



## Review

# The chemistry and behaviour of antimony in the soil environment with comparisons to arsenic: A critical review

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*A critical and comparative review of Sb and As chemistry and associations in soil systems identifies research directions needed for better understanding of risks.*

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## ABSTRACT

This article provides a critical review of the environmental chemistry of inorganic antimony (Sb) in soils, comparing and contrasting findings with those of arsenic (As). Characteristics of the Sb soil system are reviewed, with an emphasis on speciation, sorption and phase associations, identifying differences between Sb and As behaviour. Knowledge gaps in environmentally relevant Sb data for soils are identified and discussed in terms of the limitations this imposes on understanding the fate, behaviour and risks associated with Sb in environmental soil systems, with particular reference to mobility and bioavailability.

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## 1. Introduction

Antimony (Sb) and arsenic (As) are metalloids belonging to Group 15 of the periodic table. They both occur naturally in the environment at trace levels. Arsenic has long been recognised as a potentially harmful element, evidenced through its historic use as a popular poison (Azcue and Nriagu, 1994). Less is known about Sb effects. The understanding of its toxicity and environmental behaviour is much more limited (Filella et al., 2002a). Chemical similarities between the two metalloids have prompted concerns over the enrichment of this metalloid in many environments (Krachler et al., 2001; Filella et al., 2002a). Often Sb is considered to behave similarly to As, not always with justification (Casiot et al., 2007).

Antimony has a wide range of uses including the manufacture of semiconductors, diodes, flameproof retardants, lead hardener, batteries, small arms, tracer bullets, automobile brake linings, and pigments (Filella et al., 2002a). Antimony also remains the treatment of choice for several tropical protozoan diseases, such as leishmaniasis (Vasquez et al., 2006), and in treating HIV (Fowler and Goering, 1991). Arsenic is used industrially in the manufacture

of numerous products including glass, ceramics, electronics, cosmetics, and fireworks (Smith et al., 1998). In the latter half of the 20th century As was also widely used in pesticide and herbicide formulations and in wood preserving, although such use is now declining (Azcue and Nriagu, 1994).

World production for Sb is considerably larger than As. In 2008 estimated Sb mine output was 165,000 tonnes compared to 40,500 tonnes for As (U.S. Geological Survey, 2009). Environmental enrichment of both metalloids occurs naturally in areas of geological mineralisation, but also anthropogenically (Ragaini et al., 1977; McLaren et al., 1998; Filella et al., 2002a; Wilson et al., 2004; Douay et al., 2008; Telford et al., 2009) although the majority of Sb contamination appears to originate from mining and industrial emission sources, often smelting, co-occurring frequently with As (Telford et al., 2009).

Because of their identical  $s^2p^3$  outer orbital electron configuration, Sb and As display the same range of oxidation states in environmental systems (−3 to +5). Both most commonly occur as oxides, hydroxides or oxoanions either in the +5 state in relatively oxic environments (antimonates and arsenates) or in the +3 state in anoxic environments (antimonites and arsenites). Some common Sb and As species in the earth surface environment are shown in Table 1.

The toxicities of Sb and As in the environment strongly depend upon speciation (Gebel, 1997; Smith et al., 1998; Filella et al., 2002a). The general order of toxicity for Sb species is given as:

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**Table 1**  
Common Sb and As chemical species found in natural systems (Braman and Foreback, 1973; Dodd et al., 1992; Jenkins et al., 1998; Bhattacharya et al., 2002; Filella et al., 2002a,b).

	Sb		As	
	Name	Formula	Name	Formula
Minerals	Stibnite	Sb <sub>2</sub> S <sub>3</sub>	Arsenopyrite	FeAsS
	Valentinite	Sb <sub>2</sub> O <sub>3</sub> (orthorhombic)	Orpiment	As <sub>2</sub> S <sub>3</sub>
	Senarmontite	Sb <sub>2</sub> O <sub>3</sub> (cubic)	Realgar	AsS
	Cervantite	Sb <sub>2</sub> O <sub>4</sub>		
Aqueous species (+5 oxidation state)	Antimonic acid	Sb(OH) <sub>5</sub>	Arsenic acid	AsO(OH) <sub>3</sub> (or H <sub>3</sub> AsO <sub>4</sub> )
	Antimonate	Sb(OH) <sub>6</sub> <sup>-</sup> (or SbO <sub>3</sub> <sup>-</sup> )	Dihydrogen arsenate	AsO <sub>2</sub> (OH) <sub>2</sub> <sup>-</sup> (or H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup> )
			Monohydrogen arsenate	AsO <sub>3</sub> OH <sup>2-</sup> (or HAsO <sub>4</sub> <sup>2-</sup> )
Aqueous species (+3 oxidation state)	Antimonous acid	Sb(OH) <sub>3</sub> (or HSbO <sub>2</sub> )	Arsenous acid	As(OH) <sub>3</sub> (or H <sub>3</sub> AsO <sub>3</sub> )
	Antimonite	Sb(OH) <sub>2</sub> <sup>+</sup>	Arsenite	AsO(OH) <sub>2</sub> <sup>-</sup> (or H <sub>2</sub> AsO <sub>3</sub> <sup>-</sup> )
		Sb(OH) <sub>4</sub>		
				HAsO <sub>3</sub> <sup>2-</sup>
	Sulfidic complexes	H <sub>2</sub> Sb <sub>2</sub> S <sub>4</sub> HSb <sub>2</sub> S <sub>4</sub> <sup>-</sup> Sb <sub>2</sub> S <sub>4</sub> <sup>2-</sup>		
Gases	Stibine	SbH <sub>3</sub>	Arsine	AsH <sub>3</sub>
	Trimethylstibine	Sb(CH <sub>3</sub> ) <sub>3</sub>	Trimethylarsine	As(CH <sub>3</sub> ) <sub>3</sub>
Other methylated species	Methylstibonic acid (MSA)	(CH <sub>3</sub> )SbO(OH) <sub>2</sub>	Monomethylarsonic acid (MMAA)	CH <sub>3</sub> AsO(OH) <sub>2</sub>
	Dimethylstibonic acid (DMSA)	(CH <sub>3</sub> ) <sub>2</sub> Sb(O)OH	Dimethylarsinic acid (DMAA)	(CH <sub>3</sub> ) <sub>2</sub> As(O)OH
	Trimethylstiboxide	(CH <sub>3</sub> ) <sub>3</sub> Sb	Dimethylarsine	(CH <sub>3</sub> ) <sub>3</sub> As

Organoantimonials (e.g. methylated species) < antimonates (Sb (V)) < antimonites (Sb (III)) (Gebel, 1997; He and Yang, 1999; Krachler et al., 2001; Filella et al., 2002a).

This is similar to As:

Organoarsenicals (e.g. methylated species) < arsenates (As (V)) < arsenites (As (III)) (Yamauchi and Fowler, 1994).

It is debatable whether or not As is essential to human health, but there is no known human requirement for Sb (Smith et al., 1998; Bhattacharya et al., 2002; Shotyk et al., 2005). Both metalloids are clastogenic in the trivalent state, and have carcinogenic potential (Gebel, 1997). Both have a strong affinity for thiol groups and may substitute for P in biological reactions, which explains their inhibitory role in DNA replication and metabolic processes (ATSDR, 1992, 2000; Shotyk et al., 2005). There is evidence that As is detoxified via methylation in biological systems, but less evidence for the same process occurring for Sb (Gebel, 1997). Currently the World Health Organisation has set the Acceptable Daily Intake (ADI) for As at 2 µg kg<sup>-1</sup> day<sup>-1</sup> kg of body weight<sup>-1</sup> (WHO, 1989) and the Tolerable Daily Intake (TDI) for Sb at 6 µg kg<sup>-1</sup> day<sup>-1</sup> kg of body weight<sup>-1</sup> (WHO, 2003).

This review initially compares and contrasts Sb and As speciation in natural systems. Characteristics and interactions of the Sb soil system are then critically and comparatively reviewed with those of As, with an emphasis on speciation, sorption and phase associations, focussing on inorganic species. Because this review is not intended to be a review of As in soils (this has been undertaken comprehensively by other authors (Sadiq, 1997; Matera and Le Hecho, 2001; Smith et al., 1998), important findings for As are summarised first in individual sections and then comparatively discussed with Sb data available. Knowledge gaps and research needs for Sb in soil systems are identified.

## 2. Speciation in natural systems

### 2.1. Inorganic speciation in relation to pH and redox potential

System pH and redox largely determine metalloid oxidation state and environmental reactions in soil systems (Sadiq, 1997; Smith et al., 1998) and some broad similarities have been identified between As and Sb (Ashley et al., 2007). Arsenic and Sb species

present in any given system also depend upon the concentrations of co-occurring reductants and oxidants. However, the metalloid properties ensure their close association and strong bonding with oxygen and hydroxide in the environment with the oxyanionic form playing a central role in most environmental reactions.

Table 2 places some inorganic As and Sb redox reactions in the context of other common reactions that fall within the redox limits of natural systems (Lindsay, 1979; Brookins, 1988). When water-logging causes soil or sediment to become anoxic, the reduction half reactions shown in Table 2 commonly occur in sequence as microorganisms are progressively forced to select less energetic terminal electron acceptors for respiration reactions. This suggests that pentavalent Sb and As will both be reduced to the trivalent state after Fe (III) is reduced to Fe (II) but before sulfate is reduced to sulfide. Reduction of Sb (III) to elemental Sb or stibine and likewise As (III) to elemental As or arsine requires considerably lower reduction potentials, at which soluble sulfide may be present in sufficient concentration for the metalloids to form sulfide complexes.

**Table 2**

Some pertinent redox reactions in natural systems (adapted from Aylward and Findlay, 1994; Stumm and Morgan, 1996; Godfrey et al., 1998).

Reaction	pe <sup>0a</sup>	Eh <sup>0</sup> (V)
O <sub>2</sub> + 4H <sup>+</sup> + 4e <sup>-</sup> = 2H <sub>2</sub> O	20.8	1.23
2NO <sub>3</sub> <sup>-</sup> + 12H <sup>+</sup> + 10e <sup>-</sup> = N <sub>2</sub> + 6H <sub>2</sub> O	21.1	1.25
MnO <sub>2</sub> + 4H <sup>+</sup> + 2e <sup>-</sup> = Mn <sup>2+</sup> + 2H <sub>2</sub> O	20.4	1.21
Fe(OH) <sub>3</sub> (amorphous) + 3H <sup>+</sup> + e <sup>-</sup> = Fe <sup>2+</sup> + 3H <sub>2</sub> O	16.6	0.98
α-FeOOH (goethite) + 3H <sup>+</sup> + e <sup>-</sup> = Fe <sup>2+</sup> + 2H <sub>2</sub> O	13.1	0.77
Sb(OH) <sub>6</sub> <sup>-</sup> + 3H <sup>+</sup> + 2e <sup>-</sup> = Sb(OH) <sub>3</sub> + 3H <sub>2</sub> O	12.9	0.76
Sb <sub>2</sub> O <sub>5</sub> + 4H <sup>+</sup> + 4e <sup>-</sup> = Sb <sub>2</sub> O <sub>3</sub> (valentinite) + 2H <sub>2</sub> O	11.0	0.65
Sb <sub>2</sub> O <sub>5</sub> + 6H <sup>+</sup> + 4e <sup>-</sup> = 2Sb(OH) <sub>2</sub> <sup>+</sup> + H <sub>2</sub> O	9.8	0.58
H <sub>3</sub> AsO <sub>4</sub> + 2H <sup>+</sup> + 2e <sup>-</sup> = H <sub>3</sub> AsO <sub>3</sub> + H <sub>2</sub> O	9.5	0.56
SO <sub>4</sub> <sup>2-</sup> + 10H <sup>+</sup> + 8e <sup>-</sup> = H <sub>2</sub> S + 4H <sub>2</sub> O	5.3	0.31
Sb(OH) <sub>2</sub> <sup>+</sup> + 2H <sup>+</sup> + 3e <sup>-</sup> = Sb + 2H <sub>2</sub> O	3.6	0.21
CO <sub>2</sub> + 8H <sup>+</sup> + 8e <sup>-</sup> = CH <sub>4</sub> + 2H <sub>2</sub> O	2.9	0.17
Sb <sub>2</sub> O <sub>3</sub> + 6H <sup>+</sup> + 6e <sup>-</sup> = 2Sb + 3H <sub>2</sub> O	-2.5	-0.15
H <sub>3</sub> AsO <sub>3</sub> + 3H <sup>+</sup> + 3e <sup>-</sup> = As + 3H <sub>2</sub> O	-4.2	-0.25
Sb + 3H <sup>+</sup> + 3e <sup>-</sup> = SbH <sub>3</sub>	-8.6	-0.51
As + 3H <sup>+</sup> + 3e <sup>-</sup> = AsH <sub>3</sub>	-4.0	-0.61

<sup>a</sup> pe<sup>0</sup> = Eh<sup>0</sup>/0.059 V at 25 °C and Eh<sup>0</sup> is the equilibrium redox potential relative to the oxidation of H<sub>2</sub>(g).

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