

Antimony in the environment: A review focused on natural waters.

III. Microbiota relevant interactions

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Abstract

Antimony is ubiquitously present in the environment as a result of natural processes and human activities. Antimony is not considered to be an essential element for plants or animals. In this third review paper on the occurrence of antimony in natural waters, the interactions of antimony with microbiota are discussed in relation to its fate in natural waters. This paper covers the following aspects: occurrence in microbiota, uptake transport mechanisms, pathways of Sb(III) removal from cells involved in antimony tolerance, oxidation and reduction of antimony by living organisms, phytochelatin induction and biomethylation. This review is based on a careful and systematic examination of a comprehensive collection of papers on the above mentioned aspects of the subject. All data are quoted from the original sources. Relatively little existing information falls within the strict scope of this review and, when relevant, discussion on the interactions of antimony with reference microorganisms, such as *Escherichia coli*, *Saccharomyces cerevisiae* and different protozoan parasites of the genus *Leishmania*, has been included.

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1. Introduction

Antimony belongs to subgroup 15 of the periodic table of the elements. Concentrations of antimony in natural waters are low (typically less than 1 µg/L) except in geothermal waters (can be in excess of 1 g/L) and antimony-enriched mineralized areas (Filella et al., 2002a). Probably because it is lower in abundance and most of its compounds are relatively insoluble, antimony has largely been overlooked as an element

of environmental concern and its study neglected. However, the increasing number of publications that have appeared over the last five years on the presence and behaviour of antimony in environmental systems reflects the scientific community's growing interest in this element which will hopefully lead to a clarification of many aspects of antimony's environmental fate that remain virtually unexplored as yet.

Antimony is not an essential element in plants or animals (Fowler and Goering, 1991). Its bioavailability and toxicological effects depend on its chemical form and oxidation state. The two common inorganic forms of antimony present in natural waters are antimonate ($\text{Sb}(\text{OH})_6^-$) and antimonite ($\text{Sb}(\text{OH})_3$) (Filella et al.,

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2002b). Experimental and clinical trials with compounds containing antimony have shown that the trivalent compounds are generally more toxic than the pentavalent compounds (Winship, 1987; Gebel, 1997; WHO, 2006).

Antimony is considered a non-essential element and toxic to most organisms at elevated concentrations. For similar elements such as arsenic, microorganisms have evolved mechanisms to decrease uptake or to exclude them from the cytosol of the cells by active efflux or by sequestration in internal organelles. Investigations into the mechanisms of toxic metalloid interaction with living organisms have mainly focused on arsenic because of its higher concentration in nature. Nowadays, a great deal of information on the enzymes and genes involved in resistance and tolerance to arsenic is available (for review see Silver et al., 2001; Mukhopadhyay et al., 2002; Oremland and Stoltz, 2003; Silver and Phung, 2005a,b). In contrast, knowledge of the interactions of cells with antimony is still very scarce. Conclusions are often based on indirect experimental demonstrations and therefore are only tentative.

In this series of papers (Filella et al., 2002a,b), we have launched an exhaustive review of the scientific literature in order to identify and evaluate all sources of information related to antimony. The first paper focused on antimony distribution and speciation in freshwaters, marine waters, and estuaries (Filella et al., 2002a). The second paper addressed aspects of the solution chemistry of this element that are relevant to understanding its behaviour in natural waters (Filella et al., 2002b). This part describes antimony interactions with microbiota present in natural water systems. Very little information exists that, strictly speaking, falls within the scope of this review and information on some specific aspects is non-existent. For this reason, when relevant, discussion on the interaction of antimony with other microorganisms has also been included. This is particularly the case for: (1) studies on toxicity resistance mechanisms conducted in prokaryotic cells such as *Escherichia coli* and in eukaryotic unicellular microorganisms such as *Saccharomyces cerevisiae* (baker's yeast) and (2) studies on antimony drugs used to combat protozoan infections (Steck, 1974; Berman, 1988, 2003; Desjeux, 1996; Guerin et al., 2002; Sundar and Rai, 2002; Croft and Coombs, 2003; Davis et al., 2004; Ouellette et al., 2004; Murray et al., 2005). Leishmaniasis is a disease caused by protozoan parasites of the genus *Leishmania*. *Leishmania* spp. multiply as obligate intracellular amastigotes in the phagolysosome of vertebrate macrophages and are transmitted by blood-feeding sand flies in which the parasites proliferate as extracellular promastigotes. The annual incidence worldwide of visceral leishmaniasis is estimated at 500 000.

Control of the disease relies primarily on chemotherapy, and the first-line treatment against all forms of leishmaniasis is pentavalent antimonials, such as sodium stibogluconate (Pentostam) and meglumine antimonite (Glucantime). Over the years, resistant mutants have appeared in endemic regions, leading to extensive studies on antimonial resistance. As a consequence, a significant amount of information exists concerning mechanisms of resistance, including intake routes and intracellular reactions in various species of *Leishmania*.

Ecotoxicity issues concerning antimony are not included in this review and will be the subject of the next part of this series. In line with the rest of this series, all observations and values quoted come from the original sources. Multi-referencing has largely been avoided. In the few cases where it has been used, the origin of the reference is given.

2. Occurrence in microbiota

Reported concentrations for antimony in environmental microbiota deal almost exclusively with freshwater and marine algae. Concentrations are generally in the order of 0.1–0.2 µg/g dry weight as reported in Table 1. A few much higher values are reported in the same table, but they should be considered with caution. In a significant number of cases, antimony concentrations were below the detection limit of the technique used. The diversity of the algae studied, as well as differences in the pretreatment and analytical procedures used, precludes any possible comparison of the results published by the various authors, as well as the establishment of any trends. Moreover, antimony concentrations in the surrounding waters are rarely given which makes it impossible to establish any correlation between antimony content in the algae and the corresponding medium. An attempt to relate algal concentrations for a significant number of elements to water contents (Sánchez-Rodríguez et al., 2001) showed that antimony had one of the lowest absolute metal algal concentrations, as well as a relatively low enrichment factor. It is not clear whether bioaccumulation of antimony exists. Whilst some studies report no evidence of bioconcentration of antimony in aquatic algae (Bonotto et al., 1983; Mann and Fyfe, 1988; Mann et al., 1988), an accumulation of antimony was observed in freshwater algae exposed to high Sb levels (Maeda et al., 1997; Maeda and Ohki, 1998), in terrestrial plants growing in an abandoned antimony-mining area (Baroni et al., 2000) and in aquatic plants in the vicinity of ore mining industries (Hozhina et al., 2001). The authors linked this accumulation to the high concentration of antimony in the extractable fraction of soil.

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