. While agricultural lands present a contamination risk through aerial deposition and water, urban areas are facing a new important challenge: in reaction to the worldwide economic crisis, people are showing a clear desire to grow their own food in public, associative, or kitchen gardens [24]. Indeed, having a garden to produce healthy vegetables is one of the objectives highlighted by urban gardeners [25], but these areas are often either directly in contact with roads and/or industries, or set up on old industrial soils (*i.e.*, with a high risk of contamination) [26].

According to Winship [27], Sb is a toxic element, and excess intake by humans may cause vomiting, diarrhea, skin rashes, and respiratory symptoms, such as a cough. Other studies have also demonstrated the toxicity of Sb to human beings [28,29]. Cardiotoxicity has also been reported, with arrhythmias and cardiac arrest. According to the German Research Council, inhalation of Sb compounds, as well as metallic Sb dust, may cause lung tumors [12,30].

Since 1979, antimony has been considered as a priority pollutant by the United States Environmental Protection Agency (US EPA), as well as the European Union [31]. Antimony has therefore been studied widely in the water compartment [32], and the results have led to different thresholds (from 5 to 20 $\mu g\,L^{-1}$) for drinking and agricultural water in some countries [33]. Subsequently, as food represents the main source of human exposure to environmental pollutants [34], with fruits and vegetables making up the world population's major dietary components, scientists have become more and more interested in Sb transfer in soil–plant–water systems [35,36]. The consumption of polluted plants could therefore have a strong impact on human health [37,38]. Recently, Feng et al. [39] reviewed Sb interactions with terrestrial plants. However, the data dealing with edible plants are widely scattered, and unlike lead (Pb), cadmium (Cd), or mercury (Hg), there is no regulation concerning maximal Sb concentrations in marketed consumer produce.

Agricultural lands and urban areas allocated for agriculture and gardening activities are also places where the soil biodiversity can be enhanced by sustainable cultural practices, based on organic matter inputs [40]. Consequently, these areas may have an important biological activity. A better knowledge of biotic factors influencing the transfer of Sb in the soil–plant system appears as an important goal. Earthworms are known to play a key role in metal(loid) bioavailability in soils [41], as do mycorrhizal fungi, which are used as biofertilizers in current agriculture practices [42]. Both interact with different soil compartments (*i.e.*, transfer from soil solution through fungus to plant for mycorrhization for the former, and solid-phase-to-earthworm transfer for the latter).

In this review, we investigate the sanitary risks induced by human exposure to Sb, owing to the ingestion of polluted vegetables or soils (in the case of accidental soil ingestion). The scientific questions raised are therefore: (1) What are the mechanisms involved in Sb transfer to vegetables and soil fauna? (2) What is the influence of plant–earthworm, or plant–fungi interactions on the transfer? The main factors affecting Sb bioavailability in relation to its compartmentalization and speciation are summarized first. Then, relevant data, and gaps concerning edible plant and Sb bioaccumulation, are studied, with a focus on biological factors influencing such transfers (plant mycorrhization and earthworm

Table 1
Minimal and maximal Sb values in selected soil andliving organisms.

Media	Min ($mg\,kg^{-1}$)	Max ($mg\,kg^{-1}$)	References
Soil	0.3 Continental crust	2095 Battery manufacture soil	[43] [48]
Sediments	0.3 Uncontaminated sediment	2122.8 Contaminated stream sediment	[50] [46]
Mining site	1291 Mine tailing	5045 Mining soil	[47]
Urban soil	0.46 Roadside soil	4.4 Road dust	[16]
Shooting ranges	500	15000	[46]
Plants	0.004 Garlic	5112 Pterisfauriei	[39]
Edible plants	0.004 Garlic	2236 Colza	[51]
Terrestrial invertebrates	0.04 Earthworm	30.4 Spider	[52]
Aquatic invertebrates	0.43 Grammarus	3.35 aquatic sowbug	[53]
Small mammals	<0.02 Mice	8.6 Vole	[54]
Human body	0.045 Hair sclape	0.8 Urine	[29]

bioturbation in soils). Finally, data on the trophic chain and the risks threatening human health when producing edible plants in polluted areas are exposed.

2. Factors affecting Sb bioavailability

Antimony and its compounds occur naturally in relatively small quantities in rocks (0.15–2 $mg\,kg^{-1}$) [31], non-polluted water (<1 $\mu g\,mL^{-1}$) [31] and soils (0.3–8.6 $mg\,kg^{-1}$) [43]. While soil is the main plant-developing medium, it is also a major contaminant sink in various ways: fertilizers and amendments inputs, aerial deposition, and water percolation. According to the Toxics Release Inventory [44], in 1987, almost 3,061,036 pounds of Sb was released into the environment by different industrial activities in the United States. Of these Sb releases to the environment, 2% was to water, 4.4% to air, and 92.9% to land. Urban areas allocated for gardening practices and arable lands cultivated in ancient contaminated sites present then an important health risk.

Metal bioavailability can be expressed as the part of the total soil metal content that can interact with living organisms [45]. Generally, metal availability to plants and other living organisms in the soil is controlled by the pseudo-equilibrium between aqueous and solid soil phases [45]. Part of the soil metal introduced by anthropogenic activities is more mobile than naturally occurring metal in soil. The bioavailable part of a metal can be taken up by plants and other living organisms. Bioavailability of Sb in soil is controlled by several processes, such as adsorption/desorption, precipitation/dissolution, and Sb–ligand complex formation [19]. These processes depend mainly on soil characteristics, such as cation exchange capacity, soil pH, soil texture, biological and microbial conditions, amount of metals, organic and inorganic ligands, and competing cations [45]. These processes and parameters, either separately or in combination with each other, may affect Sb behavior in soil. This section reviews the actual knowledge about Sb behavior in soil.

2.1. *Antimony consideration is variable*

As shown in Table 1, because of numerous anthropogenic activities, Sb concentration is highly variable in the environment [46]. As a non-exhaustive example, its concentration in mining site, mine tailing, industrial soil (battery recycling factory), shooting range, road side soil, and road dusts can reach, respectively, (in $mg\,kg^{-1}$): 5045 [47], 1291, 2095, 13 800, 0.46, and 4.4 [16,47–49].

Interestingly, great asymmetry can be observed between the geographic areas with high Sb levels in the soils, and the scientific studies performed all around the world, so we can effectively conclude that Sb contamination often seems not to be taken into account worldwide. Countries such as China (87% of the world's Sb production [5]) have been studying Sb behavior at the soil-edible plant interface to a large extent. In the same way, the number of publications about Sb content in edible plants has doubled since 2010, with an average number of accepted publications of 2.4 publications per year (1.25 during 2000–09; none before). At the opposite end of the spectrum, Bolivia, which possesses large Sb deposits, and is the second largest Sb producer (3.3% of the world's production), neither studies nor publishes data about Sb contamination.

There is a contradiction arising around Sb with respect to its importance in remediation and risk-assessment studies. Some studies highlight the fact that this toxic element can accumulate in plants [55], especially in the case of Chinese studies, and focus mainly on mining sites with major contamination [1,36]. But on the other hand, in the same country, this element is not even systematically measured. This is the case with the recent study of Huang et al. [56], which investigated the bioaccumulation of several heavy metal(loid)s in more than 300 vegetables of 11 common types, from a large geographic area, including Zhejiang province. They reported that Sb values in water and sediments could be high [1], and were potentially responsible for contaminating arable lands and urban gardens through irrigation.

2.2. *Antimony solubilization in the soil*

The behavior of Sb in soils has gained considerable attention over the last decade. Generally, the water, $Na_2HPO^-{}_4$, and NH_4NO_3 extractable fraction of Sb is considered to represent the soluble and bioavailable form of Sb in soil [57–60]. Wilson et al. [2] reviewed Sb behavior in soil systems and concluded that soil pH greatly affects its speciation and solubility. In addition, Sb background concentration, soil mineralogy, the presence of organic and inorganic ligands, soil organic matter contents (which can be abnormally high in urban gardens: values such as 15–20% are commonly observed in comparison with 2–3% for agricultural soils), and amount and type of co-oxidants/co-reductants also influence Sb solubilization/mobilization in soil systems [2]. The reduced solubility and mobility of Sb in soil is already well documented: (1) due to partitioning to metal (hydro) oxides of Al, Fe, and Mn [61,62], (2) to secondary mineral precipitation [63,64], (3) humic acids [65] and clay mineral interactions [66,67]. The scientific community agrees that generally Sb is not highly soluble and available, but its solubility can vary widely depending on the soil's natural characteristics [68]. For example, Hou et al. [69] showed that mobilizable Sb varies in soils as follows: Primosol > Ferrosol > = Isohumosol. Flynn et al. [58] reported less than 1% Sb solubility in soil near mining and smelting sites in the United Kingdom.

Antimony has been classified as easily phytoavailable, moderately phytoavailable, and not phytoavailable, as a function of its complexation with organic and inorganic ligands, as well as its extractability from these compounds [47]. The effect of As on the uptake and bioaccumulation of Sb by plants has also been reported [70]. Biochar is reported to enhance Sb mobility in soil [71,72], which might be a result of electrostatic repulsion between anionic Sb and negatively charged biochar surfaces [72]. The water-soluble fraction of Sb (Sb_{Sf}) is calculated as the ratio between the water extractable Sb and the total Sb in soil. From available data in the literature, this ratio has been estimated between 0.5 and 2.9% (complete results available in Supplementary material Table A.1).

2.3. Antimony oxidative state and speciation in soil

It is well-known that metal speciation plays a key role in determining the biogeochemical behavior (bioavailability, bioaccumulation, toxicity, and detoxification) of metals in soil–plant systems [73–75]. Different forms of a metal are not always equally bioavailable and toxic. Therefore, total soil metal concentration is not considered a good proxy to estimate metal bioavailability and toxicity in living organisms [17,19]. Antimony is also reported to exist in different chemical forms (organic and inorganic) in soil. It occurs in various oxidation states in environmental systems (−III, 0, III, and V), but only two of them (III and V) are found mainly in soils [10,31]. The behavior of Sb depends largely on: (1) its oxidation states [77]; for example, Sb^{III} is reported to be 10 times more toxic than Sb^{V}; and (2) the plant species [35], which may more readily take up either Sb^{V} or Sb^{III}. Some studies compared accumulation of Sb^{III} and Sb^{V} species by plants. They showed that its accumulation is both Sb species and plant species dependent (*cf.* 3.1., 3.5., and 4.2.). Most commonly, Sb occurs in soil as oxides, hydroxides or oxyanions [78,79]. Inorganic species of Sb are well-known and reported compared to organic species, but the latter are reported to exist. For example, it has been shown that organic Sb species such as soil trimethylantimony dichloride – $(CH_3)_3SbCl_2$ – probably exist is solution as $[TMSbOH]^+$ [80]. The existence of Sb in different chemical forms is considered to depend on the soil's physicochemical properties, adsorption/desorption processes, and the presence of inorganic and organic ligands [2,50,77,81]. As an example, strong humic acid–Sb interaction was currently observed in polluted soils. Moreover, these humic acids participate to the oxidation level of antimony (between Sb^{III} and Sb^{V} species) with consequences on its toxicity [82] and mobility during lixiviation processes [83].

However, to date, there is very little data regarding the biogeochemical behavior of Sb in soil–plant systems, in relation to its chemical speciation. Precisely which chemical forms of Sb are more mobile, available and toxic are questions that always need to be explored, in order to better understand the biogeochemical behavior of Sb.

2.4. Antimony from soil to plant: an oxidative state dependent pathway

Although Sb does not have an essential role in plant metabolism, this metalloid can easily be taken up by plant roots from soils [1,39,84]. Different pathways have been suggested concerning Sb transporters in plants [39], but only a small amount of data exists. It has been proposed that Sb accumulation in plants seems to occur *via* a passive pathway, especially in its Sb^{III} form. But some cues indicate that an active pathway could also exist [85]. The first identification of a cellular transporter for Sb^{III} accumulation was done in *Escherichia coli* [86,87]. Kamiya and Fujiwara [88] identified an Sb transporter in *Arabidopsis thaliana* while studying the reactions of plants mutated in As^{III} transporters. They focused on the nodulin 26-like intrinsic proteins (NIPs), and showed that the NIP1;1 As^{III} transporter also transports Sb^{III} and influences *A. thaliana* sensitivity to antimonite. The problem is that, to date, an Sb^{V} pathway from soil to plant remains undiscovered, whereas the mechanism of uptake of As^{V} has been determined to occur *via* phosphate transporters [89]. The relationship between Sb speciation and localization/compartmentation inside the plant is also still to be established. Is there any link between organic or inorganic ligands and Sb speciation in soil and its bioaccumulation by plants and soil microorganisms? To what extent would gardeners' cultural practices affect Sb speciation? Finally, what are the consequences in terms of human exposure and Sb bioaccessibility if crops are cultivated in Sb-contaminated soils?

3. Antimony bioaccumulation in edible plants

3.1. Bioaccumulation factor

The bioaccumulation factor (BAF) has been defined by the US Environmental Protection Agency as: "the ratio of the contaminant in an organism to the concentration in the ambient environment at a steady state, where the organism can take in the contaminant through ingestion with its food as well as through direct content". Data in Table 2 show a high variability of BAF for Sb in edible plants. It is expressed here using two different ratios: BAF, which is the ratio between Sb concentration in plant and the total Sb concentration in soil; and BAF_w, which is calculated as the ratio between plant Sb content and the soluble fraction of Sb in soil. The limitation is that the so-called soluble fraction is obtained through numerous different extraction protocols in the literature, such as shaking soil sample with ultrapure or bi-distilled water [36], or with KNO_3

Table 2
Antimony Bioaccumulation Factor (BAF) in edible plants.

	Plant	Organ	Sb specie	BAF	BAF_w
Sb present in soil	Peanut	Shoots		0.17	9.5
	Colza	leaves		0.02	1.08
Experiment with spiked Sb	Sunflower	Leaves	Sb_2O_3-potting mix	0.07	10.19
	Spinach		KSbO-tartrate, $3H_2O$	0.8	9.07
	Maize	–	Sb_2O_3-agricultural soil	0.03	6.66

BAF represents the ratio [Sb]plant/[Sbtotal]soil. BAF_w represents the ratio [Sb]plant/[Sbsoluble]soil. When known, the bio-accumulative organ and Sb species are specified. Complete table available in Supplementary material Table A.2.

salt [85], leading sometimes to potential mistakes in results, and in comparison experiments.

In their review, Feng et al. [39] reported that Sb phytoavailability depends mainly on its solubility, and its facility of transfer from the solid phase to the soil solution. They concluded that Sb solubility in soils is generally very low, but highly dependent on soil characteristics (*cf.* §2.1). This concentration is usually less than the total Sb in the soil, but this fraction is the most easily phytoavailable, and gives a better idea of the real mechanism of bioaccumulation. It is still imperfect because it only considers the Sb soluble fraction, while the phytoavailable fraction is composed of both the water-soluble and cation-exchangeable fractions (*i.e.*, the concentration extracted from soil with $MgCl_2$ or $CaCl_2$ for example). However, insufficient data was available in Sb-related publications. Such heterogeneity in protocols and lack of data are quite common. These results are therefore to be considered cautiously. Although Sb speciation is known to be an important factor affecting its solubility, very poor information is usually provided, except concerning its oxidative state [35] (*cf.* §2.2). Various Sb speciation analyses have been tested to date. They were reviewed with stresses on their advantages and difficulties in early 21century by Krachler et al. [90]. Major difficulties come from both the lack of suitable Sb standards and the particular Sb chemistry complicating the simultaneous separation of its chemical species without changes (in comparison with the initial speciation in the environment). The development of certified materials (root, leaves, seeds, fruits *etc.*) for bioaccessibility assessment could therefore be of great interest for the scientific community.

Values range from 0.001 to 1.4 for BAF, and 0.04 to 10.19 for BAF_w, showing the potential risk of cultivating vegetables in Sb-contaminated soil (Table 2 and Supplementary material Table A.2). Such results also highlight the essential role of the Sb species in its uptake and bioaccumulation. Indeed, for the same vegetable, two different Sb species led to highly variable BAF and/or BAF_w while the exposure concentration was the same. Moreover, when exposed to $SbCl_3$ or $SbCl_5$, rye (*Secale cereal* L.) and wheat (*Triticum aestivum* L.) presented two opposite absorption preferences: rye and wheat accumulated more Sb in the presence of $SbCl_5$ and $SbCl_3$, respectively [91].

Consequently, since agricultural lands and urban gardens are submitted to frequent and sometimes major watering (*i.e.*, waterlogging), a fraction of the soil Sb pool could solubilize and convert in more phytoavailable species [35], and this has to be taken into account in both environmental and sanitary risk assessments.

3.2. Antimony in edible plants

Metal(loid) accumulation by plants occurs in different organs so it is crucial to distinguish the whole plant accumulation from the edible part one, which is the hazardous one. Table 3 summarizes the main information to date cited in the literature about Sb in edible plants. It shows that Sb can be found in every plant tissue, from roots [91] to fruits [92]. However, its range of concentration is very large (0.004–1400 mg kg^{-1}). Thus, in regard to the potential health risks induced by Sb exposure, the high concentrations sometimes observed in consumed plant parts highlight the interest in determining a threshold concentration for vegetables in the context of European regulation and beyond, to ensure food safety. However, although some studies found no obvious relationship between Sb concentrations in soil and plants [57,93], perhaps as a result of foliar pollution highlighted by Schreck et al. [22], others seemed to identify one. For example, a positive correlation between $[Sb]_{soil}$ and $[Sb]_{roots}$ ($R = 0.959$, p value = 0.01) has been found in an old mining site in Spain [26].

Antimony speciation in plants has not yet been studied in detail. The current state of knowledge has been reviewed by Feng et al. [39] with often a mixture between precise chemical compounds and oxidative degree identification. For instance, four Sb species (Sb^{III}, Sb^{V}, $Sb(CH_3)_3$ and an unidentified Sb compound) have been found in *Pteris vittata* L. when grown in the presence of Sb^{V} [51]. Moreover, the origin of $Sb(CH_3)_3$ often observed in aboveground plant parts is still unclear. But some results showed the capability of fungi and bacteria to methylate Sb in soil (*cf.* 4.2). The question remains however, if the plants can methylate Sb as it has been shown for arsenate [94], or if they accumulate it through their endophytic fungi. In some edible plants, it has been shown that the main Sb species is Sb^{V} (~95%) [95] but its uptake pathway is still unclear (*cf.* 2.4).

The truth is that roadside soils do not generally have a very high Sb contamination. However, in some cases, when arable lands or urban gardens are set up in the direct vicinity of a road, or in old industrial/mining areas, long-term exposure could lead to an increased accumulation of Sb in their soils (and then to the harvests), leading to food-chain accumulation, human exposure and, in the worst cases, disease.

As a result of this synthesis, some plants seem to fit the role of Sb phyto-extractors because of their high capability to take up and stock Sb in their shoots (rapeseed, peanut, English mace and Bladder campion, in which Sb values have reached, 2236, 340, 1367 and 1164 mg kg^{-1}, respectively; see Table 3). However, it is still necessary to measure Sb values in peanuts, which is the edible part of this plant.

On the other hand, some plants reveal a potential capacity to grow on Sb-contaminated soil without any increment in their uptake of this metalloid. These plants could, therefore, be recommended to be grown when the soil cannot be remediated (*i.e.*, in the case of a lithogenic Sb contamination). Such is the case for onions, cucumber, sunflowers and wild rosemary (Table 3).

Since farmers and gardeners can buy and grow many different varieties (cultivars) of each vegetable, investigations also need to be performed at the varietal scale, to know if different varieties of the same species behave similarly or not, with regard to Sb uptake and accumulation, as has been shown for other metal(loid)s such as Pb and Cd [102].

Differences between perennial and annual plants have also been shown [103]. For example, in seasonal plants, Sb concentrations ranged from 1 to 447 mg kg^{-1}, and in perennial plants its value was between 1 and 20 mg kg^{-1}, which is 20 fold less. Such differences highlight the potential sanitary risk, both in urban gardens and in agriculture, where seasonal plants are mainly cultivated.

3.3. Antimony in rice

Rice is one of the most consumed food crops for 3 billion people in the world. Nowadays, its cultivation in areas near towns (in Japan, Malesia, *etc.*) is seriously asked from a sustainable point of view [104]. But, the Sb accumulation by rice may cause human health threats, especially in Asia where such food could represent about 33% of direct Sb intake [95] and even more if, in addition, the possible entrance of Sb (as other potentially harmful element such as As) into food chain through cattle fed with rice straw is considered [105]. This section focuses therefore on the data concerning Sb availability and accumulation in rice plant. Actually, the relationship between rice and Sb has already been intensively studied, revealing that Sb concentration in edible parts could be potentially high. According to Ren et al. [106], rice plant can accumulate Sb up to 5.79 mg kg^{-1} in seeds. However, as shown in Table 4, Sb concentration in rice is generally relatively low. Iron plaques developed around rice root seem to play a major role in the alleviation of Sb contamination [107] through a strong bondage between Sb and Fe, leading to a decrease of Sb in plant. A competition in absorption of Sb^{III} and As^{III} has also been identified [108]. As for other edible

Table 3
Review of Sb content in edible plants in relation with the form of Sb and type of experiment.

Common name	Plant species	Sb exposed levels (mg kg^{-1}/mg L^{-1})	Chemical form	Maximum Sb concentration (mg kg^{-1} DW)	Accumulation organ	Experiment	Additional information	References
Apple	*Malus domestica*	–	–	0.011	Fruits	–	Retail network	[80]
Barley	*Hordeum vulgare*	67.3	–	0.02	Grains	F	Agricultural soil	[47]
Beet	*Beta bulgaris*	0.41	–	0.03	–	F	–	[16]
Cabbage	*Brassica oleracea*	–	–	0.021	Leaves	–	Retail network	[80]
		266.3	–	0.28		F	Garden soil	[47]
Carrot	*Daucus carota*	–	–	1.13	–	F	–	[82]
		–	–	0.008	Roots	–	Retail network	[80]
		159.4	–	0.03	Storage organ	F	Garden soil	[47]
		159.4	–	0.8	Leaves	F		
Celery	*Apium graveolens*	–	–	3.44	–	F	–	[82]
Chili pepper	*Capsicum annuum* Linn	–	–	2.87	–	F	–	
Chinese cabbage	*Brassica rapa* subsp. chinensis	–	–	3.33	–	F	–	
Colza	*Brassica campestris*	1 600	KSbO-tartrate	2236	–	P	–	[83]
		5 045	–	121	Leaves	F	–	[60]
		–	–	2.84	–	F	–	[82]
Coriander Herb	*Coriandrum sativum*	–	–	6.65	–	F	–	
Corn salad	*Valerianella locusta*	166.3	–	1	Leaves	F	Garden soil	[47]
Cucumber	*Cucumis sativus*	1 600	KSbO-tartrate	~600	–	P	gd	[83]
		–	–	0.01	Fruits	–	Retail network	[80]
Dill	*Anethum graveolens*	40.6	–	0.14	–	F	No detail for each plant	[84]
Eggplant	*Solanum melongena*	0.41	–	0.03	Fruits	F	–	[16]
Endive	*Chicorium endiva*	266.3	–	2.2	Leaves	F	Garden soil	[47]
Garlic	*Allium sativum*	–	–	0.004	Clove	–	Retail network	[80]
		–	–	3.41	–	F	–	[82]
Green bean	*Phaseolus vulgaris*	–	–	9.87	–	F	–	
Lucerne	*Medicago sativa*	14	–	1.75	–	F	–	[85]
Maize/Corn	*Zea mays*	28.75	Mining drainage	~100/78	Shoots/roots	P	–	[86]
		57.7	–	0.35	Shoots	F	Agricultural soil	[47]
		57.7	–	0.02	Grains	F	Agricultural soil	
	Zea mays cv. Magister	5 000	Sb_2O_3	~170	–	P	Agricultural soil. gd	[87]
			$KSb(OH)_6$	~180	–			
	Zea sp.	–	–	0.72	–	F	No specie details	[82]
Mung bean	*Phaseolus radiatus*	1 600	KSbO-tartrate	~1400	–	P	gd	[83]
Oat	*Avena sativa*	67.3	–	0.06	Grains	F	Agricultural soil	[47]
Onion	*Allium cepa*	–	–	0.011	Storage organ	–	Retail network	[80]

		40.6	–	0.14	–	F	No detail for each plant	[84]
		94.2	–	0.03	Storage organ		Garden soil	[47]
Oregano	*Oregano vulgare*	0.41	–	0.46	–		–	[16]
Parsley annual	*Petroselinum crispum*	159.4	–	0.42	Leaves		Garden soil	[47]
Parsley biennial		94.2	–	1.73				
Peanut	*Arachis hypogaea*	1 837	–	314	Shoots		–	[36]
Pepper	*Piper nigrum*	–	–	0.016	Bay	–	Retail network	[80]
Peppery bolete	*Chalciporus piperatus*	–	–	1423	Fruits body	F	Mushroom	[88]
Potato	*Solanum tuberosum*	82.5	–	0.02	Storage organ		Garden soil	[47]
Prickly lettuce	*Lactuca serriola*	–	–	5.12	–		–	[82]
Radish	*Raphanus sativus*	–	–	2.06	–		–	
Red beet	*Beta vulgaris*	159.4	–	0.09	Storage organ		Garden soil	[47]
Rice	Rice	–	–	0.93	–		No specie details	
Rye	*Secale cereale*	75	$SbCl_3$	52.5/26.6/12.3	Roots/seeds/leaves	H	–	[79]
			$SbCl_5$	73/44.9/44.4			–	
		142.3	–	<0.02	Grains	F	Agricultural soil	[47]
Shallot	*Allium fistulosum*	–	–	3.57	–		–	[82]
Soybean	*Glycine max*	–	–	1.01	–		–	
Spinach	*Spinacia oleracea*	500	KSbO-tartrate	399	Leaves	P	–	[47]
		266.3	–	1.13		F	Garden soil	
Sugar beet	*Beta vulgaris*	34.3	–	0.02	Storage organ		Agricultural soil	
			–	0.07	Leaves			
Sunflower	*Helianthus annuus*	10 000	Sb_2O_3	$\sim$700		P	potting mix. gd	[87]
			$KSb(OH)_6$	$\sim$200				
		5 000	Sb_2O_3	$\sim$40	–		Agricultural soil. gd	
			$KSb(OH)_6$	$\sim$25	–			
Sweet potato	*Ipomoea batatas*	–	–	2.26	–	F	–	[82]
Sword bean	*Canavalia gladiata*	–	–	4.14	–		–	
Tangerine	*Citrus tangerina*	–	–	0.02	Fruits	–	Retail network	[80]
Tomatoes	*Lycopersicum esculentum*	–	–	0,014		–		
		266.3	–	<0.02		F	Garden soil	[47]
Water spinach	*Ipomoea aquatica* Forsk	–	–	7.27	–	F	–	[82]
Wheat	*Triticum aestivum*	–	–	4.63/1.29/0.10	Roots/stems/grains		–	[26]
		142.3	–	<0.02	Grains		Agricultural soil	[47]
		1600	KSbO-tartrate	$\sim$400	–	P	gd	[83]
		75	$SbCl_3$	80.3/17.8/4.06	Roots/seeds/leaves	H	–	[79]
			$SbCl_5$	42.3/12.4/2.82			–	
White radish	*Raphanus sativus*	–	–	1,8	–	F	–	[82]
Wild Rosemary	Rosmarinus officinalis	539	–	$\sim$0.48/0.8	Stems/leaves		gd	[81]
Yacon	*Polymnia sonchifolia*	–	–	1.83	–		–	[82]
Yellow boletus	*Suillus luteus*	–	–	225	Fruits body		Mushroom	[88]

– = No information available; F = Field survey; P = Pot; H = Hydroponic; gd = graphical.

Table 4
Review of Sb content in rice in relation with the form of Sb and type of experiment.

Plant species	Sb exposition (mg kg^{-1} or mg L^{-1})	Chemical form	Maximum Sb concentration (mg kg^{-1} DW)	Sb specie	Accumulation organ	References
Oryza sativa L. cv. Jiahua	1562	Sb^{V}(~80%)	511/11.5	Sb^{V}	Root/shoot	[109]
–	–	–	0.93	–	–	[95]
O. sativa cv. Nanjing 45	0–5	$KSb(OH)_6$ KSbO-tartrate	1.4/0.30/0.28 12.5/1.30 /0.30	Sb^{V}(>75%) Sb^{V}(>78%)	Root/stem/leave	[106]
O. sativa cv. Yuhong No. 1	0–1	KSbO-tartrate $KSb(OH)_6$	~1 ~1	– –	Root/stem–leave/seed	[110]
	–	–	0.013	–	seed	[111]

– = No information available.

plants (*cf.* 3.2.), Sb accumulation in rice is both Sb species and rice cultivar dependent [106,107], which has to be carefully taken into account in risk assessment studies [1]. Finally, Sb human bioaccessibility in rice seems not to have been studied at all to this point, the authors suggest therefore focusing further studies on that topic to assess the risk of Sb human exposure in eating rice grown on a Sb contaminated site.

3.4. Antimony in herbs

In urban areas many people grow herbs *via* various methods: either on their balconies or in their gardens. These plants may be either cooked or eaten fresh. They are not always well washed, which can increase the ingestion of Sb present in soil particles. While there is no data available about Sb in such urban-grown herbs, its transfer from wild rosemary harvested in contaminated soil has been studied [93], either when used as an essential oil or in herbal tea. In the first case, the very low Sb content found in wild rosemary oils indicates that it can be used even if it grew on a highly contaminated soil ($[Sb]_{soil}$ = 309 mg kg^{-1}). Concerning the risk of contamination by boiling to prepare infusions, it depends on the elemental and leaf concentration of Sb. Under experimental conditions, the transfer ratio was low, and the final Sb value in the infusion was below the official threshold [33]. To reach this permissible value (5-6-20 μg L^{-1}) depending on different legislation [112–114], one would have to drink at least 387 L of herbal tea coming from the contaminated site. Although their results reveal no important health risk in their conditions, they ask for further research focused on Sb speciation, because it is already known that an inorganic pollutant's bioavailability is directly linked to its speciation (*cf.* §2.3 and [17,45,115,116]). The results of Affholder et al. [93] showed that for some herbs (*i.e.*, wild rosemary), Sb seems not to be a threatening element. Results on coriander, dill and parsley seem to show a low accumulation of Sb (6.65, 0.14, and 1.73 mg kg^{-1}, respectively; Table 3), but not enough detail is available concerning the accumulating organ, except for parsley, in which As has been measured in leaves. Additional studies should be performed to confirm whether or not herbs present a risk regarding Sb bioaccumulation and bioavailability. If that is not the case, such plants could be proposed to gardeners when their soils present a proven risk of Sb contamination.

3.5. Lack of data about Sb localization in plant organs

One of the issues regarding metal(loid) accumulation in edible plants is their localization (organs, tissues, *etc.*). Since different edible types exist (leaves, roots, fruits, stems, *etc.*) and some vegetables are eaten peeled and others not, for these vegetables it is necessary to determine which tissues and/or organs are Sb sinks. Many studies represent plants only as a two-compartment organism (shoot/root) (Table 3), leading to a lack of data about the real Sb-accumulating organ (stem, leave, fruit, *etc.*). This shows that actual knowledge about Sb accumulation and compartmentation in edible plants is still fuzzy. It seems essential to homogenize the methods, in order to make the results comparable.

What we actually know is that Sb localization in plant organs is variable and species-dependent. For example, in the case of some plant species, such as *Achillea ageratum* L., high Sb concentrations have been found, either in basal leaves (>1367 mg kg^{-1}) or in flowers (1105 mg kg^{-1}) [117]. On the other hand, some fern plants, such as *Pteris cretica* Retz, can accumulate up to 6405 mg kg^{-1} of Sb in their root system [55]. Recently, it has been shown that in the hyperaccumulator *P. vittata*, Sb^{III} accumulates more than Sb^{V}, with all the Sb accumulating only in the roots [89]. This fern species was also reported to hyperaccumulate different species of arsenic, mostly in its fronds (93%) [118]. Recently, Affholder et al. [93] reported 309 mg kg^{-1} of Sb in wild rosemary (*Rosmarinus officinalis* L.) roots, cultivated on multi-metal contaminated soil in southern France, under dry conditions. However, the translocation of Sb from roots to aerial parts was very limited. Similar results of reduced Sb translocation to aerial parts were also reported by Pérez-Sirvent et al. [119] for yellow fleabane (*Dittrichia viscosa* L.), when grown in mining-affected semiarid soils in southeast Spain.

Another point is that one-quarter of the above Sb values (Table 3) comes from measurements performed on fruits and vegetables, taken directly in the retail network [92], which give no information about soil content, pesticide exposure, and proximity to roads and/or factories. In some cases, Sb has been detected inside fruits (for example, apple pulp – 0.011 mg kg^{-1}; pepper bays – 0.016 mg kg^{-1}; and tomatoes – 0.014 mg kg^{-1}). These concentrations cannot only be credited to soil-to-plant transfer. Aerial deposition onto leaves and fruits could explain such results [21,22]. Moreover, with the increasing quantities of ultrafine atmospheric particles in urban and peri-urban areas, foliar plant exposure could sometimes be the main route of plant pollution in aerial organs [23,120].

Antimony is often considered to behave similarly, but not always, to arsenic (As) [2,121]. Concerning As localization, one study showed that As accumulates more in open-leaf vegetables (*e.g.*, lettuce, spinaches, *etc.*) than in others [122]. Underground products, such as carrots and potatoes, seem to stock more As in their skin than in their flesh, which is not true for aboveground products, such as apples. Such specific studies have not been done for Sb, for which data are still scattered, as shown in Table 3. Nevertheless, in Table 3, Sb preferential accumulation seems to occur more in root than in shoot, suggesting a small translocation factor, except for maize, where accumulation is higher in leaves.

All these data highlight the urgent need to define maximal Sb values for food safety in urban areas, and to determine the key relationships between the different Sb compartments (soil, water, plants, atmosphere, *etc.*), in order to develop provisional models of Sb behavior. Although various models exist to simulate and foresee metal(loid) speciation and behavior in soils and factors affecting it [123], Sb is not yet available in such tools.

Table 5
Mycorrhizal response under ETM stress.

Mechanism	Action mode	Molecules	Metal(loid) studied
Extracellular inactivation	Hyphal exudation of complexing agent	Glomalin, phenolic, citric, malic or oxalic acids	As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Zn
	Association with bacteria	aggregates chelating agents	Cd, Mn, Pb, Tl, Zn
	Exudation of redox enzymes	Superoxide dismutase	Zn
Binding in fungal walls	Structure of cell wall with ETM binding sites	glucans, chitins and galactosamines polymers, small peptides and proteins, glomalin	Cd, Cu, Ni, Zn
Intracellular inactivation	Increase of ETM efflux	Protein carriers or permeases	Cd, Cu, Zn
	Intracellular compartmentation: vacuoles, vesicles, spores	Chelators and then transporters: same molecules as above, fungal AND plant metallothionein	As, Cd, Cu, Ni, Zn
Response to oxidative stress	Synthesis of molecules of resistance to oxidative stress (enzymatic and non-enzymatic pathways)	Glutathione, vitamin C, E and B6, catalase, superoxide dismutase, thiol reductase	As, Cd, Cu

4. Bioaccumulation in microorganisms and soil fauna

As mentioned earlier, as Sb is not known as an essential element for living organisms, and as its toxicity is lower compared to Pb or Cd, it has been poorly studied. Its increase during the last decades has recently led to heightened awareness in the scientific community. Data about its accumulation in different organisms are still weak and scattered, but are gradually being enriched. Here is gathered the current knowledge concerning Sb bioaccumulation by soil flora and fauna.

4.1. The fungal case

For millions of years, terrestrial plants have developed close relationships with different kinds of bacteria and fungi, seeking to increase their performance, particularly in terms of inorganic element absorption [124], resistance to stresses such as metal(loid)s, and development capabilities through their symbiosis [125]. Mycorrhizal symbionts are associated with plant roots, and are present in almost every terrestrial ecosystem. A detailed classification of symbiotic fungi exists, and can be summarized as follows: trees are associated mainly with ectomycorrhizal fungi, while about 94% of angiosperms are associated with endomycorrhizal fungi [126]. The main difference is that ectomycorrhizal fungi develop hyphae that surround root cells, but do not enter inside, while endomycorrhizal species penetrate into cortical root cells. Plants usually present these symbioses, and non-mycorrhizal ones are very rare. This symbiosis is a mutual exchange, where the plant transfers a portion of its photosynthesized carbon compounds, while the fungus enhances phosphorus and other nutrient absorption, soil exploration [127,128], and drought tolerance. It is also well-documented that these symbioses induce physicochemical changes in the mycorrhizosphere [129].

In agriculture, such symbiosis usually leads to increased harvest yields, but sometimes the mycorrhizal growth response is negative. This can occur for different reasons, such as arbuscular mycorrhizal fungi parasitism, where the benefits of increased nutrient uptake do not outweigh the fungus' carbon sink [127].

Mycorrhizal fungi have also been studied at the soil–plant interface for their capability to be either a barrier or an enhancer of metal transfer, through a large range of metabolic pathways. These results were reviewed few years ago [130] and Table 5 presents a synthesis of current actual knowledge. For example, the study of As transfer at the soil–AMF–plant interface led to a wide range of results, showing either accumulation enhancement permitting phytoextraction/remediation [131], or a phytoprotective role with decreased As in plants [132]. In lettuce, the combined addition of phosphorus and AMF could reduce As transfer from a contaminated soil (250 mg kg^{-1} As) to plant: −34% in roots, and −60% in leaves, in comparison with the control [133].

Mechanisms of interaction between AMF and plants, with regard to metal(loid)s, have been widely described [134], but Sb never appears in such publications. Thus, even if Sb behavior in soil has been compared to As in many ways [2], further research has to be done to clearly define under which conditions and parameters it is possible to transpose As behavior to Sb at the soil–plant interface.

4.2. Antimony and fungal relationships

Very poor information has been published concerning the Sb–fungal relationship. Research has been done on non-symbiotic fungi, such as *Penicilium notatum* and *Scopulariopsis brevicaulis* [79]; the latter being already known as a methylator of As inorganic compounds [135]. *S. brevicaulis* has the capacity not to accumulate Sb, but rather to synthesize trimethylantimony – $(CH_3)_3Sb$ – in the presence of inorganic Sb (both Sb_2O_3 and Sb_2O_5), under aerobic conditions (detailed results in Supplementary material Table A.3) [135]. Interestingly, in the same year, different results were published for the same fungus, with no $(CH_3)_3Sb$ detected, with the addition of another Sb^V species – $Sb(OH)_6$ – [136]. Even if the fungus studied was the same, it is rather difficult to compare these experiments because both the growing conditions and Sb species differed, as well as the fungal form used (spores *vs.* mycelia ball). The important Sb biosorption capacity (>90%) of three macro-fungi (*Agaricus campestris*, *Amanita muscaria*, and *Trametes gibbosa*) from Sb-contaminated water has also been reported, but further investigation on metal-binding mechanisms is still needed [137].

Concerning the relationship between mycorrhizal fungi and Sb in soils, one study has been reported on ectomycorrhizal fungi [101]. These organisms, as well as endomycorrhizal fungi, are already known as metal(loid) hyperaccumulators [138]. In their study, the authors sampled fungi on tailing piles and slag dumps (old As/Sb mining sites), and found no major differences for Sb concentration between ectomycorrhizal and saprobic fungi. Interestingly, among all their samples Sb content in the soil was higher than in fruit bodies, which could indicate that mycorrhizal fungi play a barrier role against this metalloid. However, the case of some ectomycorrhizal fungi (*Chalciporus piperatus* and various *Suillus*) able to accumulate Sb up to 10^3 mg kg^{-1} is also mentioned. This suggests that these genera possess a specific biological metabolism to mobilize and concentrate Sb from the soil, while Sb is generally present in species with poor solubility (*cf.* §2.2, [57]). How then do some mycorrhizal fungi influence Sb speciation in the soil compartment? What about the reactivity of these newly formed Sb species under the influence of mycorrhizal fungi?

Other recent studies found $(CH_3)_3Sb$ and another unidentified Sb species in some herbaceous plants [51], suggesting the role of the microbial community in the synthesis and transfer of these compounds. As stated earlier, it is well-documented that herbaceous plants generally develop more endomycorrhizal symbioses (such as AMF), suggesting the role of AMF in the biosynthesis and transfer

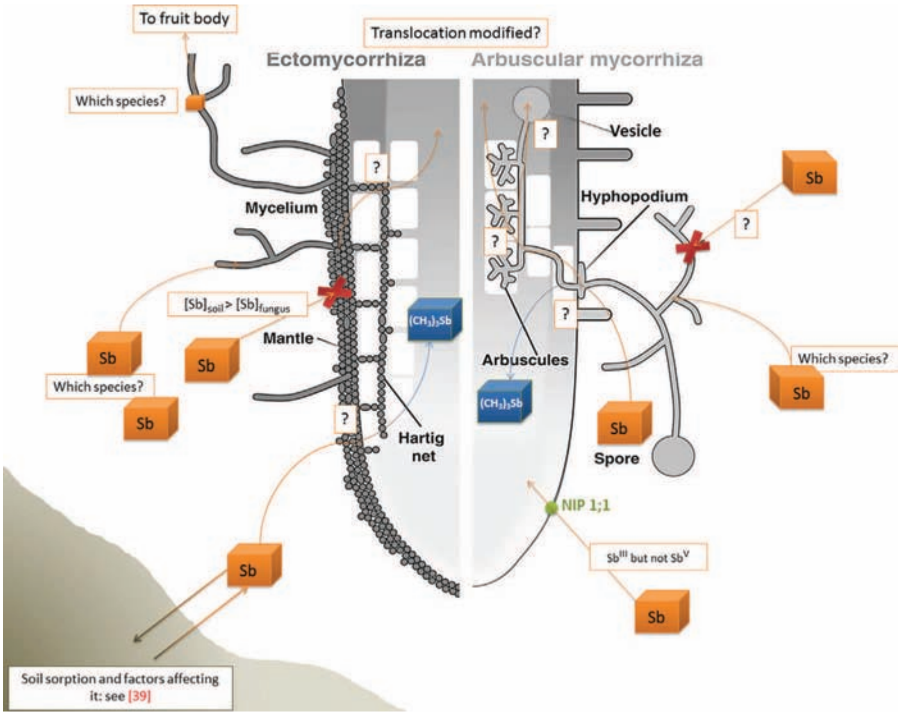


Fig. 1. Mycorrhizal role in Antimony (Sb) transfer from soil to plants.
[?] Represents the actual mechanisms to be elucidated. Sb regroups the different Sb oxidative states and species.

of $(CH_3)_3Sb$ to herbaceous plants. Fig. 1 presents the current state of knowledge of the possible ways for Sb to gain entry from soil to plants, either when associated with mycorrhizal fungi or without these organisms. 'Sb' refers without distinction to the various Sb species which have been found in soil and soil water, because not enough data exist about specific pathways for any Sb species. The different possible fluxes of Sb from soil to both plants and fungi are represented by arrows. As shown in Fig. 1, and summarized in this review, portions of these mechanisms are already known [39,88], but others have not yet been described (mostly the entirely of the fungal pathway). Nothing is known about how mycorrhizal fungi either absorb, adsorb and/or transform Sb at the soil–fungal–plant interface.

4.3. Biofertilizers in agriculture

With the development of biological agriculture, arbuscular mycorrhizal fungi are now produced and sold in almost every garden center, both for agriculture and casual gardeners, as biofertilizers [139]. As mycorrhizal symbiosis is known to affect different physiological parameters, such as stomatal conductance and fruit development [140–143], it might participate in increasing the entry of metal(loid)s through stomata (*i.e.*, leaves) and fruits. Consequently, in some cases, these biofertilizers could also be factors in the increase of metal(loid) uptake by plants [144]. Therefore, research needs to be conducted, to determine if most fungi able to methylate As have the same capability with regard to Sb, especially in the case of AMF, which could be used as a barrier between edible plants and soil on Sb-contaminated soils. Such results would also allow conclusions to be drawn as to whether or not the knowledge we already have about the relationship between AMF and As is transferable to Sb compounds, and to what extent.

4.4. Bioaccumulation by the soil fauna

In addition to their key role in soil fertility, earthworms, as the major living organisms in soils, influence metal(loid) behavior in soil through bioturbation [145]. In the case of Sb, Nannoni et al. [145] concluded that soil ingestion is the predominant means of exposure and absorption (Pearson correlation (PC) between [Sb] in earthworms and Sb extractable fraction = 0.88, $p < 0.001$). Nevertheless, they also indicated that skin penetration is not negligible (PC = 0.62, $p < 0.05$). In their experiment, total Sb concentration in earthworms varied from 0.04 to1.1 mg kg^{-1} (on clean and contaminated soils, respectively). High Sb concentrations could also cause morphological abnormalities and low activity in *Perionyx excavates* [96]. Such inhibitory effects on earthworms might cause a loss of fertility. In the case of Sb, the BAF is very low, indicating that, for earthworms, the total Sb concentration in the soil is not a good predictor of their possible contamination, while the extractable fraction seems to fit this role better. It also indicates that these species do not accumulate Sb intensively from the environment, so that Sb will not spread and accumulate through food webs *via* these organisms. Moreover, as shown for other metal(loid)s, such as Pb, Cu, Cd, Zn, Cr, Co, and Ni [18,52], earthworms can modify metal bioavailability in soils. For example, earthworm activity on a contaminated soil led to a 46% increase in Cd and Pb in lettuce leaves, owing to improved soil–plant transfer [41]. As earthworms are mainly interested in soil organic matter, the same authors also discussed Sb–soil organic matter interactions. *Eisenia fetida* has also been shown to biotransform As without excreting it after exposure, until its death [146]. This led to a decline in the As concentration in the soil during this period, but no data was given about As speciation or transfer when these organisms die and decompose in the soil. Such effects have not yet been demonstrated for Sb. Fig. 2 represents the actual state of knowledge about Sb behavior in soil–earthworm systems with excreted castings. It shows that such organisms can absorb Sb and further change its bioavailability, but the Sb species involved have not yet been clearly identified.

Typically, the bioaccumulation of Sb by soil microfauna varies with their habitat and species type. Antimony concentrations in terrestrial invertebrates (30.4 mg kg^{-1} dry wt.) are generally higher than those in aquatic invertebrates (5.2 mg kg^{-1} dry wt.) and

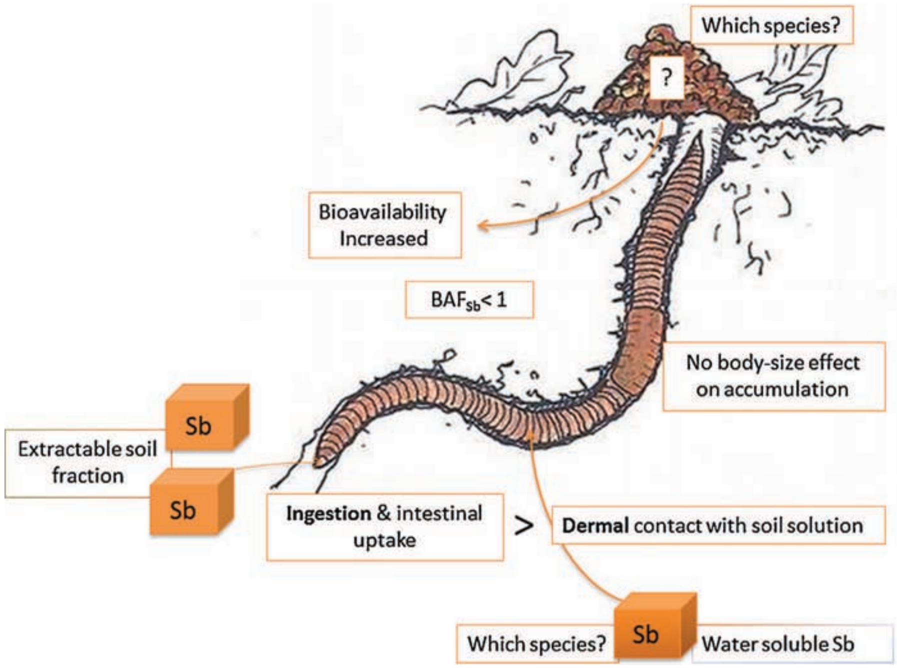


Fig. 2. Antimony bioaccumulation in earthworms. Original earthworm drawing (www.onf.fr). BAF$_{Sb}$ = bioaccumulation factor of Sb.

amphibians (2.3 mg kg^{-1} dry wt.) [147]. Some terrestrial invertebrate such as earthworms have already been shown to accumulate Sb [54]. Such disparity could be explained by differences in Sb compartmentation (in particular, soil organic matter influence) or speciation and in diet of these living organisms (soil consumption, water filtration, *etc.*). The same authors [147] also reported high Sb concentrations in *Acrida chinensis* and *Pheretima aspergillum*: 17.3 and 43.6 mg kg^{-1}, respectively, within 1 km of an Sb mining area. Pauget et al. [148] noted the high availability of Sb to snails, at three industrially impacted sites in northern France. They studied Sb accumulation kinetics from the soil into these organisms, and showed that $CaCl_2$ extract concentrations were the best predictors of Sb bioaccumulation. As noted earlier, organic matter (OM) participates in Sb availability, and the relatively high level of OM in their study area (up to 10%) could partially explain such results.

Up to the present, there is no data available concerning Sb accumulation in other living macro/meso-organisms in the soil compartment. It is, therefore, difficult to precisely identify the possible pathway of Sb through the food chain.

5. Human health risks assessment

People working with Sb compounds are subject to Sb inhalation, mostly antimony trioxide. For the rest of the population, food represents the predominant source of Sb exposure. Its absorption through the digestive tract has been estimated between 5 and 20% of the total Sb content ingested [149]. In 1992, urban dwellers were exposed to about 60–460 ng day^{-1} through inhalation [150]. Nowadays, this value has certainly increased with the increase of Sb uses (since 1992) around the world.

5.1. Food-chain biomagnification

Antimony biomagnification has not been investigated much as yet, but some studies have intended to evaluate this parameter [151,152]. However, these studies did not discover any evidence of Sb accumulation across the food chain, but their intention was not necessarily to assess trophic linkage. Therefore, this conclusion is not guaranteed. In any case, biomagnification only considers the xenobiotic accumulation in an organism through its daily alimentation [153]. For example, as shown earlier (*cf.* §4.2), some fungi have been identified as Sb hyperaccumulators [101], with concentration exceeding 1400 mg kg^{-1} in the fruiting body of *C. piperatus*. Consequently, they can become Sb sources in the food web, through slugs, then ducks or chickens, and then humans (or directly to human beings in the case of mushroom consumption). Nevertheless, these organisms are more sensitive to soil contamination than aerial deposition because of the short fruiting period (10–14 day) in which they could accumulate metalloids from dusts. However, it would be necessary to consider other sources of Sb exposure (inhalation, skin contact, *etc.*), and to focus not only on the biomagnification factor but also on the bioaccumulation factor, which takes into account every kind of exposure. Investigations need to be performed on the transfer of Sb from cereals, such as wheat and maize (which are known to accumulate Sb up to 700 mg kg^{-1}), to poultry and livestock, in order to give clues about the risk of transfer through the plant–meat–human food chain. However, little risk of Sb bioaccumulation seems to exist for herbivores, even when their grassland diet suffered major contamination near an Sb smelter [154]. Indeed, rabbits and voles presented relatively high levels of Sb in different organs (0.30 and 0.68 mg–kg^{-1} DW in voles and rabbit Liver respectively) when they fed in contaminated sites (<250 m). However, these concentrations were considered not be harmful as laboratory animals (mice and voles) presented no visible diseases when fed with even higher concentrations than in contaminated grasslands (<0.02–8.6 mg kg^{-1} DW when fed with 6700 mg of Sb per kg DW); except in mice liver which could accumulate Sb up to 46.2 mg kg^{-1} DW [84]. Same authors nonetheless suggest investigating longevity, resistance to stresses and breeding success in field experiment to complete their study. It will also be necessary to focus on soil–livestock Sb transfer, because their daily soil intake can be potentially high (up to 30% for sheep) [155]. Although no data have been published on Sb transfer from soil to cattle, the previous study on As also showed that 34 to 90% of animal intake comes from ingestion of polluted soil particles.

Concerning aquatic ecosystems, much information can be found in the review published by Filella et al. [32] about the different types of Sb speciation, transfer and pathways, with a focus on microbiota interactions. At the macrobiotic scale [156], antimony concentration in freshwater fish (Crucian, carp, wild carp, grass carp, herring, and bighead carp) can reach $809 \pm 360\,\mu g\,kg^{-1}{}_{DW}$.This might be due to highly contaminated algae (>11 mg kg^{-1}) consumption. This demonstrates that Sb could transfer and accumulate through these fish up to human beings.

Antimony can also reach human directly through food packages (plastic, ceramic, drinking cup, *etc.*) as it is used in alloy during the production processes. An accurate method has therefore been developed to measure Sb in the leaching of these packages and showed concentrations about 1.6 mg L^{-1} [157].

Consequently, many fields of investigation need to be clarified, to permit a good understanding of Sb behavior in the environment (soil, water, and living organisms), and through the food chain.

5.2. Human bioaccessibility of Sb

The human bioaccessible fraction of a metal(loid) is defined as the fraction extracted by the entire digestive system when it is ingested with polluted soil [158], or polluted vegetables [20,21]. A standardized bioaccessibility test has been developed by the BioAccessibility Research Group of Europe (BARGE): the Unified BARGE Method (UBM) [159]. The UBM simulates the digestion process with synthetic digestive solutions (mouth, gastric and gastrointestinal). It mimics all the chemical reactions occurring throughout the digestive tract, with appropriate physiological transit times and temperatures [160]. It has been validated with *in-vivo* tests for As, Cd and Pb in contaminated soils, with the measurement of these elements at four endpoints (kidney, liver, bone, and urine), in swine grown and fed with such polluted soils in their diet [161]. However, the UBM for Sb did not achieve validation *in-vivo*, except in urine, because of its low concentration in soil samples. Nevertheless, using the measured bioaccessibility it is then possible to evaluate and approach the human bioavailability of Sb.

Different studies focused on the daily intake of Sb by measuring the total Sb concentration in aliments eaten by Chinese people (between 0.252 and 9.3 $\mu g(kg\,bw)^{-1}$; details in Supplementary material Table A.4) [95,162]. However, as with almost every value cited in the literature (Table 3), they were concerned with total Sb content, but give very little information as to speciation and human bioaccessibility and bioavailability in the case of consuming polluted vegetables.

Recently, some studies focused on Sb bioaccessibility and ecotoxicity, in relation to soil remediation [159] and Sb bioaccessibility in vegetables, with regard to the context of the pollution (polluted soil or atmosphere) and plant species [20,21]. Gastric Sb bioaccessibility was 14% and 43% for spinach and cabbage, respectively. Such variations could come from differences in leaf morphology, and/or changes in Sb speciation throughout the plant [23].

Currently it remains unclear how Sb will transit through the different nodes of the food web. The question arising then is: are these Sb compounds bioaccessible to humans when digested? If they are, in what proportions, and what are the species absorbed? Finally, what about their toxicity, and what are the risks of eating vegetables grown in contaminated soils, such as urban and peri-urban soils, where the metal(loid) levels are increasingly alarming?

6. Conclusion and perspectives

The present review gathers the current state of knowledge on Sb behavior in edible plants, and the factors affecting it in the context of polluted arable lands and urban areas. While a portion of urban and peri-urban soils are used for agriculture, Sb production has been increasing continuously for 50 years (~55,000 t/year in 1960; 163,000 t/year in 2013) leading to an increasing risk for human health. Many contamination sources exist, and gardeners' cultural practices could participate in transferring Sb from soil to plants. Such practices can lead to sanitary consequences, as shown by Sb values found in some edible plants grown on polluted soils (Tables 3 and 4).

The major issue is the lack of data concerning Sb values, speciation and compartmentation in vegetables, as well as its behavior with arbuscular mycorrhizal fungi, such organisms being known to play a major role in metal(loid) transfer at the soil–plant interface. Actually, there is still no legal threshold for Sb in edible plants. Thus fields of investigation are proposed to complete our understanding of the health risks when growing food in Sb-contaminated soils.

Research needs to focus on the immobilization and transfer mechanisms of metal(loid)s such as Sb, in order to develop future strategies and guidelines for sustainable agriculture and urban agriculture. For example, a better understanding of the different pathways and interactions could lead to solutions for gardeners, such as crop association or rotation adapted to their soil contamination. To choose plant species according to their potential to absorb or exclude a few inorganic elements and to choose fertilizers and amendments in function of their composition, could enable plant quality and soil ecosystemic services to be optimized. Measuring Sb human bioaccessibility in edible plants, and modeling such transfers at soil–plant–human interfaces are finally fields of investigation to integrate into future experiments and risk assessments.

Acknowledgment

This work has received support from the National Research Agency under reference ANR-12-0011-VBDU.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat.2015.02.011.

References

[1] M. He, X. Wang, F. Wu, Z. Fu, Antimony pollution in China, Sci. Total Environ. 421–422 (2012) 41–50, http://dx.doi.org/10.1016/j.scitotenv.2011.06.009.
[2] S.C. Wilson, P.V. Lockwood, P.M. Ashley, M. Tighe, The chemistry and behaviour of antimony in the soil environment with comparisons to arsenic: a critical review, Environ. Pollut. 158 (2010) 1169–1181, http://dx.doi.org/10.1016/j.envpol.2009.10.045.
[3] M. Krachler, J. Zheng, R. Koerner, C. Zdanowicz, D. Fisher, W. Shotyk, Increasing atmospheric antimony contamination in the northern hemisphere: snow and ice evidence from Devon Island, Arctic Canada, J. Environ. Monit. 7 (2005) 1169, http://dx.doi.org/10.1039/b509373b.
[4] B.J. Alloway, Heavy Metals in Soils, Blackie A. & P., London, 1995.
[5] BRGM, RP-61342-FR.pdf, BRGM (2012).
[6] D.C. Adriano, Trace Elements in the Terrestrial Environment, Springer, New York, 1986.
[7] G. Okkenhaug, K. Amstätter, H. Lassen Bue, G. Cornelissen, G.D. Breedveld, T. Henriksen, et al., Antimony (Sb) contaminated shooting range soil: Sb mobility and immobilization by soil amendments, Environ. Sci. Technol. 47 (2013) 6431–6439, http://dx.doi.org/10.1021/es302448k.
[8] E. Randich, W. Duerfeldt, W. McLendon, W. Tobin, A metallurgical review of the interpretation of a bullet lead compositional analysis, Forensic Sci. Int. 127 (2002) 174–191.
[9] R. Keto, Analysis and comparison of bullet leads by inductively-coupled plasma mass spectrometry, J. Forensic Sci. 44 (1999) 1020–1026.
[10] A.G. Ilgen, F. Majs, A.J. Barker, T.A. Douglas, T.P. Trainor, Oxidation and mobilization of metallic antimony in aqueous systems with simulated groundwater, Geochim. Cosmochim. Acta 132 (2014) 16–30, http://dx.doi.org/10.1016/j.gca.2014.01.019.
[11] N. Yang, H. Sun, Application of arsenic, antimony and bismuth in medicine, Prog. Chem. 21 (2009) 856–865.
[12] 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. 113 (2012) 100–105, http://dx.doi.org/10.1016/j.gexplo.2011.06.006.

[13] S.E. Wagner, F.J. Peryea, R.A. Filby, Antimony impurity in lead arsenate insecticide enhances the antimony content of old orchard soils, J. Environ. Qual. 32 (2003) 736–738.
[14] R. Edwards, N.W. Lepp, C. Jones, Other less abundant elements of potential environmental significance: antimony, in: Heavy Metals in Soils, second ed., Alloway, London, 1995.
[15] F. Fujiwara, R.J. Rebagliati, J. Marrero, D. Gómez, P. Smichowski, Antimony as a traffic-related element in size-fractionated road dust samples collected in Buenos Aires, Microchem. J. 97 (2011) 62–67, http://dx.doi.org/10.1016/j.microc.2010.05.006.
[16] C.L.S. Wiseman, F. Zereini, W. Püttmann, Traffic-related trace element fate and uptake by plants cultivated in roadside soils in Toronto, Canada, Sci. Total Environ. 442 (2013) 86–95, http://dx.doi.org/10.1016/j.scitotenv.2012.10.051.
[17] M. Shahid, T. Xiong, M. Castrec-Rouelle, T. Leveque, C. Dumat, Water extraction kinetics of metals, arsenic and dissolved organic carbon from industrial contaminated poplar leaves, J. Environ. Sci. 25 (2013) 2451–2459, http://dx.doi.org/10.1016/S1001-0742(12)60197-1.
[18] T. Leveque, Y. Capowiez, E. Schreck, C. Mazzia, M. Auffan, Y. Foucault, et al., Assessing ecotoxicity and uptake of metals and metalloids in relation to two different earthworm species (*Eiseina hortensis* and *Lumbricus terrestris*), Environ. Pollut. 179 (2013) 232–241, http://dx.doi.org/10.1016/j.envpol.2013.03.066.
[19] M. Shahid, E. Ferrand, E. Schreck, C. Dumat, Behavior and impact of zirconium in the soil–plant system: plant uptake and phytotoxicity, Rev. Environ. Contam. Toxicol. 221 (2013) 107–127, http://dx.doi.org/10.1007/978-1-4614-4448-0_2.
[20] T.-T. Xiong, T. Leveque, A. Austruy, S. Goix, E. Schreck, V. Dappe, et al., Foliar uptake and metal(loid) bioaccessibility in vegetables exposed to particulate matter, Environ. Geochem. Health (2014) 1–13, http://dx.doi.org/10.1007/s10653-014-9607-6.
[21] T.-T. Xiong, T. Leveque, M. Shahid, Y. Foucault, C. Dumat, Lead and cadmium phytoavailability and human bioaccessibility for vegetables exposed to soil or atmosphere pollution by process ultrafine particles, J. Environ. Qual. 43 (5) (2014) 1593–1600, http://dx.doi.org/10.2134/jeq2013.11.0469.
[22] E. Schreck, Y. Foucault, G. Sarret, S. Sobanska, L. Cécillon, M. Castrec-Rouelle, et al., Metal and metalloid foliar uptake by various plant species exposed to atmospheric industrial fallout: mechanisms involved for lead, Sci. Total Environ. 427–427 (2012) 253–262, http://dx.doi.org/10.1016/j.scitotenv.2012.03.051.
[23] E. Schreck, V. Dappe, G. Sarret, S. Sobanska, D. Nowak, J. Nowak, et al., Foliar or root exposures to smelter particles: consequences for lead compartmentalization and speciation in plant leaves, Sci. Total Environ. 476–477 (2014) 667–676, http://dx.doi.org/10.1016/j.scitotenv.2013.12.089.
[24] R.E. Galt, L.C. Gray, P. Hurley, Subversive and interstitial food spaces: transforming selves, societies, and society–environment relations through urban agriculture and foraging, Local Environ. 19 (2014) 133–146, http://dx.doi.org/10.1080/13549839.2013.832554.
[25] S. Gojard, F. Weber, Jardins, jardinage et autoconsommation alimentaire, INRA Sci. Soc. Rech. Écon. Soc. Rural 2 (1995) 4.
[26] E. Álvarez-Ayuso, V. Otones, A. Murciego, A. García-Sánchez, I.S. Regina, Antimony, arsenic and lead distribution in soils and plants of an agricultural area impacted by former mining activities, Sci. Total Environ. 439 (2012) 35–43, http://dx.doi.org/10.1016/j.scitotenv.2012.09.023.
[27] K.A. Winship, Toxicity of antimony and its compounds, Adverse Drug React. Acute Poisoning Rev. 6 (1987) 67–90.
[28] K. Kuroda, G. Endo, A. Okamoto, Y.S. Yoo, Genotoxicity of beryllium, gallium and antimony in short-term assays, Mutat. Res. Lett. 264 (1991) 163–170.
[29] T.W. Gebel, R.H. Suchenwirth, C. Bolten, H.H. Dunkelberg, Human biomonitoring of arsenic and antimony in case of an elevated geogenic exposure, Environ. Health Perspect. 106 (1998) 33.
[30] D. Beyersmann, A. Hartwig, Carcinogenic metal compounds: recent insight into molecular and cellular mechanisms, Arch. Toxicol. 82 (2008) 493–512, http://dx.doi.org/10.1007/s00204-008-0313-y.
[31] M. Filella, N. Belzile, Y.-W. Chen, Antimony in the environment: a review focused on natural waters: I. Occurrence, Earth-Sci. Rev. 57 (2002) 125–176, http://dx.doi.org/10.1016/S0012-8252(01)70-8.
[32] M. Filella, N. Belzile, M.-C. Lett, Antimony in the environment: a review focused on natural waters III. Microbiota relevant interactions, Earth-Sci. Rev. 80 (2007) 195–217, http://dx.doi.org/10.1016/j.earscirev.2006.09.003.
[33] WHO, Guidelines for drinking-water quality, in: Incorporating First and Second Addenda, third ed., WHO, Geneva, 2008 (accessed 09.12.13) https://extranet.who.int/iris/restricted/handle/10665/75376
[34] S.A. Mansour, M.H. Belal, A.A.K. Abou-Arab, H.M. Ashour, M.F. Gad, Evaluation of some pollutant levels in conventionally and organically farmed potato tubers and their risks to human health, Food Chem. Toxicol. 47 (2009) 615–624, http://dx.doi.org/10.1016/j.fct.2008.12.019.
[35] X. Wan, S. Tandy, K. Hockmann, R. Schulin, Changes in Sb speciation with waterlogging of shooting range soils and impacts on plant uptake, Environ. Pollut. 172 (2013) 53–60, http://dx.doi.org/10.1016/j.envpol.2012.08.010.
[36] G. Okkenhaug, Y.-G. Zhu, L. Luo, M. Lei, X. Li, J. Mulder, Distribution, speciation and availability of antimony (Sb) in soils and terrestrial plants from an active Sb mining area, Environ. Pollut. 159 (2011) 2427–2434, http://dx.doi.org/10.1016/j.envpol.2011.06.028.
[37] M.A. Radwan, A.K. Salama, Market basket survey for some heavy metals in Egyptian fruits and vegetables, Food Chem. Toxicol. 44 (2006) 1273–1278, http://dx.doi.org/10.1016/j.fct.2006.02.004.
[38] K. Cooper, L. Marshall, L. Vanderlinden, F. Ursitti, Early Exposures to Hazardous Chemicals/Pollution and Associations with Chronic Disease: a Scoping Review, 2011.
[39] R. Feng, C. Wei, S. Tu, Y. Ding, R. Wang, J. Guo, The uptake and detoxification of antimony by plants: a review, Environ. Exp. Bot. 96 (2013) 28–34, http://dx.doi.org/10.1016/j.envexpbot.2013.08.006.
[40] T.T. Doan, C. Bouvier, Y. Bettarel, T. Bouvier, T. Henry-des-Tureaux, J.L. Janeau, et al., Influence of buffalo manure, compost, vermicompost and biochar amendments on bacterial and viral communities in soil and adjacent aquatic systems, Appl. Soil Ecol. 73 (2014) 78–86, http://dx.doi.org/10.1016/j.apsoil.2013.08.016.
[41] T. Leveque, Y. Capowiez, E. Schreck, T.-T. Xiong, Y. Foucault, C. Dumat, Earthworm bioturbation influences the phytoavailability of metals released by particles in cultivated soils, Environ. Pollut. (2014), http://dx.doi.org/10.1016/j.envpol.2014.04.005.
[42] T. Kangwankraiphaisan, K. Suntornvongsagul, P. Sihanonth, W. Klysubun, G.M. Gadd, Influence of arbuscular mycorrhizal fungi (AMF) on zinc biogeochemistry in the rhizosphere of *Lindenbergia philippensis* growing in zinc-contaminated sediment, BioMetals 26 (2013) 489–505, http://dx.doi.org/10.1007/s10534-013-9634-2.
[43] M. Tschan, B.H. Robinson, R. Schulin, Antimony in the soil–plant system—a review, Environ. Chem. 6 (2009) 106, http://dx.doi.org/10.1071/EN08111.
[44] Environmental Protection Agency, 1989 Toxics Release Inventory data for All US States and Territories, 1989.
[45] M. Shahid, E. Pinelli, C. Dumat, Review of Pb availability and toxicity to plants in relation with metal speciation; role of synthetic and natural organic ligands, J. Hazard. Mater. 219–220 (2012) 1–12, http://dx.doi.org/10.1016/j.jhazmat.2012.01.060.
[46] M. Tella, Impact de la matière organique sur le transport de l'antimoine dans les eaux naturelles: étude expérimentale et modélisation physico-chimique, 2009. http://core.kmi.open.ac.uk/download/pdf/12094030pdf (accessed 19.11.14).
[47] M. He, Distribution and phytoavailability of antimony at an antimony mining and smelting area, Hunan, China, Environ. Geochem. Health 29 (2007) 209–219, http://dx.doi.org/10.1007/s10653-006-9066-9.
[48] Y. Foucault, Réhabilitation écologique et gestion durable d'un site industriel urbain: cas d'une pollution historique en éléments inorganiques potentiellement toxiques (Pb, Cd, Zn, Cu, Sb et As, (2013)). http://ethesis.inp-toulouse.fr/archive/00002412/ (accessed 02.09.14).
[49] C.A. Johnson, H. Moench, P. Wersin, P. Kugler, C. Wenger, Solubility of Antimony and other elements in samples taken from shooting ranges, J. Environ. Qual. 34 (2005) 248–254.
[50] J. Xi, M. He, G. Zhang, Antimony adsorption on kaolinite in the presence of competitive anions, Environ. Earth Sci. 71 (2014) 2989–2997, http://dx.doi.org/10.1007/s12665-013-2673-8.
[51] K. Müller, B. Daus, J. Mattusch, H.-J. Stärk, R. Wennrich, Simultaneous determination of inorganic and organic antimony species by using anion exchange phases for HPLC–ICP-MS and their application to plant extracts of *Pteris vittata*, Talanta 78 (2009) 820–826, http://dx.doi.org/10.1016/j.talanta.2008.12.059.
[52] B. Wen, H. Xiao-yu, L. Ying, W. Wei-sheng, The role of earthworm (Eisenia fetida) in influencing bioavailability of heavy metals in soils, Biol. Fertil. Soils (2004) 181–187, http://dx.doi.org/10.1007/s00374-004-0761-3.
[53] M. Duran, Y. Kara, G.K. Akyildiz, A. Ozdemir, Antimony and heavy metals accumulation in some macroinvertebrates in the Yesilirmak River (N Turkey) near the Sb-mining area, Bull. Environ. Contam. Toxicol. 78 (2007) 395–399, http://dx.doi.org/10.1007/s00128-007-9183-x.
[54] N. Ainsworth, J.A. Cooke, M.S. Johnson, Distribution of Sb in contaminated grasslands 2: small mammals and invertebrates (1990).
[55] R. Feng, X. Wang, C. Wei, S. Tu, The accumulation and subcellular distribution of arsenic and antimony in four fern plants, Int. J. Phytorem. 17 (2013) 348–354, http://dx.doi.org/10.1080/15226514.2013.773281.
[56] Z. Huang, X.-D. Pan, P.-G. Wu, J.-L. Han, Q. Chen, Heavy metals in vegetables and the health risk to population in Zhejiang, China, Food Control 36 (2014) 248–252, http://dx.doi.org/10.1016/j.foodcont.2013.08.036.
[57] W. Hammel, R. Debus, L. Steubing, Mobility of antimony in soil and its availability to plants, Chemosphere 41 (2000) 1791–1798, http://dx.doi.org/10.1016/S0045-6535(00)37-0.
[58] H.C. Flynn, A.A. Meharg, P.K. Bowyer, G.I. Paton, Antimony bioavailability in mine soils, Environ. Pollut. 124 (2003) 93–100.
[59] Y. Nakamaru, K. Tagami, S. Uchida, Antimony mobility in Japanese agricultural soils and the factors affecting antimony sorption behavior, Environ. Pollut. 141 (2006) 321–326, http://dx.doi.org/10.1016/j.envpol.2005.08.040.
[60] A.M. Murciego, A.G. Sánchez, M.A.R. González, E.P. Gil, C.T. Gordillo, J.C. Fernández, et al., Antimony distribution and mobility in topsoils and plants (*Cytisus striatus*, *Cistus ladanifer* and *Dittrichia viscosa*) from polluted Sb-mining areas in Extremadura (Spain), Environ. Pollut. 145 (2007) 15–21, http://dx.doi.org/10.1016/j.envpol.2006.04.004.
[61] S. Rakshit, D. Sarkar, P. Punamiya, R. Datta, Antimony sorption at gibbsite–water interface, Chemosphere 84 (2011) 480–483, http://dx.doi.org/10.1016/j.chemosphere.2011.03.028.

[62] W. Xu, H. Wang, R. Liu, X. Zhao, J. Qu, The mechanism of antimony(III) removal and its reactions on the surfaces of Fe–Mn binary oxide, J. Colloid Interface Sci. 363 (2011) 320–326, http://dx.doi.org/10.1016/j.jcis.2011.07.026.
[63] G.A. Diemar, M. Filella, P. Leverett, P.A. Williams, Dispersion of antimony from oxidizing ore deposits, Pure Appl. Chem. 81 (2009), http://dx.doi.org/10.1351/PAC-CON-08-10-21.
[64] A.J. Roper, P.A. Williams, M. Filella, Secondary antimony minerals: phases that control the dispersion of antimony in the supergene zone, Chem. Erde – Geochem. 72 (2012) 9–14, http://dx.doi.org/10.1016/j.chemer.2012.01.005.
[65] M. Tighe, P. Lockwood, S. Wilson, Adsorption of antimony(V) by floodplain soils amorphous iron(III) hydroxide and humic acid, J. Environ. Monit. 7 (2005) 1177, http://dx.doi.org/10.1039/b508302h.
[66] J. Xi, M. He, C. Lin, Adsorption of antimony(V) on kaolinite as a function of pH, ionic strength and humic acid, Environ Earth Sci. 60 (2010) 715–722, http://dx.doi.org/10.1007/s12665-009-0209-z.
[67] A.G. Ilgen, 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. 46 (2012) 843–851, http://dx.doi.org/10.1021/es203027v.
[68] M.W.H. Evangelou, K. Hockmann, R. Pokharel, A. Jakob, R. Schulin, Accumulation of Sb, Pb, Cu, Zn and Cd by various plants species on two different relocated military shooting range soils, J. Environ. Manage. 108 (2012) 102–107, http://dx.doi.org/10.1016/j.jenvman.2012.04.044.
[69] H. Hou, N. Yao, J.N. Li, Y. Wei, L. Zhao, J. Zhang, et al., Migration and leaching risk of extraneous antimony in three representative soils of China: lysimeter and batch experiments, Chemosphere 93 (2013) 1980–1988, http://dx.doi.org/10.1016/j.chemosphere.2013.07.017.
[70] K. Müller, B. Daus, J. Mattusch, D. Vetterlein, I. Merbach, R. Wennrich, Impact of arsenic on uptake and bio-accumulation of antimony by arsenic hyperaccumulator *Pteris vittata*, Environ. Pollut. 174 (2013) 128–133, http://dx.doi.org/10.1016/j.envpol.2012.10.024.
[71] M. Uchimiya, D.I. Bannon, L.H. Wartelle, Retention of heavy metals by carboxyl functional groups of biochars in small arms range soil, J. Agric. Food Chem. 60 (2012) 1798–1809, http://dx.doi.org/10.1021/jf2047898.
[72] M. Ahmad, S.S. Lee, J.E. Lim, S.-E. Lee, J.S. Cho, D.H. Moon, et al., Speciation and phytoavailability of lead and antimony in a small arms range soil amended with mussel shell, cow bone and biochar: EXAFS spectroscopy and chemical extractions, Chemosphere 95 (2014) 433–441, http://dx.doi.org/10.1016/j.chemosphere.2013.09.077.
[73] M. Shahid, E. Pinelli, B. Pourrut, J. Silvestre, C. Dumat, Lead-induced genotoxicity to *Vicia faba* L. roots in relation with metal cell uptake and initial speciation, Ecotoxicol. Environ. Saf. 74 (2011) 78–84, http://dx.doi.org/10.1016/j.ecoenv.2010.08.037.
[74] M. Shahid, C. Dumat, B. Pourrut, M. Sabir, E. Pinelli, Assessing the effect of metal speciation on lead toxicity to *Vicia faba* pigment contents, J. Geochem. Explor. (2014), http://dx.doi.org/10.1016/j.gexplo.2014.01.003.
[75] A. Austruy, M. Shahid, T. Xiong, M. Castrec, V. Payre, N.K. Niazi, et al., Mechanisms of metal-phosphates formation in the rhizosphere soils of pea and tomato: environmental and sanitary consequences, J. Soils Sediments 14 (2014) 666–678, http://dx.doi.org/10.1007/s11368-014-0862-z.
[77] M. Iqbal, A. Saeed, R.G.J. Edyvean, Bioremoval of antimony(III) from contaminated water using several plant wastes: optimization of batch and dynamic flow conditions for sorption by green bean husk (*Vigna radiata*), Chem. Eng. J. 225 (2013) 192–201, http://dx.doi.org/10.1016/j.cej.2013.03.079.
[78] M. Dodd, S.L. Grundy, K.J. Reimer, W.R. Cullen, Methylated antimony(V) compounds: synthesis, hydride generation properties and implications for aquatic speciation, Appl. Organomet. Chem. 6 (1992) 207–211, http://dx.doi.org/10.1002/aoc.590060215.
[79] R.O. Jenkins, P.J. Craig, W. Goessler, D. Miller, N. Ostah, K.J. Irgolic, Biomethylation of inorganic antimony compounds by an aerobic fungus: *Scopulariopsis brevicaulis*, Environ. Sci. Technol. 32 (1998) 882–885.
[80] J. Lintschinger, O. Schramel, A. Kettrup, The analysis of antimony species by using ESI–MS and HPLC–ICP-MS, Fresenius J. Anal. Chem. 361 (1998) 96–102, http://dx.doi.org/10.1007/s002160050841.
[81] M. Vithanage, A.U. Rajapaksha, X. Dou, N.S. Bolan, J.E. Yang, Y.S. Ok, Surface complexation modeling and spectroscopic evidence of antimony adsorption on iron-oxide-rich red earth soils, J. Colloid Interface Sci. 406 (2013) 217–224, http://dx.doi.org/10.1016/j.jcis.2013.05.053.
[82] S. Steely, D. Amarasiriwardena, B. Xing, An investigation of inorganic antimony species and antimony associated with soil humic acid molar mass fractions in contaminated soils, Environ. Pollut. 148 (2007) 590–598, http://dx.doi.org/10.1016/j.envpol.2006.11.031.
[83] V. Ettler, M. Mihaljevič, O. Šebek, Z. Nechutný, Antimony availability in highly polluted soils and sediments—a comparison of single extractions, Chemosphere 68 (2007) 455–463, http://dx.doi.org/10.1016/j.chemosphere.2006.12.085.
[84] N. Ainsworth, J.A. Cooke, M.S. Johnson, Biological significance of antimony in contaminated grassland, Water Air Soil Pollut. 57 (1991) 193–199.
[85] M. Tschan, B.H. Robinson, M. Nodari, R. Schulin, Antimony uptake by different plant species from nutrient solution, agar and soil, Environ. Chem. 6 (2009) 144–152.
[86] O.I. Sanders, C. Rensing, M. Kuroda, B. Mitra, B.P. Rosen, Antimonite is accumulated by the glycerol facilitator GlpF in *Escherichia coli*, J. Bacteriol. 179 (1997) 3365–3367.
[87] R. Mukhopadhyay, H. Bhattacharjee, B.P. Rosen, Aquaglyceroporins: generalized metalloid channels, Biochim. Biophys. Acta (BBA) – Gen. Subj. 1840 (2014) 1583–1591, http://dx.doi.org/10.1016/j.bbagen.2013.11.021.
[88] T. Kamiya, T. Fujiwara, Arabidopsis NIP1;1 transports antimonite and determines antimonite sensitivity, Plant Cell Physiol. 50 (2009) 1977–1981, http://dx.doi.org/10.1093/pcp/pcp130.
[89] R. Tisarum, J.T. Lessl, X. Dong, L.M. de Oliveira, B. Rathinasabapathi, L.Q. Ma, Antimony uptake, efflux and speciation in arsenic hyperaccumulator *Pteris vittata*, Environ. Pollut. 186 (2014) 110–114, http://dx.doi.org/10.1016/j.envpol.2013.11.033.
[90] M. Krachler, H. Emons, J. Zheng, Speciation of antimony for the 21st century: promises and pitfalls, TrAC Trends Anal. Chem. 20 (2001) 79–90.
[91] I. Shtangeeva, E. Steinnes, S. Lierhagen, Uptake of different forms of antimony by wheat and rye seedlings, Environ. Sci. Pollut. Res. 19 (2012) 502–509, http://dx.doi.org/10.1007/s11356-011-0589-y.
[92] M. Koreňovská, Determination of arsenic antimony, and selenium by FI-HG-AAS in foods consumed in Slovakia, J. Food Nutr. Res. 45 (2006) 84–88.
[93] M.-C. Affholder, P. Prudent, V. Masotti, B. Coulomb, J. Rabier, B. Nguyen-The, et al., Transfer of metals and metalloids from soil to shoots in wild rosemary (*Rosmarinus officinalis* L.) growing on a former lead smelter site: human exposure risk, Sci. Total Environ. 454–455 (2013) 219–229, http://dx.doi.org/10.1016/j.scitotenv.2013.02.086.
[94] F.J. Zhao, J.F. Ma, A.A. Meharg, S.P. McGrath, Arsenic uptake and metabolism in plants, New Phytol. 181 (2009) 777–794, http://dx.doi.org/10.1111/j.1469-8137.2008.02716. x.
[95] F. Wu, Z. Fu, B. Liu, C. Mo, B. Chen, W. Corns, et al., Health risk associated with dietary co-exposure to high levels of antimony and arsenic in the world's largest antimony mine area, Sci. Total Environ. 409 (2011) 3344–3351, http://dx.doi.org/10.1016/j.scitotenv.2011.05.033.
[96] Y.-W. Baek, W.-M. Lee, S.-W. Jeong, Y.-J. An, Ecological effects of soil antimony on the crop plant growth and earthworm activity, Environ. Earth Sci. (2013), http://dx.doi.org/10.1007/s12665-013-2492-y.
[101] J. Borovička, Z. Řanda, E. Jelínek, Antimony content of macrofungi from clean and polluted areas, Chemosphere 64 (2006) 1837–1844, http://dx.doi.org/10.1016/j.chemosphere.2006.01.060.
[102] P.D. Alexander, B.J. Alloway, A.M. Dourado, Genotypic variations in the accumulation of Cd, Cu, Pb and Zn exhibited by six commonly grown vegetables, Environ. Pollut. 144 (2006) 736–745, http://dx.doi.org/10.1016/j.envpol.2006.03.001.
[103] G. Levresse, G. Lopez, J. Tritlla, E.C. López, A.C. Chavez, E.M. Salvador, et al., Phytoavailability of antimony and heavy metals in arid regions: the case of the Wadley Sb district (San Luis, Potosí, Mexico), Sci. Total Environ. 427–428 (2012) 115–125, http://dx.doi.org/10.1016/j.scitotenv.2012.04.020.
[104] N.G. Dowling, S.M. Greenfield, K.S. Fischer, Sustainability of Rice in the Global Food System, International Rice Research Institute, 1998.
[105] M.J. Abedin, M.S. Cresser, A.A. Meharg, J. Feldmann, J. Cotter-Howells, Arsenic accumulation and metabolism in rice (*Oryza sativa* L.), Environ. Sci. Technol. 36 (2002) 962–968, http://dx.doi.org/10.1021/es0101678.
[106] J. Ren, L.Q. Ma, H. Sun, F. Cai, J. Luo, Antimony uptake, translocation and speciation in rice plants exposed to antimonite and antimonate, Sci. Total Environ. 475 (2014) 83–89, http://dx.doi.org/10.1016/j.scitotenv.2013.12.103.
[107] Y. Huang, Z. Chen, W. Liu, Influence of iron plaque and cultivars on antimony uptake by and translocation in rice (*Oryza sativa* L.) seedlings exposed to Sb(III) or Sb(V), Plant Soil 352 (2012) 41–49, http://dx.doi.org/10.1007/s11104-011-0973-x.
[108] A.A. Meharg, L. Jardine, Arsenite transport into paddy rice (*Oryza sativa*) roots, New Phytol. 157 (2003) 39–44, http://dx.doi.org/10.1046/j.1469-8137.2003.00655.x.
[109] G. Okkenhaug, Y.-G. Zhu, J. He, X. Li, L. Luo, J. Mulder, Antimony (Sb) and arsenic (As) in Sb mining impacted paddy soil from Xikuangshan, China: differences in mechanisms controlling soil sequestration and uptake in rice, Environ Sci. Technol. 46 (2012) 3155–3162, http://dx.doi.org/10.1021/es2022472.
[110] M. He, J. Yang, Effects of different forms of antimony on rice during the period of germination and growth and antimony concentration in rice tissue, Sci. Total Environ. 243–244 (1999) 149–155, http://dx.doi.org/10.1016/S0048-9697(99)370-8.
[111] B.L. Batista, V.C. De Oliveira Souza, F.G. Da Silva, F. Barbosa Jr., Survey of 13 trace elements of toxic and nutritional significance in rice from Brazil and exposure assessment, Food Addit. Contam. Part B. 3 (2010) 253–262, http://dx.doi.org/10.1080/19393210.2010.516024.
[112] GB 5749, Standards for drinking water quality (2006).
[113] USEPA, Drinking water regulations and health advisories, Washington (2006).
[114] WHO, Antimony in Drinking-Water—Background Document for Development WHO Guidelines for Drinking-Water Quality, WHO, Geneva, 2003 (accessed 09.12.13) https://extranet.who.int/iris/restricted/handle/10665/75376
[115] B. Pourrut, M. Shahid, C. Dumat, P. Winterton, E. Pinelli, Lead uptake, toxicity, and detoxification in plants, in: D.M. Whitacre (Ed.), Reviews of Environmental Contamination and Toxicology, vol. 213, Springer, New York, 2011, pp. 113–136 (accessed 10.04.14) http://link.springer.com/chapter/10.1007/978-1-4419-9860-6_4
[116] A.G. Oomen, C.J.M. Rompelberg, M.A. Bruil, C.J.G. Dobbe, D.P.K.H. Pereboom, A.J.A.M. Sips, Development of an in vitro digestion model for estimating the

bioaccessibility of soil contaminants, Arch. Environ. Contam. Toxicol. 44 (2003) 281–287, http://dx.doi.org/10.1007/s00244-002-1278-0.
[117] F. Baroni, A. Boscagli, G. Protano, F. Riccobono, Antimony accumulation in *Achillea ageratum*, *Plantago lanceolata* and *Silene vulgaris* growing in an old Sb-mining area, Environ. Pollut. 109 (2000) 347–352.
[118] L.Q. Ma, K.M. Komar, C. Tu, W. Zhang, Y. Cai, E.D. Kennelley, A fern that hyperaccumulates arsenic, Nature 409 (2001) 579, http://dx.doi.org/10.1038/35054664.
[119] C. Pérez-Sirvent, M.J. Martínez-Sánchez, S. Martínez-López, J. Bech, N. Bolan, Distribution and bioaccumulation of arsenic and antimony in *Dittrichia viscosa* growing in mining-affected semiarid soils in southeast Spain, J. Geochem. Explor. 123 (2012) 128–135, http://dx.doi.org/10.1016/j.gexplo.2012.08.002.
[120] E. Schreck, C. Laplanche, M. Le Guédard, J.-J. Bessoule, A. Austruy, T. Xiong, et al., Influence of fine process particles enriched with metals and metalloids on *Lactuca sativa* L. leaf fatty acid composition following air and/or soil–plant field exposure, Environ. Pollut. 179 (2013) 242–249, http://dx.doi.org/10.1016/j.envpol.2013.04.024.
[121] C. Casiot, M. Ujevic, M. Munoz, J.L. Seidel, F. Elbaz-Poulichet, Antimony and arsenic mobility in a creek draining an antimony mine abandoned 85 years ago (upper Orb basin, France), Appl. Geochem. 22 (2007) 788–798, http://dx.doi.org/10.1016/j.apgeochem.2006.11.007.
[122] G. Norton, C. Deacon, A. Mestrot, J. Feldmann, P. Jenkins, C. Baskaran, et al., Arsenic speciation and localization in horticultural produce grown in a historically impacted mining region, Environ. Sci. Technol. 47 (2013) 6164–6172, http://dx.doi.org/10.1021/es400720r.
[123] B. Lange, M.-P. Faucon, P. Meerts, M. Shutcha, G. Mahy, O. Pourret, Prediction of the edaphic factors influence upon the copper and cobalt accumulation in two metallophytes using copper and cobalt speciation in soils, Plant Soil (2014), http://dx.doi.org/10.1007/s11104-014-2068-y.
[124] W. Jiang, G. Gou, Y. Ding, Influence of arbuscular mycorrhizal fungi on growth and mineral element absorption of chenglu hybrid bamboo seedlings, Pak. J. Bot. 45 (2013) 303–310.
[125] M.A. Abiala, O.O. Popoola, O.J. Olawuyi, J.O. Oyelude, A.O. Akanmu, A.S. Killani, et al., Harnessing the potentials of vesicular arbuscular mycorrhizal (VAM) fungi to plant growth–a review, Int. J. Pure Appl. Sci. Technol. 14 (2013) 61–79.
[126] M.C. Brundrett, Mycorrhizal associations and other means of nutrition of vascular plants: understanding the global diversity of host plants by resolving conflicting information and developing reliable means of diagnosis, Plant Soil 320 (2009) 37–77, http://dx.doi.org/10.1007/s11104-008-9877-9.
[127] S.E. Smith, F.A. Smith, Roles of arbuscular mycorrhizas in plant nutrition and growth: new paradigms from cellular to ecosystem scales, Annu. Rev. Plant Biol. 62 (2011) 227–250, http://dx.doi.org/10.1146/annurev-arplant-042110-103846.
[128] A.-R. Li, K.-Y. Guan, R. Stonor, S.E. Smith, F.A. Smith, Direct and indirect influences of arbuscular mycorrhizal fungi on phosphorus uptake by two root hemiparasitic Pedicularis species: do the fungal partners matter at low colonization levels? Ann. Bot. 112 (2013) 1089–1098, http://dx.doi.org/10.1093/aob/mct177.
[129] P. Hinsinger, C. Plassard, C. Tang, B. Jillard, Origins of root-mediated pH changes in the rhizosphere and their responses to environmental constraints: a review, Plant Soil 248 (2002) 43–59, http://dx.doi.org/10.1023/A.1022371130939.
[130] H. Amir, P. Jourand, Y. Cavaloc, M. Ducousso, Role of mycorrhizal fungi on the alleviation of heavy metal toxicity on plant, in: Mycorrhizal Fungi: Use in Sustainable Agriculture and Forestry, Springer, 2014.
[131] L.T. Danh, P. Truong, R. Mammucari, N. Foster, A critical review of the arsenic uptake mechanisms and phytoremediation potential of *Pteris vittata*, Int. J. Phytorem. 16 (2014) 429–453, http://dx.doi.org/10.1080/15226514.2013.798613.
[132] W. de, M. Rangel, J. Schneider, E.T. de, S. Costa, C.R.F.S. Soares, L.R.G. Guilherme, F.M. de, Moreira, phytoprotective effect of arbuscular mycorrhizal fungi species against arsenic toxicity in tropical leguminous species, Int. J. Phytorem. 16 (2014) 840–858, http://dx.doi.org/10.1080/15226514.2013.856852.
[133] V. Cozzolino, M. Pigna, V. Di Meo, A.G. Caporale, A. Violante, Effects of arbuscular mycorrhizal inoculation and phosphorus supply on the growth of *Lactuca sativa* L. and arsenic and phosphorus availability in an arsenic polluted soil under non-sterile conditions, Appl. Soil Ecol. 45 (2010) 262–268, http://dx.doi.org/10.1016/j.apsoil.2010.05.001.
[134] A. Sharma, H. Sharma, Role of vesicular arbuscular mycorrhiza in the mycoremediation of heavy toxic metals from soil, Int. J. Life Sci. Bt. Pharm. Res. 2 (2013) 2418–2431.
[135] W.R. Cullen, K.J. Reimer, Arsenic speciation in the environment, Chem. Rev. 89 (1989) 713–764, http://dx.doi.org/10.1021/cr00094a002.
[136] P. Andrewes, W.R. Cullen, J. Feldmann, I. Koch, E. Polishchunk, K.J. Reimer, The production of methylated organoantimony compounds by *Scopulariopsis brevicaulis*, Appl. Organomet. Chem. 12 (1998) 827–842.
[137] J. Tomko, M. Bačkor, M. Štofko, Biosorption of heavy metals by dry fungi biomass, Acta Metall. Slovaca 12 (2006) 447–451.
[138] L.K. Long, Q. Yao, J. Guo, R.H. Yang, Y.H. Huang, H.H. Zhu, Molecular community analysis of arbuscular mycorrhizal fungi associated with five selected plant species from heavy metal polluted soils, Eur. J. Soil Biol. 46 (2010) 288–294, http://dx.doi.org/10.1016/j.ejsobi.2010.06.003.
[139] A.M. Kavoo-wangi, E.M. Kahangi, E. Ateka, J. Onguso, R.W. Mukhongo, E.K. Mwangi, et al., Growth effects of microorganisms based commercial products inoculated to tissue cultured banana cultivated in three different soils in Kenya, Appl. Soil Ecol. 64 (2013) 152–162, http://dx.doi.org/10.1016/j.apsoil.2012.12.002.
[140] J. Beltrano, M. Ruscitti, M.C. Arango, M. Ronco, Effects of arbuscular mycorrhiza inoculation on plant growth, biological and physiological parameters and mineral nutrition in pepper grown under different salinity and p levels, J. Soil Sci. Plant Nutr. 13 (2013) 123–141.
[141] M.J. Sánchez-Blanco, T. Ferrández, M. Morales, A. Morte, J.J. Alarcón, Variations in water status gas exchange, and growth in *Rosmarinus officinalis* plants infected with *Glomus deserticola* under drought conditions, J. Plant Physiol. 161 (2004) 675–682.
[142] Q.-S. Wu, R.-X. Xia, Arbuscular mycorrhizal fungi influence growth, osmotic adjustment and photosynthesis of citrus under well-watered and water stress conditions, J. Plant Physiol. 163 (2006) 417–425, http://dx.doi.org/10.1016/j.jplph.2005.04.024.
[143] I. Zouari, A. Salvioli, M. Chialva, M. Novero, L. Miozzi, G.C. Tenore, et al., From root to fruit: RNA-Seq analysis shows that arbuscular mycorrhizal symbiosis may affect tomato fruit metabolism, BMC Genomics 15 (2014) 221.
[144] W.F. Chan, H. Li, F.Y. Wu, S.C. Wu, M.H. Wong, Arsenic uptake in upland rice inoculated with a combination or single arbuscular mycorrhizal fungi, J. Hazard. Mater. 262 (2013) 1116–1122, http://dx.doi.org/10.1016/j.jhazmat.2012.08.020.
[145] F. Nannoni, G. Protano, F. Riccobono, Uptake and bioaccumulation of heavy elements by two earthworm species from a smelter contaminated area in northern Kosovo, Soil Biol. Biochem. 43 (2011) 2359–2367, http://dx.doi.org/10.1016/j.soilbio.2011.08.002.
[146] B.-T. Lee, K.-W. Kim, Toxicokinetics and biotransformation of As(III) and As(V) in *Eisenia fetida*, Hum. Ecol. Risk Assess. Int. J. 19 (2013) 792–806, http://dx.doi.org/10.1080/10807039.2012.708285.
[147] Z. Fu, F. Wu, C. Mo, B. Liu, J. Zhu, Q. Deng, et al., Bioaccumulation of antimony, arsenic, and mercury in the vicinities of a large antimony mine, China, Microchem. J. 97 (2011) 12–19, http://dx.doi.org/10.1016/j.microc.2010.06.004.
[148] B. Pauget, F. Gimbert, M. Coeurdassier, N. Crini, G. Pérès, O. Faure, et al., Assessing the in situ bioavailability of trace elements to snails using accumulation kinetics, Ecol. Indic. 34 (2013) 126–135, http://dx.doi.org/10.1016/j.ecolind.2013.04.018.
[149] ANSES, Fiche 1: Evaluation des risques sanitaires liés au dépassement de la limite de qualité de l'antimoine dans les eaux destinées à la consommation humaine (2004).
[150] W. Slooff, P. Bont, J. Hesse, B. Loos, Exploratory report. Antimony and antimony compounds (1992). http://rivm.openrepository.com/rivm/handle/10029/261256 (accessed 26.11.14).
[151] L.M. Campbell, R.J. Norstrom, K.A. Hobson, D.C.G. Muir, S. Backus, A.T. Fisk, Mercury and other trace elements in a pelagic Arctic marine food web (Northwater Polynya, Baffin Bay), Sci. Total Environ. 351–352 (2005) 247–263, http://dx.doi.org/10.1016/j.scitotenv.2005.02.043.
[152] T. Ikemoto, N.P.C. Tu, N. Okuda, A. Iwata, K. Omori, S. Tanabe, et al., Biomagnification of trace elements in the aquatic food web in the mekong delta, South Vietnam using stable carbon and nitrogen isotope analysis, Arch. Environ. Contam. Toxicol. 54 (2007) 504–515, http://dx.doi.org/10.1007/s00244-007-9058-5.
[153] F. Gobas, H.A. Morrison, Bioconcentration and Biomagnification in the Aquatic Environment, Lewis Publishers, Boca Raton, FL, 2000 (accessed 4.12.13) http://research.rem.sfu.ca/downloads/rem-610/readings/gobas.pdf
[154] N. Ainsworth, J.A. Cooke, M.S. Johnson, Distribution of antimony in contaminated grassland: 2 – small mammals and invertebrates, Environ. Pollut. 65 (1990) 79–87, http://dx.doi.org/10.1016/0269-7491(90)90166-A.
[155] I. Thornton, P. Abrahams, Soil ingestion – a major pathway of heavy metals into livestock grazing contaminated land, Sci. Total Environ. 28 (1983) 287–294, http://dx.doi.org/10.1016/S0048-9697(83)80026-6.
[156] Z. Fu, F. Wu, D. Amarasiriwardena, C. Mo, B. Liu, J. Zhu, et al., Antimony, arsenic and mercury in the aquatic environment and fish in a large antimony mining area in Hunan, China, Sci. Total Environ. 408 (2010) 3403–3410, http://dx.doi.org/10.1016/j.scitotenv.2010.04.031.
[157] X. Jiang, S. Wen, G. Xiang, Cloud point extraction combined with electrothermal atomic absorption spectrometry for the speciation of antimony(III) and antimony(V) in food packaging materials, J. Hazard. Mater. 175 (2010) 146–150, http://dx.doi.org/10.1016/j.jhazmat.2009.09.141.
[158] G. Pascaud, T. Leveque, M. Soubrand, S. Boussen, E. Joussein, C. Dumat, Environmental and health risk assessment of Pb, Zn, As and Sb in soccer field soils and sediments from mine tailings: solid speciation and bioaccessibility, Environ. Sci. Pollut. Res. Int. 21 (2014) 4254–4264, http://dx.doi.org/10.1007/s11356-013-2297-2.
[159] Y. Foucault, T. Lévêque, T. Xiong, E. Schreck, A. Austruy, M. Shahid, et al., Green manure plants for remediation of soils polluted by metals and metalloids: ecotoxicity and human bioavailability assessment, Chemosphere 93 (2013) 1430–1435, http://dx.doi.org/10.1016/j.chemosphere.2013.07.040.
[160] S. Denys, K. Tack, J. Caboche, P. Delalain, Bioaccessibility, solid phase distribution, and speciation of Sb in soils and in digestive fluids,

Chemosphere 74 (2009) 711–716,
http://dx.doi.org/10.1016/j.chemosphere.2008.09.088.

[161] S. Denys, J. Caboche, K. Tack, G. Rychen, J. Wragg, M. Cave, et al., In vivo validation of the unified BARGE method to assess the bioaccessibility of arsenic, antimony, cadmium, and lead in soils, Environ. Sci. Technol. 46 (2012) 6252–6260, http://dx.doi.org/10.1021/es3006942.

[162] S.W. Cheung Chung, K.P. Kwong, J. Yau, W. Wong, Dietary exposure to antimony, lead and mercury of secondary school students in Hong Kong, Food Addit. Contam. Part A 25 (2008) 831–840, http://dx.doi.org/10.1080/02652030701697751.