

Antimony in the environment: a review focused on natural waters

I. Occurrence

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Abstract

Antimony is ubiquitously present in the environment as a result of natural processes and human activities. It exists mainly as Sb(III) and Sb(V) in environmental, biological and geochemical samples. Antimony and its compounds are considered to be priority pollutants interest by the USEPA and the EU. In this first review paper on antimony occurrence in natural waters, 420 papers on freshwaters, marine waters, estuaries, soils, and sediments have been reviewed. All data are quoted from the original sources. Typical concentrations of total dissolved antimony are usually less than 1.0 $\mu\text{g}/\text{l}$ in non-polluted waters. When redox speciation determinations are performed, most studies report the dominance of Sb(V) under oxic conditions. However, the presence of significant proportions of Sb(III) is sometimes detected. This is in contrast with thermodynamic equilibrium predictions and discrepancies are often attributed to biological activity or kinetic effects but proofs are lacking. Similarly, the existence of Sb(V), although not thermodynamically predicted, is often reported under anoxic conditions. Low concentrations of methylated antimony species are mentioned in a few studies. Antimony is not considered to be a highly reactive element in oceans, with concentrations of the order of 200 ng/l. In estuarine waters, both conservative and non-conservative behaviours are reported depending on the estuaries' characteristics. Elevated concentrations of antimony in soils and sediments are either related to anthropogenic sources or associated with high arsenic concentrations in sulfidic ores. Antimony appears to be highly unreactive in soils. Low accumulation factors are reported in algae. Airborne supply of antimony to aquatic and terrestrial systems seems to be important in systems far from direct pollution sources. However, the limited available data do not allow firm conclusions to be drawn on the reactivity and cycling of the element in natural systems and a list of research priorities is given. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: antimony; freshwater; seawater; estuaries; sediments; soils; speciation

Abbreviations: AAS, atomic absorption spectrometry; AES, atomic emission spectrometry; AFS, atomic fluorescence spectrometry; ASV, anodic stripping voltammetry; CL, competing ligand; CMCPE, chemically modified carbon paste electrode; CRM, certified reference material; CSV, cathodic stripping voltammetry; DPASV, differential pulse ASV; ETAAS, electrothermal AAS; ETV, electrothermal volatilisation; FAAS, flame atomic absorption spectrometry; FIA, flow injection analysis; GC, gas chromatography; GF, graphite furnace; HG, hydride generation; HMDE, hanging mercury dropping electrode; HPLC, high performance liquid chromatography; IC, ion chromatography; ICP, inductively coupled plasma; LTGC, low temperature GC; MS, mass spectrometry; NAA, neutron activation analysis; OES, optical emission spectrometry; PAA, photon activation analysis; PID, photo ionisation detection; RM, reference material; RDE, rotating disc electrode; SFC, supercritical fluid chromatography; SMDE, static mercury drop electrode; USS, ultrasonic slurry sampling.

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1. Introduction

A good deal of research on geochemical and biogeochemical processes in natural waters has been, and continues to be, devoted to trace elements, particularly transition metals. Rather less attention has been focused on the so-called metalloid elements. Among them, antimony is the one that has received the scantiest attention.

Antimony is a naturally occurring element. It belongs to the group 15 of the Periodic Table of the Elements. Antimony can exist in a variety of oxidation states (–III, 0, III, V) but it is mainly found in two oxidation states (III and V) in environmental, biological and geochemical samples. The relative abundance of antimony in different terrestrial systems is given in Table 1.

According to the classical classification of Goldschmidt, antimony is a strong chalcophile element and as such mainly occurs in nature as Sb_2S_3 (stibnite, antimonite) and Sb_2O_3 (valentinite), which is a transformation product of stibnite. These compounds

of antimony are commonly found in ores of copper, silver, and lead. Antimony is also a common component of coal and petroleum.

Little information is available on the transformation and transport of antimony in the different environmental compartments. Even information on antimony speciation and total content in the various media is scarce and often contradictory. This lack of understanding of antimony behaviour and fate in the environment hinders further research. In this series of papers, we have launched an exhaustive review of the scientific literature in order to identify and evaluate all sources of information related to antimony. In this first paper, we have attempted to include all studies devoted to freshwaters, marine waters, and estuaries. To illustrate key aspects of antimony occurrence in nature, some selected information on sediments and soils is also included. Values quoted come from the original sources. Multireferencing has been avoided. In the very few cases where it has been used, the origin of the reference is given. A total of 420 papers have been reviewed. Other studies on subjects such as relevant aquatic chemistry, antimony in biota, etc., will follow.

Table 1
Antimony abundance

| Material | Sb ^a | Reference |
|-------------------------|--------------------|-------------------------------------------|
| Cosmic abundance | 0.246 ^b | Suess and Urey, 1956 |
| Chondrites | 0.1 | Onishi and Sandell, 1955; Onishi, 1969 |
| Mean crustal average | 0.2 ^c | Onishi and Sandell, 1955 |
| Upper continental crust | 0.31 ^d | Wedepohl, 1995 |
| Lower continental crust | 0.30 ^d | |
| Terrestrial abundance | 0.7 | Boyle and Jonasson, 1973 |
| Basic rocks (basalt) | 0.15 | Onishi and Sandell, 1955 ^e |
| Granitic rocks | 0.2 | |
| Sedimentary rocks | | |
| Shales | 1–2 | |
| Carbonates | 0.2 | |
| Deep sea clays | 1 | |

^aAll values in ppm, except for the cosmic abundance.

^bAtomic abundance relative to Si (= 1,000,000) deduced from the following mean composition of meteorites: silicate = 100, sulfide = 7, metal = 10.6 parts per weight.

^cMost often cited value of antimony crustal average (Taylor, 1964; Ahrens, 1965; Mason, 1966; Wedepohl, 1968).

^dCalculated by the author from rock averages of Onishi and Sandell (1955).

^eVery often the sources cited for these values are either Turekian and Wedepohl (1961) or Onishi (1969). Both papers give Onishi and Sandell (1955) as the only reference.

2. Uses

Antimony was already known to the ancients. Since it can dissolve many other metals including gold, this property was used for purifying gold from copper and silver up to the 18th century. A peat core from an ombrotrophic Swiss bog revealed significant enrichments of antimony extending back to Roman times, indicating that the anthropogenic fluxes of this metal have exceeded natural ones for more than 2000 years. The present day enrichment factor (relative to the element/Sc ratios of typical crust rocks) is of the order of 70 times (for comparison, it is 20 for As, 130 for Pb) (Shotyk et al., 1996).

World reserves of antimony are in excess of 2 million tons and are located principally in Bolivia, China, Russia, South Africa, and Mexico (Carlin, 2000). Current world production of antimony is about 140,000 tons per year. Table 2 shows world mine production by the main producing countries in 1999.

Antimony is used in semiconductors for making infrared detectors, diodes and Hall-effect devices.

Table 2
World mine production of antimony by country in 1999 (Carlin, 2000)

| Country | Sb production (metric tons) |
|-----------------|--------------------------------|
| Bolivia | 5000 |
| China | 120,000 |
| Kyrgyzstan | 200 |
| Russia | 3000 |
| South Africa | 3000 |
| Tajikistan | 1200 |
| USA | 480 |
| Other countries | 5000 |
| Total | 138,000 |

The presence of antimony greatly increases the hardness and the mechanical strength of lead. Batteries, antifriction alloys, type-metal, small arms and tracer bullets, and cable sheathing are the main products containing antimony. Antimony trioxide, Sb_2O_3 , has many uses including as a flame-proof retardant of textiles, papers, plastics and adhesives; as a paint pigment, ceramic opacifier, catalyst, mordant and glass decolouriser. Antimony tetroxide, Sb_4O_{10} , is used as an oxidation catalyst, particularly for the oxidative dehydrogenation of olefins.

For years, the major industrial use of antimony was the production of alloys. Nowadays, antimony is mostly used in large quantities as a flame retarding additive. The situation has largely evolved from the early 1950s when antimony was qualified as a “cheap metal which can be used in certain instances as a substitute for more expensive metals” (Latimer and Hildebrand, 1951). In 1999, the USA consumption of antimony was 36,480 tons (domestic mine production plus secondary production from old scrap plus net import reliance) and the estimated distribution of antimony uses was as follows: flame retardants, 55%; transportation, including batteries, 18%; chemicals, 10%; ceramics and glass, 7%; and other, 10% (Carlin, 2000).

Antimony is used in certain therapeutic agents against major tropical diseases, although in recent years, it has been increasingly replaced by other agents. Antimony is still the treatment of choice for several tropical protozoan diseases, such as leishmaniasis, schistosomiasis, ascariasis, trypanosomiasis and bilharziasis. Pentostam and Glucantime, pentava-

lent antimony-containing drugs, are widely used in the treatment of leishmaniasis (Berman, 1988). Antimony compounds were once used in the treatment of syphilis.

Traditionally, the bulk of secondary antimony has been recovered as antimonial lead, most of which was generated and then also consumed by the battery industry. However, the current trend to avoid the use of antimony in lead alloys towards its use in fire-retardant treatments and other applications, which do not permit recycling, have caused lesser amounts of secondary antimony to be produced. This decrease in antimony recycling is of environmental concern.

3. Toxicity

Antimony and its compounds were considered as pollutants of priority interest by the Environmental Protection Agency of the United States (USEPA, 1979) and the European Union (Council of the European Communities, 1976). The USEPA drinking water standards are: maximum contaminant level goal (MCLG) and maximum contaminant level (MCL), both $6 \mu\text{g}/\text{l}$ (USEPA, 1999). The European Union established a maximum admissible concentration of antimony in drinking water of $5 \mu\text{g}/\text{l}$ (Council of the European Union, 1998). Antimony is on the list of hazardous substances under the Basel convention concerning the restriction of transfer of hazardous waste across borders (United Nations Environmental Program, 1999).

Antimony has no known biological function and, like arsenic, it is toxic. Trivalent species are reported to be more toxic than pentavalent forms (Bencze, 1994).

Antimony is usually present at levels less than $1.0 \mu\text{g}/\text{g}$ in all human tissues. Lung, lymph nodes and hair contain the largest amounts (Fergusson, 1990; Emsley, 1991). Most of the work on the toxic effects of antimony has been focused on its uses in medicine or on occupational exposure. The small number of laboratory animal experiments have tended to involve forms of antimony, doses and routes of administration, which are not relevant to its possible effects as an environmental pollutant. A wide range of effects has been reported but they will not be given

Table 3
Published antimony concentrations in freshwater systems (filtered samples)

| System ^a | System details | Total Sb (ng/l) | [Sb(III)] (ng/l) | [Sb(V)] (ng/l) | [MSA] ^b (ng/l) | [DMSA] ^c (ng/l) | Experimental technique ^d | Reference |
|-----------------------------------|---------------------------------------|---------------------------------------|---------------------|-------------------|------------------------------|-------------------------------|----------------------------------------|----------------------------|
| Waters from 15 regions of Siberia | 3770 samples (Sb found in 95 samples) | 0.1–31.2 | | | | | Precipitation (sulfide) + spectroscopy | Udodov and Parilov, 1961 |
| River waters, SV | unfiltered samples | | | | | | NAA | Landström and Wenner, 1965 |
| Skellefte River | | 50 | | | | | | |
| Une River | | 70 | | | | | | |
| Ångerman River | | 80 | | | | | | |
| Groundwaters, SV | | | | | | | | |
| Near Skellefteå | 2 locations | 10, 20 | | | | | | |
| Brån | 2 locations | 30, 200 | | | | | | |
| Sollefteå | 3 locations | 60, 40, 500 | | | | | | |
| Rivers, US | 7 rivers | 270–980 | | | | | Precipitation (sulfide) + NAA | Kharkar et al., 1968 |
| Rhone River, Avignon, FR | average value | 1530 | | | | | | |
| Amazon River, Santarem, BR | average value | 4900 | | | | | | |
| World average | | 1100 | | | | | | |
| Columbia River, US, 14/11/68 | | 2000 | | | | | NAA | Tanner et al., 1972 |
| Bavarian rivers, GE | unfiltered samples | | | | | | NAA | Schramel et al., 1973 |
| Illerkanal | | 50 | | | | | | |
| Donau (Ulm) | | 60 | | | | | | |
| Donau (Böfingerhalde) | | 100 | | | | | | |
| Lech (Augsburg) | | 1000 | | | | | | |
| Lechkanal (Gersthofen) | | 5200 | | | | | | |
| Lechkanal (Langweid) | | 2300 | | | | | | |
| Subsurface waters, IT | | < 6.1–73 ^e (mean: 12.2) | | | | | NAA | Clemente and Mastinu, 1974 |

| | | | | |
|--------------------------------------------------|------------|-----------------------|-----------------------------------------------------------------------------------------------|------------------------------------------------------|
| Northern New Mexico surface and groundwaters, US | 27 samples | ND ^f -1100 | Ion exchange (Al ₂ O ₃) + NAA | Gladney and Owens, 1976 |
| 15th Fairway Pond, USF Golf Course, US | | | HG-AES + discharge atomic emission detector | Braman and Tompkins, 1978 |
| 05/09/75 | | ≈ 14 | | |
| 08/09/75 | | ≈ 14 | | |
| 07/11/75 | | 110 | | |
| 28/01/76 | | < 7 | | |
| Research Pond, USF, US | | | | |
| 08/09/75 | | 92 | | |
| 07/11/75 | | < 7 | | |
| Hillsborough River, Tampa, US | | | | |
| 08/09/75 | | < 7 | | |
| 15/09/75 | | 48 | | |
| Lake Carroll, Tampa, US | | | | |
| 15/09/75 | | < 7 | | |
| 07/11/75 | | < 7 | | |
| Lake West, Tampa, US | | | | |
| 05/09/75 | | < 7 | | |
| 07/11/75 | | < 7 | | |
| Lake Eckles, Tampa, US | | < 7 | | |
| Pond, Brandon, US | | < 7 | | |
| Average world rivers | | 1000 ^g | Based on Kharkar et al., 1968 | Martin and Meybeck, 1979; Martin and Whitfield, 1983 |
| Average 11 rivers, NR | | < 160–2100 (mean 350) | NAA | Salbu et al., 1979 |
| Lake Celyn, GB | | 80 | Precipitation | Abu-Hilal and Riley, 1981 |
| Gowy River, GB | | 420 | (zirconium oxide) + colorimetry (ion pair SbCl ₆ ⁻ with crystal violet) | |
| Conwy River, GB | | 130 | | |

(continued on next page)

Table 3 (continued)

| System ^a | System details | Total Sb (ng/l) | [Sb(III)] (ng/l) | [Sb(V)] (ng/l) | [MSA] ^b (ng/l) | [DMSA] ^c (ng/l) | Experimental technique ^d | Reference |
|------------------------------------------------|----------------------------------|--------------------|---------------------|-------------------|------------------------------|-------------------------------|-------------------------------------------------------|------------------------------------------|
| Ochlockonee River, US | | | 3.2 | 22.9 | 0.5 | ND ^f | HG-AAS | Andreae et al. 1981; Andreae, 1983 |
| Trinity River, US | | | 1.9 | 30.3 | ND ^f | ND ^f | | |
| Mississippi River, US | | | < 0.3 | 148.0 | 2.3 | ND ^f | | |
| Escambia River, US | | | < 0.3 | 12.8 | 0.8 | ND ^f | | |
| Apalachicola River, US | | | 0.4 | 55.0 | 0.6 | ND ^f | | |
| Rhine River at Oppenheim, GE | highly polluted | | 0.4 | 231.0 | 1.2 | ND ^f | | |
| Main River at Frankfurt, GE | highly polluted | | 0.3 | 311.0 | 1.8 | ND ^f | | |
| Tap water, Okayama, JP | | 46 | | | | | Flotation (Fe(OH) ₃ + surfactant) + AAS | Nakashima, 1981 |
| Takahashi River, JP | | 28 | | | | | | |
| Muddy pond, Waverley, US | | 5130 | | | | | Precipitation (Se(IV) + SnCl ₂) + NAA | Elson et al., 1982 |
| Domestic well, Waverley, US | | 1070 | | | | | | |
| Thames River, GB | | 270 ^g | | | | | NAA | Habib and Minski, 1982 |
| Rhine River, NL | | | | | | | HG-AAS | Haring et al., 1982 |
| Lobith | | 800 | | | | | | |
| Gorkum | | 600 | | | | | | |
| Tejo River, Santarem, PT, 30/04/82 | | 102 | | | | | HG-AAS | Andreae et al., 1983 |
| Tejo River, Santarem, PT, Dec. '79 | | 230 | | | | | | |
| 20 small lakes, South SV, Mar.–Apr. '80 | acidic lakes 2.5 m depth | 140 | | | | | In situ dialysis + NAA | Borg, 1983 |
| 18 small lakes, North SV, Mar.–Apr. '80 | samples (2 m below ice cover) | 130 | | | | | | |
| River water, Yakushima Island, JP, Dec. '79 | 9 sites | 3–29 (mean: 13) | | | | | NAA | Tanizaki and Nagatsuka, 1983 |
| Rhine, Bregenz, GE, 12/05/82 | | 80.4 ^e | | | | | HG-AAS | Andreae and |

| | | | | | | |
|--------------------------------------------------|--------------------------------------------------|------------------------|------------------|--|--------|-------------------------------|
| Rhine, Oppenheim, GE, 02/04/82 | | 232 | | | | Froelich, 1984 |
| Rhine, Mainz, GE, 06/12/82 | | 528 | | | | |
| Main, Frankfurt, GE, 13/04/81 | | 313 | | | | |
| Danube, Neuberg, GE, 10/05/82 | | < 3.7 | | | | |
| Tejo, Santarem, PT, 30/04/82 | | 102 | | | | |
| Tejo, Vilafranca, PT, 06/12/82 | | 229 | | | | |
| Guadalquivir, Coira, ES, 18/12/82 | | 539 | | | | |
| Elbe, below Hamburg, GE, 09/06/81 | | 256 | | | | |
| Rhône, Arles, FR, 05/09/81 | | 335 | | | | |
| Isère, Domène, FR, 02/09/81 | | 326 | | | | |
| Average, European Rivers | | 248 | | | | |
| Yukon, CA, Aug. '81–Sep. '82 | average 8 samples | 332 | | | | |
| St. Lawrence, Massena, US, Dec. '81– Aug. '82 | average 5 samples | 197 | | | | |
| Tama River, Tokyo, JP | | | | | NAA | Tanizaki et al., 1984 |
| Hamura dam, 01/11/82 | low TOC | 176 ^g | | | | |
| Tamagawara bridge, 16/12/83 | high TOC | 376 | | | | |
| Tama River, Tokyo, JP | | | | | NAA | Tanizaki et al., 1985 |
| Hamura dam, 01/11/82 | | 176 ^g | | | | |
| Kinuta, 31/10/83 | | 264 | | | | |
| Denenchofu, 12/12/83 | | 258 | | | | |
| Lake Yssel, NL, Apr. '78 | 3 stations | 365–475 ^{e,g} | | | HG-NAA | van der Sloot et al., 1985 |
| River Rhine, NL, Feb. '75 | 3 stations | 329–1059 ^e | | | | |
| Loch Ewe, NW Scotland, GB, 1983 | spring diatom bloom, no temporal variation | 156 ^e | 3 ^{e,h} | | HG-AAS | Apte et al., 1986 |
| Loch Ewe, NW Scotland, GB | | | | | HG-AAS | Apte and Howard, 1986 |
| 26/03/83 | | 168 | 2 | | | |
| 09/04/83 | | 145 | 3 | | | |
| River Arakawa, JP, Jan.–Feb. '86 | unfiltered samples | | | | HG-AAS | Narasaki, 1986 |
| Mitsumine (137.8 km mouth) | | 420, 480 | | | | |

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Table 3 (continued)

| System ^a | System details | Total Sb (ng/l) | [Sb(III)] (ng/l) | [Sb(V)] (ng/l) | [MSA] ^b (ng/l) | [DMSA] ^c (ng/l) | Experimental technique ^d | Reference |
|-----------------------------------|----------------|--------------------|---------------------|-------------------|------------------------------|-------------------------------|-------------------------------------------------------------------------------------------|------------------------------|
| Kami-Nagatoro (110.6 km mouth) | | 160, 180 | | | | | | |
| Kumagaya (76.4 km mouth) | | 180, 200 | | | | | | |
| Urawa (37.0 km mouth) | | 270, 310 | | | | | | |
| Toda (25.2 km mouth) | | 310, 390 | | | | | | |
| Yotsugi (8.8 km mouth) | | 910, 930 | | | | | | |
| River waters, JP | | | | | | | HG-AAS | Tanaka et al., 1986 |
| Yagamigawa River | | 260 | < 1 | | | | | |
| Sagamigawa River | | 150 | < 1 | | | | | |
| Kamogawa River | | 290 | < 1 | | | | | |
| Katsuragawa River | | 110 | < 1 | | | | | |
| Yuragawa River | | 70 | < 1 | | | | | |
| Lake waters, JP | | | | | | | | |
| Lake Biwako | | 90 | < 1 | | | | | |
| Lake Hamanako | | 460 | < 1 | | | | | |
| Mean 41 Norwegian lakes, 1977 | | 32 | | | | | NAA | Allen and Steinnes, 1987 |
| Snake River, Lewiston, US | mining area | | 5 | 190 | | | Solvent Extraction (pyrrolidinedicarbo dithionate)+ NAA | Mok and Wai, 1987 |
| Coeur d' Alene River, Cataldo, US | | | 44 | 1890 | | | | |
| Coeur d' Alene River, Kellogg, US | | | 30 | 7030 | | | | |
| Great Lakes | surface water | | | | | | HG-AAS | Rossmann and Barres, 1988 |
| Lake Huron, 1980 | | 500 ^g | | | | | | |
| Lake Erie, 1981 | | 170 | | | | | | |
| Lake Michigan, 1981 | | 230 | | | | | | |
| Lake Superior, 1983 | | 82 | | | | | | |
| Lake Ontario | | | | | | | | |
| 1981 | | 180 | | | | | | |
| 1985 | | 160 | | | | | | |
| Pond water | | 120 | ND ^f | 120 | | | Solvent extraction | Abbasi, 1989 |
| Reservoir water, surface | | ND ^f | ND ^f | ND ^f | | | (<i>N-p</i> -methoxy- phenyl-2-furyl- acrylohydroxamic acid) + flameless AAS | |
| Reservoir water, near-bottom | | 330 | 170 | 160 | | | | |

| | | | | | | |
|--------------------------------------------|--------------------|-----------------------|-----------------------|-------------------|---------------------------------------------------------|----------------------------------|
| Lake water 1 | | 1250 | | | | Li et al., 1989 |
| Lake water 2 | | 1550 | | | | |
| Solo River, ID | wet season | | 24.4 ^{e,g} | 244 ^e | HG-NAA | van der Sloot et al., 1989 |
| | dry season | | 21.9 | 244 | | |
| Porong River, ID | dry season | | 12.2 | 158 | | |
| Rivers TH, Oct. '86 | 6 rivers/locations | 42.6–190 ^e | | | HG-AAS | Byrd, 1990 |
| Rivers TW, Oct. '86 | 10 | 35.3–540 | | | | |
| Rivers KR, Oct. '86 | 6 | 53.6–315 | | | | |
| Rivers JP, Nov. '86 | 6 | 56.0–431 | | | | |
| Rivers US, 1986–1987 | 18 | 1.2–1157 | | | | |
| Rivers CA, 1987 | 3 | 24.4–212 | | | | |
| Glenshanna River, Scotland, GB | | | | | HG-AAS | Mohammad et al., 1990 |
| Disused Sb mine entrance | | 5300 | ND ^f | 5300 | | |
| Soil heap drainage | | 60,400 | 2200 | 58,200 | | |
| River (2 m downstream soil heap) | | 14,300 | ND ^f | 14,300 | | |
| Coeur d'Alene River, US, Dec. '86–June '87 | mining area | | | | Solvent extraction (pyrrolidinedicarbo dithionate)+ NAA | Mok and Wai, 1990 |
| Mean values | 9 stations | 59–8245 | 0–125 | | | |
| North Fork, 26/06/87 | | 164 | | | | |
| Southern Lake Coeur d'Alene, 15/08/87 | | 480 | | | | |
| Delta Area, 15/08/87 | | 1656 | | | | |
| St. Joe River, 15/08/87 | | 44 | | | | |
| Sacramento River, US, 24/09/86 | | | < 0.37 ^{e,g} | 67 ^{e,g} | HG-GC-PID | Cutter et al., 1991 |
| Tap water, Warsaw, PO | unfiltered samples | 130 | | | HMDE-DPASV | Postupolski and Golimowski, 1991 |
| Surface water, Vistula River, PO | | 600 | | | | |

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Table 3 (continued)

| System ^a | System details | Total Sb (ng/l) | [Sb(III)] (ng/l) | [Sb(V)] (ng/l) | [MSA] ^b (ng/l) | [DMSA] ^c (ng/l) | Experimental technique ^d | Reference |
|--------------------------------------------------------|----------------------------------------------------|--------------------|---------------------|-------------------|------------------------------|-------------------------------|----------------------------------------------------------------------------------|---------------------------|
| Lake Constance, GE, 1986–1987 | | 100–170 | | | | | HG-AAS | Stabel et al., 1991 |
| Coeur d'Alene River sediment interstitial water, US | mining area | | | | | | Solvent extraction (lithium bis(trifluoro ethyl)dithio carbamate) + SFC | Laintz et al., 1992 |
| Lake Harrison | | | 1700 | 1500 | | | | |
| St. Joe River | | | 300 | 1500 | | | | |
| Smeltonville | | | 1700 | 2100 | | | | |
| Lake Constance, GE Spring, 03/04/90 | constant with depth (mean 9 samples 0–140 m) | 117 ^{g,h} | | | | | FIA-HG-GF-AAS | Sinemus et al., 1992 |
| Autumn, 14/11/90 | surface | 110 ^{g,h} | | | | | | |
| | 20 m | 116 ^{g,h} | | | | | | |
| | 60 m | 114 ^{g,h} | | | | | | |
| | 140 m | 108 ^{g,h} | | | | | | |
| Tamagawa River, JP Hamura, 18/11/85 | | 163 ^g | | | | | NAA | Tanizaki et al., 1992a |
| Sekidobashi, 04/06/90 | | 301 | | | | | | |
| Noborito, 01/12/86 | | 270 | | | | | | |
| Kinuta, 31/10/83 | | 264 | | | | | | |
| Futagotamagawa (flooding), 04/09/89 | | 1050 | | | | | | |
| Denenchoufu, 12/12/83 | | 258 | | | | | | |
| Sagamigawa River, JP Sagamiko, 18/06/85 | | 184 | | | | | | |
| Atsugi, 13/12/88 | | 204 | | | | | | |
| Asakawa River, JP, 1984–1986–1989 | | 366 ^g | | | | | NAA | Tanizaki et al., 1992b |
| Nogawa River, JP, 1984–1986–1989 | | 271 | | | | | | |
| Hirasegawa River, JP, 1985 | | 196 | | | | | | |
| Tamagawa River, JP | | | < 9.4 | 283 | | | HG-GC-PID | Yamamoto et al., 1992 |

| | | | | | | |
|--------------------------------------------|---------------------------|---------------------|-----------------------|-----|------------------------------------|----------------------------|
| Rhône River, FR | | 487 ^{e,g} | | | NAA | Guieu et al., 1993 |
| Coeur d'Alene River, US | mining area | | | | Solvent extraction + NAA | Shieh, 1993 |
| River water | | < 100–4600 | < 100 | | | |
| Sediment interstitial water | | 1200–4000 | 100–1900 ^h | | | |
| Blackfoot Disease Area, TW | high As concentr. | | | | | |
| Groundwater 1989 | | 500–1200 | 80–470 | | | |
| Groundwater 1990 | | 680–1530 | 110–500 | | | |
| Porewater | | 560–920 | 90–100 | | | |
| Lake water | | 280 | 5 | 275 | Coprecipitation (thionalide) + NAA | Sun et al., 1993 |
| Groundwater | | 20 | 8 | 12 | | |
| Amazonian waters, BR, 1990–1991 | | | | | ICP-MS | Konhauser et al., 1994 |
| Rio Negro | | < 100 | | | | |
| Rio Solimões | | < 150 | | | | |
| Shield streams in Carajás | | < 110 | | | | |
| Creek in Gidea, North SV, Sep. '90 | | < 36.5 ^e | | | ICP-MS | Carbol et al., 1995 |
| Manzanares River, ES | | | ND ^f | 390 | HPLC-HG-ICP-AAS | Smichowski et al., 1995 |
| Tap water, Kaohsiung, TW | | 1000 | | | FIA-HG-ICP-MS | Chen and Jiang, 1996 |
| Onion Creek, Washington, US, Aug.–Oct. '92 | Near Van Stone Pb/Zn mine | | | | ICP-MS | Routh and Ikramuddin, 1996 |
| Near abandoned tailings pond | | 3200–44800 | | | | |
| Near new tailings pond | | 1800–4300 | | | | |
| New tailings pond | | 2500–14900 | | | | |
| Tap water, Warsaw, PO | | 180 | ND ^f | | Sorption on Polyorgs 31 + AAS | Garboś et al., 1997 |
| | | 580 | 190 | | | |

(continued on next page)

Table 3 (continued)

| System ^a | System details | Total Sb (ng/l) | [Sb(III)] (ng/l) | [Sb(V)] (ng/l) | [MSA] ^b (ng/l) | [DMSA] ^c (ng/l) | Experimental technique ^d | Reference |
|--------------------------------|------------------------------------------------------------------|--------------------|---------------------|-------------------|------------------------------|-------------------------------|----------------------------------------|-------------------------------|
| Lake Pavin, FR | small meromictic lake | 31.7 ^e | 15.8 ^e | 15.8 ^e | | | HG-AAS | Takayanagi and Cossa, 1997 |
| Surface | | 42.6 | ND ^f | 42.6 | | | | |
| Deep oxic water | | < 7.3 | | | | | | |
| Bitterfeld, GE | both sites are polluted by mining and industrial wastes | 31,000 | 2000 | 28,000 | | | IC-ICP-AES | Ulrich, 1998 |
| Pfälzer Bergland, GE | | 96,000 | 9000 | 85,000 | | | | |
| Arakawa River, JP, Dec. '98 | | | | | | | HG-ICP-MS | Hou and Narasaki, 1999 |
| Mitsumine (137.8 km mouth) | | | 147.7 | 66.0 | | | | |
| Kami-nagatoro (110.6 km mouth) | | | 156.2 | 40.9 | | | | |
| Kumagaya (76.4 km mouth) | | | 169.6 | 49.3 | | | | |
| Urawa (37.0 km mouth) | | | 173.4 | 37.0 | | | | |
| Lake water, Sudbury, CA | surface water | | | | | | HG-AFS | Deng et al., 2000 |
| Lake Geneva | | 119.3 ⁱ | ND ^f | 39.6 | | | | |
| Lake Bethel | | 141.2 ⁱ | 21.4 | 72.5 | | | | |
| Lake Laurentian | | 139.3 ⁱ | ND ^f | 46.8 | | | | |
| Lower Trent River, GB | | | | | | | ICP-OES and ICP- MS | Jarvie et al., 2000 |
| Cromwell Lock | non-tidal | 1940 ^g | | | | | | |
| Torksey | freshwater tidal | 1970 ^g | | | | | | |
| Gainsborough | freshwater tidal | 2110 ^g | | | | | | |
| Amazon River | | 30 | | | | | HG-GC-PID | Cutter et al., 2001 |

^a International country codes follow the ISO 3166 convention; specific sampling dates are given as dd/mm/yy, otherwise the month and year are given if reported.

^b MSA = methylstibonic acid.

^c DMSA = dimethylstibonic acid.

^d See corresponding list for meaning of abbreviations.

^e In molar scale units in the original.

^f ND = not detected.

^g Particulate concentrations also given.

^h Estimated from graph by digitisation of the corresponding figure (Silk Scientific, 1998).

ⁱ Data obtained after UV oxidation and operationally defined as organic-Sb also given.

here as it is out of the scope of this review. Further information may be found in Elinder and Friberg (1986) and Gebel (1997).

4. Occurrence in natural waters

Antimony is present in the aquatic environment as a result of rock weathering, soil runoff and anthropogenic activities. Typical concentrations of dissolved antimony in unpolluted waters are less than 1 $\mu\text{g/l}$. However, in the proximity of anthropogenic sources, concentrations can reach up to 100 times natural levels.

Antimony is present in substantial concentrations in precipitates from hot springs and boreholes and in geothermal waters. Concentrations ranging from 500 mg/l up to 10 wt.% have been reported (Ritchie, 1961; Sabadell and Axtmann, 1975; Weissberg et al., 1979; Stauffer and Thompson, 1984). Field data are sparse on antimony pollution caused by the proximity of geothermal areas. Klein et al. (1975) suggested that, at that time, antimony weathering and mobilisation from these areas might largely exceed mobilisation from industrial operations but this hypothesis was not further investigated. Geothermal systems will not be considered further in the present paper.

Total concentrations of antimony present in aqueous and solid environmental samples can be readily determined using present day analytical techniques. This has primarily resulted from the development of microwave-digestion techniques for solid samples and NAA and plasma-based analyte detection systems. Both ICP-AES and ICP-MS techniques are nowadays widely used, with ICP-MS having less spectral interferences and a lower detection limit (pg/ml). Determination of antimony speciation still represents a challenging analytical problem. Data reported in the literature are almost exclusively based on hydride generation methods and often only oxidation state data are obtained.

An excellent critical review on the methodologies currently available for the environmental analysis of antimony has recently been published (Nash et al., 2000) and this issue will not be addressed in detail in this paper.

Antimony concentration values given in the following sections correspond to antimony contents in

filtered samples (usually, 0.45 μm pore size filters). The few studies where antimony contents in the particulate fraction are also given (Gohda, 1972, 1974, 1975; Habib and Minski, 1982; Tanizaki et al., 1984, 1985; van der Sloot et al., 1985, 1989; Rossmann and Barres, 1988; Van der Weijden et al., 1989; Sinemus et al., 1992; Tanizaki et al., 1992a,b; Guieu et al., 1993; Jarvie et al., 2000) show that antimony exists almost exclusively in the so-called “dissolved” fraction.

4.1. Freshwater systems

The distribution and speciation of antimony in freshwater systems have not been extensively studied. Published results on dissolved antimony concentrations in freshwaters are shown in Table 3. Concentrations range from a few ng/l to a few $\mu\text{g/l}$ depending on location, thus reflecting the wide range of physical and chemical conditions existing in freshwater systems and the proximity of pollution sources (e.g. Mok and Wai, 1987, 1990; Mohammad et al., 1990; Shieh, 1993; Ulrich, 1998).

4.2. Oceans

Antimony concentration in oceans is about 200 ng/l. Published results are shown in Table 4. Fig. 1 shows the evolution of published values for open surface sea water as a function of their year of publication. The observed decrease in antimony concentrations as well as in data scatter with time reflect the parallel improvement of the analytical techniques available. Antimony behaviour in open oceans is not considered to be highly reactive. Some authors report that antimony behaves conservatively: Brewer et al., 1972 (Sargasso Sea); Andreae et al., 1981 (Gulf of Mexico); Bertine and Lee, 1983 (Saanich Inlet); Middelburg et al., 1988 (Atlantic Ocean); Van der Weijden et al., 1989 (Kau Bay); Van der Weijden et al., 1990 (Tyro and Bannock basins in Eastern Mediterranean Sea); Takayanagi et al., 1996 (Western Mediterranean Sea, Northern part). Other researchers state that antimony shows a pattern corresponding to a mildly scavenged element with surface (atmospheric) input: Andreae and Froelich, 1984 (Baltic Sea); Cutter and Cutter, 1995 (Eastern Atlantic Ocean); Cutter and Cutter, 1998 (North At-

Table 4
Published antimony concentrations in seawater (filtered samples)

| System ^a | System details | Total Sb (ng/l) | [Sb(III)] (ng/l) | [Sb(V)] (ng/l) | [MSA] ^b (ng/l) | [DMSA] ^c (ng/l) | Experimental technique ^d | Reference |
|----------------------------------------------------------------|---------------------------------------------------------|--------------------------|---------------------|-------------------|------------------------------|-------------------------------|-----------------------------------------------------------------------------------------------------------------|------------------------------|
| Gullmarf fjord, NR | shallow water | < 500 | | | | | Spectrophotometry | Noddack and Noddack, 1940 |
| Ocean average | | 330 | | | | | Precipitation (sulfide) + NAA | Schutz and Turekian, 1965 |
| Caribbean | | 260 | | | | | | |
| Gulf of Mexico | | 460 | | | | | | |
| NW Atlantic | | 240 | | | | | | |
| NE Atlantic | | 210 | | | | | | |
| SW Atlantic | | 250 | | | | | | |
| Indian Ocean | | 370 | | | | | | |
| Central Pacific | | 510 | | | | | | |
| East Pacific | | 260 | | | | | | |
| Antarctic | | 240 | | | | | | |
| Long Island Sound, Gulf of Mexico | | 430 | | | | | | |
| Irish Sea | surface waters | 130–400 (median: 220) | | | | | Precipitation (MnO ₂) + solvent extraction (CCl ₄) + colorimetry (rhodamine B) | Portmann and Riley, 1966 |
| Tampa Bay | | 10–30 | | | | | HG-AES | Braman et al., 1972 |
| Sargasso Sea, North Atlantic Ocean (GEOSECS-II test cruise) | 1–5069 m (28 samples), no variation with depth | 180–250 (median: 215) | | | | | NAA of evaporated sea salts | Brewer et al., 1972 |
| Sea water, JP, Nov. '69 | | | | | | | Precipitation (thionalide) + NAA | Gohda, 1972 |
| Surface | 8 samples | 150–440 ^e | | | | | | |
| 20 m | | 320 ^e | | | | | | |
| 100 m | | 200 ^e | | | | | | |
| 300 m | | 170 ^e | | | | | | |
| 500 m | | 220 ^e | | | | | | |

| | | | | | | |
|-----------------------------------------------|--------------------------------|-------------------------------------|--------|---------|--------------------------------------------|------------------------------|
| Boston Light-Ship | 2 m | 180 | | | ASV (Hg-covered graphite electrode) | Gilbert and Hume, 1973 |
| Caribbean Deep | 3000 m (2 samples) | 390, 440 | | | | |
| Bahia Honda Key, FL, US | 1 m (4 samples) | 400–480 (median: 435) | | | | |
| Coastal sea water, JP | | | | | Precipitation (thionalide) + NAA | Gohda, 1974 |
| Shirahama, Wakayama, 30/10/70 | 0 m (3 samples) | 360–440 ^e | 50–90 | 310–380 | | |
| Kojima, Osaka, 01/12/70 | 0 m (5 samples) | 300–570 ^e | 30–100 | 230–490 | | |
| Suruga, Shizuokaa, 15/12/70 | 0 m (5 samples) | 220–550 ^e | 30–160 | 180–390 | | |
| | 10–1200 m (4 samples) | 290–670 ^e | 30–240 | 220–430 | | |
| Suruga Bay, Shizuoka, 04/10/72 | 0 m (1 sample) | 270 ^e | 40 | 240 | | |
| | 50–800 m (4 samples) | 200–280 ^e | 30–80 | 180–230 | | |
| Sea water, JP | | | | | Precipitation (thionalide) + NAA | Gohda, 1975 |
| Shirahama, Wakayama, 30/10/70 | 0 m (3 samples) | 360–440 ^e | 50–90 | 310–380 | | |
| Uragami, Wakayama, 04/11/71 | 0 m (4 samples) | 160–220 ^e | 30–60 | 120–190 | | |
| | 40 m (1 sample) | 230 ^e | 50 | 180 | | |
| Kojima, Osaka, 01/12/70 | 0 m (4 samples) | 470–570 ^e | 30–100 | 410–490 | | |
| North Adriatic sea water | (5 locations) | 190–530 ^e (mean: 310) | | | Precipitation (MnO ₂) + NAA | Strohal et al., 1975 |
| Cirus Jetty sea water, IN | | 96 | | | Precipitation (eosin) + NAA | Doshi, 1977 |
| Kalwa Bridge sea water, IN | | 140 | | | | |
| Hillsborough Bay, Seddon Channel, US | | | | | HG-AES | Braman and Tompkins, 1978 |
| 10/09/75 | | 21 | | | | |
| 12/09/75 | | 30 | | | | |
| McKay Bay, US | | < 7 | | | | |
| Old Tampa Bay, Courtney Campbell Causeway, US | | < 7 | | | | |
| North Sea, off the Belgian Coast | 3 m depth water (5 samples) | 300–820 | | | HMDE-DPASV | Gillain et al., 1979 |

(continued on next page)

Table 4 (continued)

| System ^a | System details | Total Sb (ng/l) | [Sb(III)] (ng/l) | [Sb(V)] (ng/l) | [MSA] ^b (ng/l) | [DMSA] ^c (ng/l) | Experimental technique ^d | Reference |
|------------------------------------------------|-------------------|--------------------|---------------------|-------------------|------------------------------|-------------------------------|------------------------------------------------------------------------------------------------|------------------------------------------------------|
| Sea water world average | | 240 | | | | | | Martin and Meybeck, 1979; Martin and Whitfield, 1983 |
| Irish Sea | | 260 | | | | | Precipitation (zirconium oxide) + colorimetry (ion pair SbCl_6^- with crystal violet) | Abu-Hilal and Riley, 1981 |
| Gulf of Mexico | | | 4.4 | 149.0 | 5.3 | 3.2 | HG-AAS | Andreae et al. 1981 |
| Apalachee Bay | | | 1.9 | 164.0 | 8.5 | ND ^f | | |
| Hiroshima Bay, JP | surface water | 220 | ND ^f | | | | HG-FAAS | Yamamoto et al., 1981 |
| Northwest Arm, Halifax Harbour, CA | | 380 | | | | | Precipitation (Se(IV) + SnCl_2) + NAA | Elson et al., 1982 |
| North Sea | | 300 | | | | | HG-AAS | Haring et al., 1982 |
| Sea water | | 300 | ND ^f | 300 | | | Solvent extraction (<i>N</i> -benzoyl- <i>N</i> -phenylhydroxylamine) + GF-AAS | Sun et al., 1982 |
| Pacific Ocean (GEOSECS station 227) | | | | 92–141 | | | HG-AAS | Andreae, 1983 |
| Atlantic Ocean, off Tejo estuary, PT, 26/04/82 | surface sea water | 155 | | | | | HG-AAS | Andreae et al., 1983 |
| Saanich Inlet, BC, CA Jan. '81 | oxygen in all | | | | | | HG-AAS | Bertine and Lee, 1983 |

| | | | | | | | |
|---------------------------------------------------------|---------------------------|--------------------------|--------------------------|------------------------|------------------------|----------------------------------------------------|----------------------------|
| 10–200 m | samples | 72–170 ^g | < 0.05–12.2 ^g | 72–160 ^g | < 0.5–3.7 ^g | | |
| < 200 m | | 158–228 | 3.7–11.0 | 155–220 | 2.4 | | |
| bottom water | | 580–772 | 42.6–503 | 269–538 | ND ^f | | |
| May '81 | | | | | | | |
| 0–170 m | oxic | 140–188 | 2.4–17.0 | 138–180 | | | |
| < 170 m | anoxic | 180–185 (+ 17 Sb(III)–S) | 3.7–8.5 | 157–177 | | | |
| Sediment interstitial waters | | | | | | | |
| SI-3 | 205–5 cm | 1449–17045 | 195–6500 | 1218–10532 | | | |
| SI-5 | 205–2 cm | 450–12420 | 50–4554 | 329–9144 | | | |
| North Sea, off the Belgian coast | same sample, 2 techniques | 160 | | | | HMDE-DPASV | Brihaye et al., 1983 |
| | | 120 | | | | RDE-ASV | |
| Sea water, 34°25'N, 133°54'E, JP | | 120 | | | | Flotation (Fe(OH) ₃ + surfactant) + AAS | Nakashima and Yagi, 1983 |
| Baltic Sea | | | | | | | |
| Station BY5, 11/06/81 | 10–95 m (10 samples) | 37.7–106 ^g | | | 0.7–9.7 ^g | < 0.7 ^g | Andreae and Froelich, 1984 |
| Station BY11, 12/06/81 | 10–210 m (15 samples) | 39.0–82.8 | | | 1.3–8.0 | < 0.7 | |
| Station BY15, 13/06/81 | 10–235 m (19 samples) | 18.3–73.1 | 0.2–18.8 ^g | 19.5–68.2 ^g | 1.6–5.0 | < 0.7 | |
| Station BY26, 14/06/81 | 10–90 m (8 samples) | 42.6–95.0 | 0.6–1.1 | 63.3–82.8 | < 0.6–11.0 | < 1.2 | |
| Station BY23, 15/06/81 | 10–65 m (6 samples) | 46.3–67.0 | | | < 0.6–8.5 | < 1.2–4.9 | |
| North Sea, off the Belgian coast, Jul. '83 | 19 stations | 50–380 (median: 120) | < 5–39 | 15–250 | | | Gillain and Brihaye, 1985 |
| North Sea, Southern Bight and British Channel, Oct. '81 | 10 stations | 195–365 ^{c,g} | | | | | van der Sloot et al., 1985 |
| Dutch Wadden Sea, Apr. '78 | 12 stations | 183–353 ^{c,g} | | | | | |
| Atlantic coastal water | unfiltered samples | | | | | HMDE-DPASV | Whang, 1985 |

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Table 4 (continued)

| System ^a | System details | Total Sb (ng/l) | [Sb(III)] (ng/l) | [Sb(V)] (ng/l) | [MSA] ^b (ng/l) | [DMSA] ^c (ng/l) | Experimental technique ^d | Reference |
|--------------------------------------|------------------------|------------------------|------------------------|------------------------------------|------------------------------|-------------------------------|-------------------------------------------------------------------------------------------------|------------------------------|
| Sample 1 | | 150 | | | | | | |
| Sample 2 | | 240 | | | | | | |
| Sea water (140°E, 51.5°S), AU | | 170 | | | | | HG-AAS | Maher, 1986 |
| Sea water, JP | | | | | | | HG-AAS | Tanaka et al., 1986 |
| Oiso | pH = 8.5 | 180 | 2 | | | | | |
| Wakasa | pH = 8.0 | 180 | 2 | | | | | |
| Sea water | 6 month storage | 13.4 ^g | | | | | CL-CSV (CL = catechol) | Capodaglio et al., 1987 |
| Lagoon water | freshly collected | 53.6 | | | | | | |
| Sea water, Bainbridge Island, WA, US | | | 5 | 240 | | | Solvent extraction (pyrrolidinecarbo dithioate) + NAA | Mok and Wai, 1987 |
| Atlantic Ocean (50–70°N) | 0–4000 m | | 3.7–23.1 ^g | 121–149 ^g (mean 141) | | | Preconcentration of hydrides on active carbon + NAA | Middelburg et al., 1988 |
| Sea water | | 280 | ND ^f | 280 | | | Solvent extraction (<i>N-p</i> -methoxy-phenyl-2-furylacryloylhydroxamic acid) + flameless AAS | Abbasi, 1989 |
| Java Sea | | 170 ^g | | | | | HG-NAA | van der Sloot et al., 1989 |
| Strait Madura | | 146 | | | | | | |
| Bali Basin | | 195 | | | | | | |
| Indian Ocean | | 231 | | | | | | |
| Southern Bight | | 158 | | | | | | |
| NW Atlantic | | 146 | | | | | | |
| Kau Bay, Halmahera, IN | (400 m depth) | | | | | | HG-NAA | Van der Weijden et al., 1989 |
| in the bay | low [O ₂] | 122–200 ^{g,g} | 110–176 ^{g,h} | 12.0–24.4 ^{g,h} | | | | |
| outside the bay | high [O ₂] | 152–225 | 135–200 | 17.0–24.0 | | | | |

| | | | | | | | | |
|------------------------------------------------------------------------|------------------|----------------------|-----------------------|----------------------|----------------------|-----------------|------------------------------------|-----------------------------------|
| Tyro basin (Eastern Mediterranean) | | | | | | | HG-NAA | Van der Weijden et al., 1990 |
| 10–3347 dbar | oxic | 200–235 ^g | 7.3–43.8 ^g | 183–208 ^g | | | | |
| 3379–3563 dbar | anoxic brine | 343–846 | 106–644 | 202–319 | | | | |
| Bannock basin (Eastern Mediterranean) | | | | | | | | |
| 2–3300 dbar | oxic | 196–239 | 23.1–36.5 | 163–208 | | | | |
| 3320–3470 dbar | anoxic brine | 666–767 | 390–649 | 118–276 | | | | |
| Coastal sea water, Qingdao, CN | | 800–900 | | | | | FIA-HG-AAS | Xiankun et al., 1990 |
| Black Sea, 3-16/06/88 | | | | | | | HG-GC-PID | Cutter, 1991 |
| Station BS3-2 (42°50'N, 32°00'E) | | | | | | | | |
| Surface | oxic | 192 ^g | ND ^f | 192 ^g | 7.3 ^g | ND ^f | | |
| 20–65 m | anoxic | 35.3–140 | ND ^f | 35.3–140 | ND ^f –6.1 | ND ^f | | |
| 70–600 m | (sulfide detect. | 8.5–127 | 3.7–90.1 ^g | ND ^f –127 | ND ^f | ND ^f | | |
| 800–2000 m | at 90 m) | 85.2–115 | ND ^g –24.4 | 63.3–95.0 | ND ^f | ND ^f | | |
| Station BS3-6 (43°04'N, 34°00'E) | | | | | | | | |
| Surface | oxic anoxic | 166 | ND ^g | 166 | 8.5 | ND ^f | | |
| 15–90 m | (sulfide detect. | 40.1–122 | ND ^g | 40.2–122 | ND ^f –8.5 | ND ^f | | |
| 95–800 m | at 110 m) | 41.4–112 | ND–63.3 | 28.0–88.9 | ND ^f –3.7 | ND ^f | | |
| 1500–2192 m | | 56.0–99.8 | 35.3–59.7 | 7.3–43.8 | ND ^f | ND ^f | | |
| Mid-Chesapeake Bay, 4 m, 14/06/88 | | | < 0.4 ^g | 58.4 ^g | | | HG-GC-PID | Cutter et al., 1991 |
| sed. porewater, mid Ches., 15/06/88 | | | 415 | 1924 | | | | |
| Spanish Mediterranean Sea coast | | 140 | ND ^f | | | | FIA-HG-AAS | de la Calle Guntiñas et al., 1991 |
| Sea water | | 160 | 33 | 127 | | | Coprecipitation (thionalide) + NAA | Sun et al., 1993 |
| Surface water Eastern Atlantic Ocean, transect from 24°S to 31°N, 1990 | mean value | 136 ^g | | | | | HG-GC-PID | Cutter and Cutter, 1995 |
| Deep waters Eastern Atlantic Ocean | | | | | | | | |
| 34°N, 13°W | 2300–4400 m | 128 | | | | | | |
| 24°N, 23°W | 2000–4100 m | 136 | | | | | | |
| 15°N, 0°W | 2000–4600 m | 132 | | | | | | |

(continued on next page)

| | | | | |
|---------------------------------------------------------|--------|-----------------|-----------------|-----------------|
| Mixed layer | 178 | 2.4 | 39 | ND ^f |
| AAIW ⁱ | 44 | ND ^f | ND ^f | ND ^f |
| UCDW | 83 | ND ^f | ND ^f | ND ^f |
| NADW | 88 | ND ^f | ND ^f | ND ^f |
| AABW | 97 | ND ^f | ND ^f | ND ^f |
| RF (0.59°S, 20.03°W) | | | | |
| Mixed layer | 268 | 1.2 | | |
| AAIW ⁱ | 106 | ND ^f | | |
| NADW | 130 | ND ^f | | |
| AABW | 138 | ND ^f | | |
| Station 6 (80°N, 45°W) | | | | |
| Surface | 185 | 3.6 | | |
| NADW ⁱ | 130 | ND ^f | | |
| AABW | 155 | ND ^f | | |
| Amazone River plume (upper 500 m) | 61 | 7.3 | | |
| Horizontal transect, 11,000 km (Montevideo-Barbados) | 151–91 | < 3.6 | 16 | ND ^f |

^aInternational country codes follow the ISO 3166 convention; specific sampling dates are given as dd/mm/yy, otherwise the month and year are given if reported.

^bMSA = methylstibonic acid.

^cDMSA = dimethylstibonic acid.

^dSee corresponding list for meaning of abbreviations.

^eParticulate concentrations also given.

^fND = not detected.

^gIn molar scale units in the original.

^hEstimated from graph by digitisation of the corresponding figure (Silk Scientific, 1998).

ⁱAABW = Antarctic Bottom Water, NADW = North Atlantic Deep Water, AAIW = Antarctic Intermediate Water, UCDW = Upper Circumpolar Deep Water.

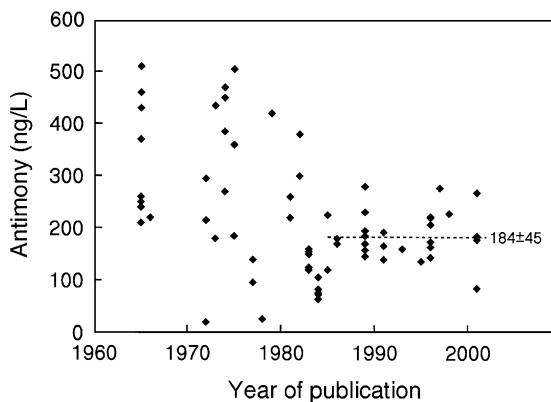


Fig. 1. Published total dissolved antimony concentrations for surface seawater as a function of their year of publication. Values taken from Table 4. The value shown in the figure corresponds to the mean and standard deviation of the values published since 1985.

lantic Ocean); Van der Weijden et al., 1990 (Western Mediterranean); Takayanagi et al., 1996 (Western Mediterranean Sea, Southern part); Cutter et al., 2001 (subtropical–equatorial Atlantic Ocean). Andreae and Froelich, (1984) attributed the scavenging nature of antimony in the Baltic Sea to a higher particle flux and longer water residence time in this sea as compared to the oceans. Thus, antimony concentrations seem to reflect regional geochemical characteristics in coastal environments.

Comparison of antimony contents in deep waters of the different oceans indicates that no antimony accumulation is produced during deep-water oceanic circulation (Cutter and Cutter, 1998).

4.3. Estuaries

Antimony behaviour in estuaries seems to be rather variable depending on the estuary characteristics. Different behaviour has even been observed in the same estuary in different years (van der Sloot et al., 1985). Table 5 provides the sparsely available published data. In estuaries without large pollutant sources, antimony behaves conservatively according to Andreae (1983), Andreae et al. (1983) and van der Sloot et al. (1985). However, in the Scheldt estuary, antimony showed a non-conservative behaviour with a mid-estuary maximum (van der Sloot et al., 1985). Similar behaviour was observed in surface waters

from two Texas estuaries, Galveston Bay and Corpus Christi Bay (Stordal, 1996). van den Berg et al. (1991) found a mixed behaviour, with antimony being conservative for salinities higher than five parts per thousand and scavenged at lower salinities. These data indicate antimony removal at very low salinities (turbidity maximum) followed by a release at intermediate salinities thereby causing a broad mid-estuarine maximum. The same author reported antimony removal at low salinities and release at intermediate salinities, with adsorption–desorption reactions probably playing a role in the Tamar estuary (van den Berg, 1993).

Byrd (1990) studied a large number of estuaries ranging from pristine to highly polluted and from inorganically dominated to very organic-rich ones. His results confirm that antimony behaviour strongly depends upon estuary characteristics. Arsenic and antimony often showed different behaviour. The authors attributed this to the association of arsenic with low molecular weight organic matter and to the possible association of antimony with particles, which increase the possibility of sedimentation during estuarine mixing.

5. Occurrence in sediments and soils

Antimony concentrations in sediments and soils are of the order of a few $\mu\text{g/g}$ (Tables 6 and 7). Higher concentrations are directly related to anthropogenic sources, mainly proximity to smelting plants (O'Toole et al., 1971; Crecelius et al., 1974; Cawse et al., 1975; Ragaini et al., 1977; Ainsworth et al., 1990a; Asami et al., 1992). Elevated concentrations in sediments near the outfalls of sewage and fertiliser facilities have also been reported (Papakostidis et al., 1975; Grimanis et al., 1977).

Unfortunately, not much is known about antimony mobility in soils. According to the Toxics Release Inventory (USEPA, 1998), antimony and antimony compounds releases to land and water in the US totaled 5.5 million kg from 1987 to 1993. These releases were nearly all on land (land: 5,456,079 kg, water: 150,029 kg). Antimony fate in soils may thus be a key element in antimony cycling in the environment. The few data available points to an antimony accumulation near the soil surface, fol-

lowed by a concentration decrease with depth (Ragaini et al., 1977; Ainsworth et al., 1990a). This indicates that the source is most probably atmospheric and that antimony is rather non-reactive in these media. Antimony in geogenetically polluted soils is mostly immobile according to Hammel et al. (1998). It is possible that much of the antimony in contaminated soils remains as the non-reactive oxides when it is deposited in this form. On the other hand, antimony in contaminated soils does not seem to be readily bioavailable, its concentrations in invertebrates and the shrews which feed on them have been measured and no significant increase has been observed (Ainsworth et al., 1990b).

High antimony concentrations are generally associated with high arsenic concentrations in sulfide ores and the use of antimony concentration in soils has been proposed as pathfinder for gold, confirming the chalcophilic nature of this element (Hawkes and Webb, 1962; Hale, 1981).

6. Reference materials

In comparison with other trace elements, reference materials (RM) with certified antimony contents are scarce. The most often used and easily available environmental reference materials containing antimony are given in Table 8. Data quoted in Tables 3–7 do not contain any published result for this type of samples. However, the reader can find complementary information on the use of these reference materials in the following selection of recent papers where these compounds are analysed: Sturgeon et al. (1985a,b), Anderson and Isaacs (1994, 1995) Sturgeon and Grégoire (1994), D'Ulivo et al. (1995), Ding and Sturgeon (1996), and Zhang and Combs (1996) for water reference materials; and de Oliveira et al. (1983), McLaren et al. (1988), Donaldson (1990), de la Calle Guntiñas et al., 1992, Anderson and Isaacs (1994, 1995), D'Ulivo et al., 1995 and López-García et al. (1997) for sediments and/or soils reference materials.

7. Occurrence in biota

There is no evidence of bioconcentration of antimony in aquatic algae (Bonotto et al., 1983; Mann

and Fyfe, 1988; Mann et al., 1988). Reported concentrations for antimony in freshwater and marine algae are 0.1–0.2 $\mu\text{g/g}$ dry weight (range from 0.02 to 1 $\mu\text{g/g}$ dry weight) (Leatherland and Burton, 1974; Strohal et al., 1975; Payer et al., 1976; Bowen, 1979; Abu-Hilal and Riley, 1981; Kantin, 1983; Andreae and Froelich, 1984; Maher, 1986; Djingova et al., 1987; Mann and Fyfe, 1988; Mann et al., 1988; Cutter et al., 1991; Jayasekera, 1994; Bondavalli et al., 1996; Esen et al., 1999; Hou and Yan, 1998; Hou, 1999; Kut et al., 2000).

Not much is known about the distribution of antimony in algae. Bonotto et al. (1983) in a study on ^{125}Sb uptake by four species of marine algae showed that most of the antimony was present in the cytosol, with very little being retained by cell walls or associated in organelles. Phytoplankton uptake of antimonate has not been reported. The different behaviour of antimonate, as compared to arsenate and phosphate, may be explained by the weaker Lewis acidity and larger ionic radius of antimonate.

Although algae bioaccumulation and detoxifying mechanisms may be important because of their possible role in antimony redox speciation, not many studies have been performed. Kantin (1983) sampled three marine algae in San Diego Bay seawater. In all of them, Sb(V) was the dominant species. Only *Sargassum* sp. was found to contain up to 30% of Sb(III), thus demonstrating an ability to form the reduced compound. Incubation of the diatom *Thalassiosira nana* with $^{125}\text{SbCl}_3$ readily yielded a protein-bound antimony, a stibnolipid, and a group of water soluble radioactive products (Benson, 1988). Andreae and Froelich, (1984) found both Sb(III) and Sb(V) to be present in phytoplankton from the Eastern North Pacific. After exposure to Sb(III), the freshwater algae *Chlorella vulgaris*, isolated from an arsenic-polluted environment, excreted 40% Sb(V) and 60% Sb(III), suggesting that a change in oxidation state is used by this alga as a detoxifying mechanism (Maeda et al., 1997; Maeda and Ohki, 1998). In the cell, antimony was found combined with proteins of molecular weight 4×10^4 Da.

There is little evidence of biomagnification of antimony in food chains represented by soil–vegetation–invertebrate–insectivore pathway of grasslands, and little indication of significant accumulation by

Table 5
Published antimony concentrations in estuarine systems (filtered samples)

| System ^a | System details | Total Sb (ng/l) | [Sb(III)] (ng/l) | [Sb(V)] (ng/l) | [MSA] ^b (ng/l) | [DMSA] ^c (ng/l) | Experimental technique ^d | Reference |
|-----------------------------------|----------------------------|-----------------------|---------------------|-------------------|------------------------------|-------------------------------|----------------------------------------|------------------------------------------|
| Ochlockonee Bay estuary, 15/03/81 | | | | | | | HG-AAS | Andreae et al. 1981; Andreae, 1983 |
| 4.3 ^e | | | 2.8 | 42.0 | 0.8 | ND ^f | | |
| 12.3 | | | 6.6 | 81.5 | 1.4 | ND ^f | | |
| 18.9 | | | 8.3 | 113.0 | 2.2 | ND ^f | | |
| 23.8 | | | 5.4 | 122.0 | 5.1 | 0.6 | | |
| 30.2 | | | 8.8 | 126.0 | 10.9 | 1.1 | | |
| 33.4 | | | 11.1 | 136.0 | 12.6 | 1.5 | | |
| Tejo River estuary, PT, 26/04/82 | pH ≈ 8 | | | | | | HG-AAS | Andreae et al., 1983 |
| 0.06 ^e (Tejo River) | [O ₂] ≈ 7 mg/l | 102 | | | | | | |
| 1.5 | | 143 | | | | | | |
| 2.7 | | 203 | | | | | | |
| 4.3 | | 219 | | | | | | |
| 8.7 | | 257 | | | | | | |
| 20.3 | | 514 | | | | | | |
| 26.1 | | 626 | | | | | | |
| 26.5 | | 669 | | | | | | |
| 32.0 | | 645 | | | | | | |
| 32.9 | | 460 | | | | | | |
| 33.9 | | 225 | | | | | | |
| 36.0 (surface sea water) | | 155 | | | | | | |
| Rhine River estuary, NL, Feb. '75 | | | | | | | HG-NAA | van der Sloot et al., 1985 |
| 0.6 ^e | | 329–1059 ^g | | | | | | |
| 2.4 | | 877 | | | | | | |
| 4.5 | | 852 | | | | | | |
| 12.2 | | 1912 | | | | | | |
| 32 | | 158 | | | | | | |

Scheldt River estuary, NL, 1975

| | |
|----------------|---------------------|
| 2 ^e | 3250 ^{g,h} |
| 4 | 2520 |
| 8 | 1500 |
| 22 | 535 |
| 26 | 560 |
| 29 | 160 |
| 33 | 330 |

Scheldt River estuary, NL, 1978

| | |
|----------------|----------------------|
| 2 ^e | 770 ^{g,h,i} |
| 4 | 730 |
| 11 | 510 |
| 17 | 185 |
| 21 | 95 |
| 26 | 365 |
| 33 | 170 |

Scheldt River estuary, NL, 1982

| | |
|----------------|----------------------|
| 1 ^e | 305 ^{g,h,i} |
| 4 | 915 |
| 9 | 210 |
| 12 | 1545 |
| 14 | 1230 |
| 20 | 330 |
| 22 | 1170 |
| 31 | 415 |
| 34 | 220 |

Tamar River estuary, GB, 18/07/83

| | | |
|------------------|-----|-----|
| < 2 ^e | 352 | 10 |
| 16 | 616 | < 1 |
| 33 | 382 | 5 |

HG-AAS

Apte and
Howard, 1986

(continued on next page)

Table 5 (continued)

| System ^a | System details | Total Sb (ng/l) | [Sb(III)] (ng/l) | [Sb(V)] (ng/l) | [MSA] ^b (ng/l) | [DMSA] ^c (ng/l) | Experimental technique ^d | Reference |
|-------------------------------|-------------------------------------------------------|-------------------------|---------------------|-------------------|------------------------------|-------------------------------|----------------------------------------|------------|
| St Mary's estuary, FL, US | DOC > 30 mg/l linear increase between 0° and 31 | 4.7–124 ^{g,h} | | | | | HG-AAS | Byrd, 1990 |
| Satilla River estuary, GA, US | DOC > 40 mg/l linear increase between 0° and 31 | 10.0–139 ^{g,h} | | | | | | |
| Medway River estuary, NS, CA | DOC > 6 mg/l linear increase between 0° and 30 | 142–494 ^{g,h} | | | | | | |
| Savannah River estuary, US | small variation | | | | | | | |
| | 2 ^e | 147 ^{g,h} | | | | | | |
| | 9 (max) | 182 | | | | | | |
| | 31 | 109 | | | | | | |
| Geum River estuary, KR | sediment input at > 15° | | | | | | | |
| | 3 ^e | 88 ^{g,h} | | | | | | |
| | 12 | 54 | | | | | | |
| | 22 (max) | 521 | | | | | | |
| | 27 | 239 | | | | | | |
| Tama River estuary, JP | highly polluted input at low salin. | | | | | | | |
| | 2 ^e | 855 ^{g,h} | | | | | | |
| | 8 | 812 | | | | | | |
| | 13 | 275 | | | | | | |
| | 30 | 291 | | | | | | |

| | | | | | |
|-----------------------------------|--------------------------------------|----------------|----------------------|-----------------------|-----------------------------------------------------|
| Tan Shui estuary, TW | highly polluted scattered concen. | 3 ^e | 385 ^{g,h} | | |
| | | 12 | 323 | | |
| | | 20 | 423 | | |
| | | 33 | 198 | | |
| Tamar River estuary, GB, Jul. '86 | (turbid. max.) | | ND ^f | CL-CSV (CL = oxine | van den Berg et al., 1991; van den Berg, 1993 |
| < 2 ^e | | | 24 ^{g,h} | | |
| 5 | | | 69 | | |
| 6 | | | 145 | | |
| 8 | | | 193 | | |
| 9 | | | 191 | | |
| 11 | | | 198 | | |
| 13 | | | 217 | | |
| 18 | | | 223 | | |
| 28 | | | 236 | | |
| 31 | | | 258 | | |
| 34 | | | | | |
| Galveston Bay, US | surface waters | | 100–755 ^g | | Stordal, 1996 |
| Corpus Christi Bay, US | | | | | |

^aInternational country codes follow the ISO 3166 convention; specific sampling dates are given as dd/mm/yy, otherwise the month and year are given if reported.

^bMSA = methylstibonic acid.

^cDMSA = dimethylstibonic acid.

^dSee corresponding list for meaning of abbreviations.

^eSalinity on the Practical Salinity Scale.

^fND = not detected.

^gIn molar scale units in the original.

^hEstimated from graph by digitisation of the corresponding figure (Silk Scientific, 1998).

ⁱParticulate concentrations also given.

Table 6
Published antimony concentrations in sediments

| Sites(s) sampled ^a | System details | Total Sb ($\mu\text{g}/\text{g}^{\text{b}}$) | Experimental technique ^c | Reference |
|-------------------------------------------|----------------------------|------------------------------------------------|-------------------------------------|------------------------------|
| Southampton Water and Solent, GB | | 0.67–2.3 | NAA | Leatherland and Burton, 1974 |
| River Mersey, GB | | 2.9 | | |
| Puget Sound estuary, Washington, US | | | NAA | Crecelius et al., 1975 |
| Bellingham Bay | | 0.83–1.43 | | |
| Strait Juan de Fuca–N. Puget Sound | | 0.35–1.13 | | |
| Hood Canal | | 0.33–1.16 | | |
| Central Puget Sound–Seattle area | | 0.47–12 | | |
| Tacoma area | smelter | 0.68–12,500 | | |
| Southern Puget Sound | | 0.28–12 | | |
| Upper Saronikos Gulf, GR | Athens sewage outfall area | 0.16–18 | NAA | Papakostidis et al., 1975 |
| Danube River and Danube Canal, Vienna, AT | | 8.22–22.22 | NAA | Rehwoldt et al., 1975 |
| North Adriatic Sea | | 20 | NAA | Strohal et al., 1975 |
| Upper Saronikos Gulf, GR | | | NAA | Grimanis et al., 1977 |
| Minimum concentration | | 0.4 | | |
| Elefsis Bay | | 2 | | |
| Athens outfall | | 15 | | |
| Piraeus Harbor | | 65 | | |
| Wateree River, SC, US, Jul. '77 | | < 0.05 | GF-AAS | Friant and Koerner, 1981 |
| Ginsheim sediments (Rhine River), GE | polluted | 7.95–96.1 | NAA | Dissanayake et al., 1983 |
| Average North-Sea sediments | | 0.92 | | |

| | | | | |
|----------------------------------------|--------------------------|---------------------|---------|------------------------------|
| US sediments | | | AAS | Brannon and Patrick, 1985 |
| Black Rock Harbour | | 2.1 | | |
| Corpus Christi Ship Channel | | 1.6 | | |
| Detroit River | | 5.9 | | |
| Indiana Harbour | | 17.5 | | |
| Johnson Creek, Bridgeport Harbour | | 7.1 | | |
| Menominee River | | 0.5 | | |
| Michigan City Harbour | | 11.8 | | |
| Milwaukee Harbour | | 0.8 | | |
| Oakland Inner Harbour | | 1.2 | | |
| Seattle, Duwamish Waterway | | 3.7 | | |
| Recent sediments, AU | | | ICP-OES | Hirner et al., 1990 |
| Mangrove sed., Broad Sound, Eastern AU | | 53 ^d | | |
| Algal mats, Spencer Gulf, South AU | | 32 ^d | | |
| Ancient sediments | | 2/7/12 ^e | | |
| Polluted algal mats, AU | smelter | 100 ^d | | |
| Rhine River, GE | polluted | 3/1/38 ^e | | |
| Coeur d'Alene River, ID, US | | | NAA | Mok and Wai, 1990 |
| North Fork | non-polluted | 1.91 | | |
| Main Stem (five sampling sites) | polluted | 48.72–60.19 | | |
| South Fork | mining wastes present | 136.81 | | |
| Delta area, vertical distribution | | | | |
| 0.5 cm | | 58.06 | | |
| 4.5 cm | | 47.13 | | |
| 8.5 cm | | 2.99 | | |
| 14.5 cm | | 1.96 | | |
| 18.0 cm | | 1.82 | | |
| 21.5 cm | | 2.20 | | |

(continued on next page)

Table 6 (continued)

| Sites(s) sampled ^a | System details | Total Sb ($\mu\text{g}/\text{g}^{\text{b}}$) | Experimental technique ^c | Reference |
|---------------------------------------------------|------------------------------------------|------------------------------------------------|-------------------------------------|----------------------------|
| Black Sea sediments, 14/06/88 | | | HG-GC-PID | Cutter et al., 1991 |
| 0–11 cm | | 1.37 | | |
| 10–11 cm | | 0.67 | | |
| 80 m sedim. trap material, N Pacific Ocean | | 0.49 | | |
| Black Sea sediments | | | HG-GC-PID | Cutter, 1992 |
| 1–2 cm | | 1.29 ^{f,g} | | |
| 6–7 cm | | 0.47 | | |
| 11–12 cm | | 0.96 | | |
| Antarctica lakes | | 0.04 | HG-AFS | Barghigiani et al., 1995 |
| Arno River, IT | | 0.2 | | |
| Venice Lagoon, IT | | 0.14–0.74 | | |
| Sediment Saudi Coast, Arabian Gulf, SA, 1991–1994 | possible effect of Gulf War | 7.4–29.5 | ICP-OES | Sadiq et al., 1995 |
| Lagoon Sacca di Goro, Po River delta, IT | high water renewal slow water renewal | 2.03 1.02 | NAA | Bondavalli et al., 1996 |
| River in West GE | | 0.5–11.9 ^h | LTGC-ICP-MS | Krupp et al., 1996 |
| Orion Creek, Washington, US, Aug.–Oct. '92 | near Van | | ICP-MS | Routh and Ikramuddin, 1996 |
| Near abandoned tailings ponds | Stone Pb/Zn | 0.79 | | |
| Near new tailings pond | mine | 0.35 | | |
| New tailings pond | | 0.59 | | |

| | | | | |
|-------------------------|-------------|-----------|------------|---------------------------|
| River sediment | | 127 | Slurry | López-García et al., 1997 |
| Marine sediment | | 8.3 | sampling + | |
| Marine sediment | | 19.1 | GF-AAS | |
| Küçükçekmece Lagoon, TR | 0–2 cm | | NAA | Esen et al., 1999 |
| Apr. '94 | | 1.07 | | |
| Oct. '94 | | 1.47 | | |
| Marmara Sea, TR | 0–2 cm | | | |
| Apr. '94 | | 0.28 | | |
| Oct. '94 | | 0.46 | | |
| Küçükçekmece Lagoon, TR | | | | |
| Sediment core, Apr. '94 | 0–2 cm | 1.18 | | |
| | 2–4 cm | 0.95 | | |
| | 4–9 cm | 0.90 | | |
| Sediment core, Oct. '94 | 0–2 cm | 1.23 | | |
| | 2–4 cm | 1.70 | | |
| | 4–9 cm | 1.64 | | |
| Bosphorous, TR, 1993 | 3 locations | 0.36–0.44 | NAA | Kut et al., 2000 |

^a International country codes follow the ISO 3166 convention; specific sampling dates are given as dd/mm/yy, otherwise the month and year are given if reported.

^b Dry weight basis.

^c See corresponding list for meaning of abbreviations.

^d Kerogen fraction (acid resistant organics).

^e Dichloromethane extracted fraction/reflux alkaline extractable fraction (humic fraction)/acid-resistant organics (kerogen fraction).

^f Sb(III) concentrations also given.

^g In nmol/g units in the original.

^h In ng/g units, only alkylic Sb compounds: 0.2–9.8 ng/g SbMeH₂, 0.1–1.2 ng/g SbMe₂H, 0.1–0.9 ng/g SbMe₃, 0.1 ng/g SbEt₃.

Table 7
Published antimony concentrations in soils

| Site(s) sampled ^a | System details | Total Sb ($\mu\text{g}/\text{g}^{\text{b}}$) | Experimental technique ^c | Reference |
|-------------------------------------------------------------------------|-------------------------|---------------------------------------------------|----------------------------------------|---------------------------------------|
| Soils Idaho and North Carolina, US | | 2.3–9.5 | Colorimetry (rhodamine B) | Ward and Lakin, 1954; Onishi, 1969 |
| Soils Nyeba lead–zinc district, NG | | | not given | Hawkes, 1954; Onishi, 1969 |
| Soils 30–120 m distant from the Ameri lode | | 1–5 | | |
| Soils 30–90 m distant from Palm Wine lode | | 1–2 | | |
| Residual soils, Jenó Hill–Galena Hill area, YT, CA | | 1–3 | Colorimetry | Boyle, 1965; Onishi, 1969 |
| Soils | | 2–10 (mean: 6) | | Bowen, 1966 |
| Yellow Knife, NW Territories; soils near stack in gold refining site | | 280 | | O’Toole et al., 1971 |
| Soils | | 0.5 | Not given | Brooks, 1972 |
| Soils, Holland Marsh, NL | market- garden soils | | PAA | Chattopadhyay and Jervis, 1974 |
| Surface | | 1.85–2.11 | | |
| 0–7.5 cm | | 1.73 | | |
| 7.5–15.0 cm | | 0.66 | | |
| 15.0–22.5 cm | | 0.58 | | |
| 22.5–30.0 cm | | 0.93 | | |
| 30.0–37.5 cm | | 0.75 | | |
| 37.5–45.0 cm | | 0.70 | | |
| Soils close to a Cu smelter site, US | | | NAA | Crececius et al., 1974 |
| Vashon Island | | 8–61 | | |
| Maury Island | | 49–204 | | |
| Tacoma area | | 31 | | |
| East of Tacoma | | 65–109 | | |
| West of Tacoma | | 11–63 | | |
| North of Seattle | | 3–5 | | |

| | | | | |
|--------------------------------------------------------------|------------------------------------------------|---------------------------------|---------------------------------|------------------------------------------|
| Sandstone and sands, ZW | arsenical soils | 50–5000 | | Wild, 1974 |
| On a former Sn smelter site | | 176 | | Cawse et al., 1975 |
| US unpolluted soils, B horizon (1000 samples) | | < 150 | | Connor and Shacklette, 1975 |
| Rural soil, SE England, GB | acid sandy soil (pH = 4.9) | 0.7 | AAS | Cornfield, 1977 |
| Soils, BG | large variety, various depths | 0.82–2.32 | NAA | Naidenov and Travesi, 1977 |
| Close to a Pb smelting complex (Kellogg, Idaho) (0–2 cm), US | sites located 0.4 to 19 km from smelter | 5–260 | NAA | Ragaini et al., 1977 |
| Twelve organic soils, NR | | 0.17–2.20 | NAA | Allen and Steinnes, 1979; Steinnes, 1980 |
| Arable surface soils, Scotland, GB | | ≈ 1 | | Mitchell and Burridge, 1979 |
| Scottish soils, GB | 10 samples, different soil types and locations | 0.29–1.3 (mean: 0.64) | Spark source MS | Ure et al., 1979 |
| Vicinity Pb/Zn smelter, BC, CA | | | ICP-AES | Lynch et al., 1980 |
| Immediately adjacent smelter (Trail) | | 49 | | |
| 50 km from smelter (Nelson) | | 11 | | |
| Humus layer of Norwegian soils | 10 regions | 0.17–2.20 | NAA | Steinnes, 1980 |
| Lekkerkerk highly polluted soils, NL | comparison of three techniques | 0.24–3.2 0.32–3.2 0.4–3.0 | Colorimetry HG-AAS GF-AAS | Haring et al., 1982 |

(continued on next page)

Table 7 (continued)

| Site(s) sampled ^a | System details | Total Sb ($\mu\text{g}/\text{g}^{\text{b}}$) | Experimental technique ^c | Reference |
|--------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------|---------------------------------------------------|----------------------------------------------------|-------------------------------|
| World soil average | | 1 | | Martin and Whitfield, 1983 |
| Normal levels in top soils (0–10 cm) Upper limit unpolluted soil, BE | all types clay-rich | < 0.2–0.5 0.1–3.0 1.0 | GF-AAS | De Temmerman et al., 1984 |
| US unpolluted soils, B horizon | (1000 samples) | < 1–8.8 (mean: 0.52) | | Shacklette and Boerngen, 1984 |
| Soil, Christchurch, NZ | | 4.33–7.95 (mean: 5.94) | NAA | Fergusson et al., 1986 |
| Mean of 24 surface soils, JP | | 0.13–0.91 (mean: 0.37) | HG-AAS | Asami et al., 1988 |
| Rural soil, Northumberland, GB 0–5 cm 10–15 cm | | 6.9 7.6 | AAS and NAA | Ainsworth et al., 1990a |
| Prox. Sb smelter (River Tyne, GB) 100 m from smelter 250 m from smelter 450 m from smelter | concentration decreases with depth | 170–360 90–200 120–180 | | |
| Soil horizons (Indiana Dunes), US | Sb more concentrated in clay fractions | 0.19–11.4 | NAA | Esser et al., 1991a,b |
| Various soil types, CN | | 0.38–2.98 (mean: 1.06) | | Qi and Cao, 1991 |
| Surface soils, JP Konosu IF Konosu OM Nagano Near Kunitomi smelter | eutric gleysol eutric gleysol eutric cambisol | 1.16 1.22 0.64 3.19 | Automated HG- electrochemical heating-AAS | Asami et al., 1992 |
| Old mining area, Derbyshire, GB Winster village and farm A Topsoil (0–15 cm) Subsoil (15–20 cm) Subsoil (30–45 cm) | | 23.4 21.8 17.1 | ICP-AES | Li and Thornton, 1993 |

| | |
|-------------------------------------|------|
| Control site (farm B) | |
| Topsoil (0–15 cm) | 1.43 |
| Subsoil (15–20 cm) | 1.11 |
| Subsoil (30–45 cm) | 1.20 |
| Old smelter site, Derbyshire, GB | |
| Old smelter site (stone Edge) | |
| Topsoil (0–15 cm) | 103 |
| Subsoil (15–20 cm) | 41.3 |
| Subsoil (30–45 cm) | 17.3 |
| Smelter surrounding area | |
| Topsoil (0–15 cm) | 1.10 |
| Subsoil (15–20 cm) | 1.03 |
| Subsoil (30–45 cm) | 0.63 |
| Old zinc mining area in Shipman, GB | |
| Shipham mining area | |
| Topsoil (0–15 cm) | 37.9 |
| Subsoil (15–20 cm) | 36.1 |
| Subsoil (30–45 cm) | 28.9 |
| Old Red sandstone area | |
| Topsoil (0–15 cm) | 1.01 |
| Subsoil (15–20 cm) | 0.68 |
| Subsoil (30–45 cm) | |
| Old mining area, Cornwall, GB | |
| Old mining site, Fraddam | |
| Topsoil (0–15 cm) | 2.21 |
| Subsoil (15–20 cm) | 2.32 |
| Subsoil (30–45 cm) | 1.95 |
| Old mining site, Wheal Sister farm | |
| Topsoil (0–15 cm) | 0.65 |
| Subsoil (15–20 cm) | 0.53 |
| Subsoil (30–45 cm) | 0.51 |

(continued on next page)

Table 7 (continued)

| Site(s) sampled ^a | System details | Total Sb ($\mu\text{g}/\text{g}^{\text{b}}$) | Experimental technique ^c | Reference |
|-------------------------------------------------------|-----------------------------------|---------------------------------------------------|----------------------------------------|---------------------------|
| Old As calciner and Sn smelter sites, Cornwall, GB | | | | |
| New Mill Farm | | | | |
| Topsoil (0–15 cm) | | 5.49 | | |
| Subsoil (15–20 cm) | | 6.33 | | |
| Subsoil (30–45 cm) | | 3.91 | | |
| Mean world soils | | 3.6 | Literature survey | Frink, 1996 |
| Soil | | 3.8 | CMCPE-DPASV | Khoo and Zhu, 1996 |
| Soil samples associated with gray copper ore, GE | | 222–333 | GF-AAS + HG-AAS | Gebel et al., 1997 |
| Polluted soil, Bavaria, GE | 2 samples | 232, 268 | HPLC-ICP-MS | Lintschinger et al., 1997 |
| Soil 1 | | 6.5 | Slurry sampling + GF-AAS | López-García et al., 1997 |
| Soil 2 | | 17.1 | | |
| Bitterfeld industrial area, GE | | | | |
| 10 cm | accumulation in A _h | 5.8 | PAA | Schulze et al., 1997 |
| 50 cm | horizon, | 2.8 | | |
| 100 cm | decrease with | 2.4 | | |
| 150 cm | depth but | 1.3 | | |
| 10 cm | peak at 1 m | 9.0 | NAA | |
| 50 cm | depth (Gor- | 40 | | |
| 100 cm | horizon acts | 36 | | |
| 150 cm | as a barrier) | 2.0 | | |
| Southern Norway surface soil | decrease along a | 2.4 | NAA | Steinnes et al., 1997 |
| Northern Norway surface soil | northerly gradient | 0.22 | | |
| Agricultural (unpolluted) soils, GE | | | | |
| Luvisol | | 1.0 | AAS | Hammel et al., 1998 |
| Chernozem | | 4.0 | | |

| | | | | |
|---------------------------------------------------------------|-------------------|---------------------------|-------------|-------------------------|
| Polluted soils from a mining area in Nordpfälzer Bergland, GE | | | | |
| Fallow meadow | | 13 (12 ^d) | | |
| Agriculturally used meadow | | 82 (30 ^d) | | |
| Vineyard | | 153 (24 ^d) | | |
| Vineyard | | 18 (33 ^d) | | |
| Former mine dump | | 1317 (2717 ^d) | | |
| Bitterfeld, GE | strongly polluted | > 100 ^e | IC-ICP-MS | Ulrich, 1998 |
| Guadamar valley, ES | | | | |
| Soils unaffected by acidic mining sludges | | 0.71–3.31 (mean: 1.80) | ICP-MS | Cabrera et al., 1999 |
| Soils affected by a toxic flood from acidic mining sludges | | 0.89–323 (mean: 13.7) | | |
| unpolluted sites | | | | |
| Soil 1 | | 0.29 | USS + ETAAS | Cal-Prieto et al., 1999 |
| Soil 2 | | 0.46 | | |
| Soil 3 | | 0.68 | | |
| 0–10 cm soil horizon Thetford Forest, GB | | | | |
| Control soil | pH 3.3 | 0.0 | ICP-MS | Hartley et al., 1999 |
| Contaminated soil | pH 3.9 | 8.7 | | |
| Bitterfeld, GE | | 2487 ^f | FIA-ICP-MS | Ulrich, 2000 |

^a International country codes follow the ISO 3166 convention; specific sampling dates are given as dd/mm/yy, otherwise the month and year are given if reported.

^b Dry weight basis.

^c See corresponding list for meaning of abbreviations.

^d Mobile content (NH₄NO₃ extraction). Units, µg/kg.

^e The dominant species was Sb(V) (90%), followed by Sb(III) (10%). TMSbO was found in small concentrations.

^f Concentration in soil extracts. Units, µg/l. Sb(III), Sb(V) and TMeSbO values determined.

Table 8
Concentration of antimony in Reference Materials (RM)

| Type and origin | Supplier | Identification | Value (mg/kg) | Value ($\mu\text{g/l}$) |
|--------------------------------|--------------------|-------------------|-------------------|---------------------------|
| <i>Soils</i> | | | | |
| San Joaquin | NIST ¹ | 2709 | 7.9 ± 0.6^a | |
| Montana (high) | NIST ¹ | 2710 | 38.4 ± 3.0^a | |
| Montana (moderate) | NIST ¹ | 2711 | 19.4 ± 1.8^a | |
| Regosolic | CCRMP ² | SO-1 | 0.2^b | |
| Podzolic | CCRMP ² | SO-2 | 0.1^b | |
| Calcareous C horizon | CCRMP ² | SO-3 | 0.3^b | |
| Chernozemic A horizon Lanark | CCRMP ² | SO-4 | 0.7^b | |
| Ontario horizon B and C Cobalt | CCRMP ² | TILL-1 | 7.8^b | |
| Ontario horizon B and C | CCRMP ² | TILL-3 | 0.9^b | |
| Peruvian soil | NBS ³ | 4355 ^c | 14.3^b | |
| Metals in soil | RTC ⁴ | 025–050 | 3.2^b | |
| Dry soil | RTC ⁴ | 026–050 | 3.2^b | |
| Dry soil No. 2 | RTC ⁴ | 021–100 | 8.38 ± 0.84^a | |
| Dry soil No. 3 | RTC ⁴ | 020–050 | 4955 ± 1784^a | |
| Soil/Sediment No. 4 | RTC ⁴ | 008–050 | 2.55^b | |
| Dry soil No. 5 | RTC ⁴ | 022–030 | 0.2^b | |
| Soil | IRANT ⁵ | 12-1-07 | 4.58 ± 0.23^a | |
| Soil | IRANT ⁵ | 12-1-08 | 1.92 ± 0.08^a | |
| Soil | IRANT ⁵ | 12-1-09 | 2.11 ± 0.08^a | |
| Metals in soils | ERA ⁶ | 540–237 | 34.4^a | |
| Soil | IAEA ⁷ | SOIL-7 | 1.7 ± 0.2^a | |
| Soil | UMM ⁸ | SO-1 | 0.5 ± 0.1^a | |
| Podzolic soil | GBW ⁹ | 7401 | 0.87 ± 0.64^a | |
| Chesnut soil | GBW ⁹ | 7402 | 1.3 ± 0.6^a | |
| Yellow–brown soil | GBW ⁹ | 7403 | 0.45 ± 0.30^a | |
| Limy–yellow soil | GBW ⁹ | 7404 | 6.3 ± 3.4^a | |
| Yellow–red soil | GBW ⁹ | 7405 | 35.4 ± 1.4^a | |
| Yellow–red soil | GBW ⁹ | 7406 | 60 ± 20^a | |
| Laterite | GBW ⁹ | 7407 | 0.42 ± 0.26^a | |
| Loess | GBW ⁹ | 7408 | 1.04 ± 0.65^a | |
| Soil | GBW ⁹ | 7409 | 0.21 ± 0.06^a | |
| Soil | GBW ⁹ | 7410 | 0.93 ± 0.64^a | |
| Soil | GBW ⁹ | 7411 | 9.2 ± 2.9^a | |
| Soil | GBW ⁹ | 7418 | 0.73 ± 0.13^a | |
| Soil | GBW ⁹ | 7419 | 0.84 ± 0.18^a | |
| Soil | GBW ⁹ | 7420 | 0.65 ± 0.12^a | |
| Soil | GBW ⁹ | 7421 | 0.78 ± 0.16^a | |
| Soil | GBW ⁹ | 7422 | 0.70 ± 0.15^a | |
| Tibet soil | GBW ⁹ | 8302 | 0.4^b | |
| <i>Freshwater sediments</i> | | | | |
| Buffalo River | NIST ¹ | 8704 | 3.07 ± 0.32^a | |
| NY–NJ Waterway sediment | NIST ¹ | 1944 | 5^b | |
| River sediment | NBS ³ | 1645 ^c | 51^b | |
| River sediment | NBS ³ | 2704 ^c | 0.79 ± 0.15^a | |
| Lavant Creek stream sediment | CCRMP ² | STSD-1 | 3.3^b | |
| Hirok stream sediment | CCRMP ² | STSD-2 | 4.8^b | |
| Composite stream sediment | CCRMP ² | STSD-3 | 4.0^b | |
| Composite stream sediment | CCRMP ² | STSD-4 | 7.3^b | |
| Lake sediment | CCRMP ² | LKSD-1 | 1.2^b | |
| Lake sediment | CCRMP ² | LKSD-2 | 1.1^b | |

Table 8 (continued)

| Type and origin | Supplier | Identification | Value (mg/kg) | Value ($\mu\text{g/l}$) |
|---------------------------------|--------------------|---------------------|--------------------------|-------------------------------|
| <i>Freshwater sediments</i> | | | | |
| Lake sediment | CCRMP ² | LKSD-3 | 1.3 ^b | |
| Lake sediment | CCRMP ² | LKSD-4 | 1.7 ^b | |
| Baikal silt | IAEA ⁷ | SL-3 | 0.56 ± 0.10 ^a | |
| Lake sediment | IAEA ⁷ | SL-1 | 1.31 ± 0.12 ^a | |
| Stream sediment | GBW ⁹ | 7301 | 0.22 ± 0.20 ^a | |
| Stream sediment | GBW ⁹ | 7302 | 0.46 ± 0.34 ^a | |
| Stream sediment | GBW ⁹ | 7303 | 5.4 ± 1.6 ^a | |
| Stream sediment | GBW ⁹ | 7304 | 1.84 ± 0.55 ^a | |
| Stream sediment | GBW ⁹ | 7305 | 3.9 ± 1.4 ^a | |
| Stream sediment | GBW ⁹ | 7306 | 1.25 ± 0.65 ^a | |
| Stream sediment | GBW ⁹ | 7307 | 2.6 ± 0.6 ^a | |
| Stream sediment | GBW ⁹ | 7308 | 0.24 ± 0.18 ^a | |
| Stream sediment | GBW ⁹ | 7309 | 0.81 ± 0.46 ^a | |
| Stream sediment | GBW ⁹ | 7310 | 6.3 ± 1.8 ^a | |
| Stream sediment | GBW ⁹ | 7311 | 14.9 ± 3.7 ^a | |
| Stream sediment | GBW ⁹ | 7312 | 24.3 ± 1.7 ^a | |
| River sediment | BCR ¹⁰ | 320 | 0.6 ^b | |
| Alumosilicate loose sediment | IGI ¹¹ | SGHM-4 | 170 ± 31 ^a | |
| Baikal bottom silt | IGI ¹¹ | BIL-1 | 0.95 ^b | |
| Stream sediment | GSJ ¹² | JSd-2 | 12.5 ^b | |
| Stream sediment | GSJ ¹² | JSd-3 | 2.78 ^b | |
| Lake sediment | GSJ ¹² | JLK-1 | 1.68 ^b | |
| Green River shale | USGS ¹³ | SGR-1 | 3.4 ± 0.5 ^a | |
| <i>Estuarine sediments</i> | | | | |
| | NIST ¹ | 1646 | 0.3 ^b | |
| | NBS ³ | 1646 ^c | 0.4 ^b | |
| <i>Ocean sediments</i> | | | | |
| Ocean sediment radioactivity | NIST ¹ | 4357 | 68 ^b | |
| Organics in marine sediment | NIST ¹ | 1941a | 11.4 ± 0.5 ^b | |
| Marine sediment | GBW ⁹ | 7313 | 1.85 ± 0.67 ^a | |
| Marine sediment | GBW ⁹ | 7314 | 1.4 ^b | |
| Marine sediment | GBW ⁹ | 7315 | 2 ^a | |
| Marine sediment | GBW ⁹ | 7316 | 1.3 ^a | |
| Gulf of St. Lawrence | NRCC ¹⁴ | BCSS-1 ^c | 0.59 ± 0.06 ^a | |
| Gulf of St. Lawrence | NRCC ¹⁴ | MESS-1 ^c | 0.73 ± 0.08 ^a | |
| Beaufort Sea | NRCC ¹⁴ | MESS-3 | 1.02 ± 0.09 ^a | |
| Esquimalt harbour | NRCC ¹⁴ | PACS-1 ^c | 171 ± 14 ^a | |
| Esquimalt harbour | NRCC ¹⁴ | PACS-2 | 11.3 ± 2.6 ^a | |
| Hibernia Shelf (Nfl) | NRCC ¹⁴ | HISS-1 | 0.13 ^b | |
| Gulf of Maine | USGS ¹³ | MAG-1 | 0.96 ± 0.01 ^a | |
| <i>Sea water</i> | | | | |
| Open-ocean water, Bermuda | NRCC ¹⁴ | NASS-1 ^c | | 0.21–0.24 ± 0.01 ^b |
| Open-ocean water, Bermuda | NRCC ¹⁴ | NASS-4 | | 0.21 ± 0.01 ^b |
| Halifax harbour | NRCC ¹⁴ | CASS-1 ^c | | 0.18–0.21 ± 0.04 ^b |
| <i>Riverine water</i> | | | | |
| Ottawa River | NRCC ¹⁴ | SLRS-2 ^c | | 0.26 ± 0.05 ^a |
| Ottawa River | NRCC ¹⁴ | SLRS-3 ^c | | 0.12 ± 0.01 ^a |
| Ottawa River | NRCC ¹⁴ | SLRS-4 | | 0.23 ± 0.04 ^a |

(continued on next page)

Table 8 (continued)

| Type and origin | Supplier | Identification | Value (mg/kg) | Value ($\mu\text{g/l}$) |
|-----------------------------|---------------------|------------------------|---------------|---------------------------|
| <i>Natural waters</i> | | | | |
| Clear Creek | NIST ¹ | 1640 | | 13.79 ± 0.42^a |
| Artificial freshwater | NIST ¹ | 1643 | | 54.1 ± 1.1^a |
| Water | ERA ⁶ | 2913 ^c | | 53^b |
| Trace metal fortified water | NWRI ¹⁵ | TM-23 | | 4.6 ± 2.2^a |
| Trace metal fortified water | NWRI ¹⁵ | TM-24 | | 13.7 ± 4.0^a |
| Trace metal fortified water | NWRI ¹⁵ | TM-26 | | 2.1 ± 1.5^a |
| Trace metal fortified water | NWRI ¹⁵ | TM-27 | | 3.0 ± 1.9^a |
| Trace metal fortified water | NWRI ¹⁵ | TM-28 | | 3.7 ± 2.5^a |
| Trace metal fortified water | NWRI ¹⁵ | TMDA-51 | | 12.6 ± 3.9^a |
| Trace metal fortified water | NWRI ¹⁵ | TMDA-52 | | 15.8 ± 4.7^a |
| Trace metal fortified water | NWRI ¹⁵ | TMDA-54 | | 11.0 ± 2.6^a |
| TM fortified rain water | NWRI ¹⁵ | TMRAIN-95 | | 0.35 ± 0.10^a |
| Hard drinking water | LGC ¹⁶ | 6010 | | 1.2 ± 0.2^a |
| Water | USEPA ¹⁷ | WP 379 #1 ^c | | 8^b |

^a Certified values.

^b Values suggested or recommended (not certified) by the supplier.

^c No longer available.

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¹⁷ United States Environmental Protection Agency.

herbivorous mammals despite marked contamination of their diet (Ainsworth et al., 1990b).

8. Speciation in natural waters

It is nowadays well recognised that the understanding of biogeochemical processes depends upon the knowledge of the chemical forms, or species, that are present in the natural environment. Despite this well-known requirement, the speciation of many ele-

ments in the natural environments is not adequately known. Antimony is not an exception.

Antimony occurs in two oxidation states in natural waters and, thus, its behaviour can be affected by changes in the redox status of the aquatic environment. As pointed out in Section 4, studies on antimony speciation have mainly focused on the separation and identification of Sb(III) and Sb(V) species. Determination of tri-methylated Sb species has also received some attention. When considering existing antimony speciation data, the following points should be considered: (i) nearly all published papers dealing

with inorganic antimony speciation are based on the determination of Sb(III), with Sb(V) being determined as the difference between total antimony and Sb(III); (ii) there is a lack of commercially available soluble antimony compounds: at present, the only compounds widely available are potassium antimony(III)tartrate and potassium hexahydroxyantimonate(V); and (iii) no certified reference materials exist.

8.1. Oxic waters

Antimony(V) is the predominant species present in oxygenated systems but thermodynamically unstable Sb(III) has also been detected in different marine water (Gohda, 1974, 1975; Andreae et al., 1981; Andreae, 1983; Bertine and Lee, 1983; Andreae and Froelich, 1984; Tanaka et al., 1986; Mok and Wai, 1987; Middelburg et al., 1988; Van der Weijden et al., 1990; Cutter, 1991; Cutter et al., 1991, 2001; Sun et al., 1993; Takayanagi and Michel, 1996; Cutter and Cutter, 1998; Sun and Yang, 1999), freshwater (Apte et al., 1986; Apte and Howard, 1986; Andreae et al., 1981; Mok and Wai, 1987, 1990; van der Sloot et al., 1989; Mohammad et al., 1990; Shieh, 1993; Sun et al., 1993; Takayanagi and Cossa, 1997; Hou and Narasaki, 1999; Deng et al., 2000), groundwater (Sun et al., 1993) and rain water (Cutter et al., 1991). This is in contrast with thermodynamic equilibrium predictions, which suggest that Sb(V) concentration should exceed Sb(III) by several orders of magnitude.

For thermodynamically unstable species to be present in water, mechanisms for their production and slow rates of interconversion must exist. Most authors invoke biological activity as the cause for Sb(III) presence. Although possible, a detailed analysis of published data shows that too often there is no proof to validate this hypothesis: Bertine and Lee, (1983) observed a surface enrichment of Sb(III) in Saanlich Inlet, Canada, and suggested that Sb(III) production occurs in the photic zone. Andreae and Froelich, (1984) observed a maximum of Sb(III) in the surface mixed layer of the Baltic Sea and attributed it to the presence of biological activity in this layer. Takayanagi and Cossa (1997) attributed the slight antimony depletion observed at the surface of Lake Pavin, France, to the uptake by phytoplank-

ton. In the surface layer of this lake, Sb(III) and Sb(V) coexist at a similar concentration level. Only two studies are universally cited to support the biological origin of the presence of Sb(III) in oxic waters: Kantin (1983) and Andreae and Froelich, (1984) (see Section 7). Recently, Cutter et al. (2001) found no correlation between Sb(III) and biotic tracers in an extensive study covering subtropical and equatorial Atlantic Ocean and pointed out the convenience of considering photochemical reduction of Sb(V) as a potential source of Sb(III).

Persistence of Sb(III) in oxic waters requires kinetic stabilisation. Cutter (1992) estimated a pseudo first-order rate constant of 0.008 day^{-1} (residence time = $1/k = 125$ days) for Sb(III) removal in oxic waters of the Black Sea. This rate includes all forms of removal (i.e., oxidation but also scavenging by adsorption to particles). A recent study, where Sb(III) was completely oxidised by amorphous iron (5 days) and manganese (3 days) oxyhydroxides, showed that Sb(III) can persist in an oxidizing environment for short periods of time (Belzile et al., 2001). Thus, the above rate constant should be considered as a maximum estimation because it was calculated at the suboxic–oxic interface of the Black Sea where the presence of manganese and iron oxides is likely to increase the rate. Possible stabilisation of Sb(III) in natural aquatic systems by the presence of organic matter could not be discarded; Sb(III) oxidation is known to be prevented by some organic ligands such as tartaric acid (Sun et al., 1982; Abbasi, 1989).

8.2. Anoxic waters

The true speciation of antimony under anoxic conditions remains unclear. On the basis of thermodynamic calculations, antimony should be completely present in the trivalent form in the absence of oxygen. However, the occurrence of oxidised antimony species in anoxic waters has been reported in different systems. In the Saanich Inlet, Bertine and Lee, (1983) found that only about 50% of Sb exists as Sb(III) + Sb(III) – S. In the Baltic Sea, Sb(III) accounted for 44% of total inorganic Sb; only in the deepest sample did this percentage increase to 93%, more as a result of a decrease in total Sb rather than an increase in Sb(III) (Andreae and Froelich, 1984). In the Black Sea, Cutter (1991) reported that Sb(III)

concentrations increased rapidly near the sulfide interface (up to 94% of total Sb). Below 200 m, however, Sb(V) was the predominant form of antimony present.

A variety of mechanisms have been postulated to explain these results, including (i) delivery of Sb(V) on sinking detritus from oxic waters (Andreae and Froelich, 1984; Cutter, 1991, 1992), (ii) formation of thiocomplexes by the pentavalent element (Bertine and Lee, 1983; Andreae and Froelich, 1984), and (iii) advection of surface waters containing high concentrations of antimonate (Cutter, 1991). All these mechanisms must be coupled with relatively slow rates of reduction, as suggested by Peterson and Carpenter (1983) for arsenate. Only one value for a pseudo first-order rate constant (0.0004 year^{-1}) for the reduction of antimonate has been estimated using Black Sea data by Cutter (1991).

Efficient removal of antimony has been observed close to the oxic–anoxic interface (Spencer et al., 1972; Andreae and Froelich, 1984; Cutter et al., 1991). This has been attributed to the adsorption of antimony onto manganese and iron oxide particles. The very low concentrations of antimony detected in Lake Pavin at pH 7 and pe below 4.2 (Takayanagi and Cossa, 1997) have been attributed to the formation of insoluble antimony sulfide.

8.3. Formation of methylated species

The presence of methylated species has been detected in the Gulf of Mexico (Andreae et al., 1981); Ochlockonee Bay estuary (Andreae et al., 1981; Andreae, 1983); Saanich Inlet (Bertine and Lee, 1983); the Baltic Sea (Andreae and Froelich, 1984); surface waters of the Black Sea (Cutter, 1991); surface waters of the subtropical–equatorial Atlantic Ocean (Cutter et al., 2001) and in some rivers (Andreae et al., 1981). They usually account for 10% or less of the total dissolved Sb. The monomethyl species is more abundant than the dimethyl form (Andreae et al., 1981). There is a tendency towards higher values at the surface. Krupp et al. (1996) have detected mono-, di-, tri-methyl and triethyl antimony derivatives in sediments from rivers and harbours.

For many years, biological methylation of inorganic antimony could not be demonstrated directly by use of experimental organisms. The chemical

similarity between antimony and Sn, Pb, As, Se and Te, which surround antimony in the periodic table and all of which had shown to be subject to biomethylation, suggested the existence of a biomethylation pathway for antimony, but there was no experimental evidence.

Andreae and Froelich, (1984) did not find methylated species in algae in the Baltic Sea while these compounds were present in the water column. This fact, plus the presence of methylated species outside the photic zone, led them to suggest that methylated species could be produced by bacteria rather than by algae, as it is the case for mercury compounds.

Dodd et al. (1992) warned against earlier reports in the literature on the presence of antimony methylated compounds in marine and freshwaters. According to these authors, methylantimony(V) compounds are either environmentally inaccessible or polymeric in nature. They also showed that the behaviour of methylated antimony compounds to hydride generation is entirely different from that exhibited by arsenic. The same research group (Dodd et al., 1996) first described the presence of organoantimony compounds in samples of biological origin in a freshwater plant extract (*Potamogetan pectinatus*). This pondweed had a high total antimony content, 48 $\mu\text{g/g}$, as compared to other plants from lakes (3.7 $\mu\text{g/g}$ for cattail and 1.6 $\mu\text{g/g}$ for snail). These compounds and a stibnolipid isolated from a marine diatom (Benson, 1988) have been for some time the only organoantimony compounds with unequivocal biological origin.

Recently, Jenkins et al. (1998) reported for the first time the production of gaseous trimethylantimony from Sb_2O_3 substrate by a pure aerobic organism, the filamentous fungus *Scopulariopsis brevicaulis*. They reported that the biovolatilisation of inorganic compounds occurred more readily from Sb(III) substrates than from Sb(V) substrates. Previously, a mixed culture of micro-organisms present in soil samples was shown to be able to volatilise antimony into the headspace of anaerobic vessels (Gürleyük et al., 1997) but the organism(s) producing this were not identified and a chemical transmethylation route could be another possibility. Earlier attempts to produce these compounds had failed. Earlier studies by Barnard (1947) suggested that the fungus *Penicillium notatum*, under aerobic condi-

tions, can convert KSbO_3 salt to unspecified gaseous derivatives (identified by the Gutzeit test). More recently, the reductive methylation of antimony has retained much attention in view of the Richardson hypothesis (Richardson, 1990) that toxic hydrides of antimony produced from components of PVC mattress covers by the action of *S. brevicaulis* were the cause of cot deaths (Sudden Infant Death Syndrome, SIDS). Several attempts (Gates et al., 1995, 1997; Thompson and Faull, 1995; Warnock et al., 1995) failed to convert antimony trioxide or potassium antimonyl tartrate to volatile derivatives under aerobic conditions using *S. brevicaulis* and other fungal species. Very recently, antimony has been shown to inhibit arsenic biomethylation while arsenic enhances antimony biomethylation but no model has been proposed yet to explain these observations (Andrewes et al., 2000).

9. Importance of atmospheric input

Airborne supply to aquatic and terrestrial systems is important for the environmental fate of some elements. Although existing data are sparse, this seems to be the case for antimony in systems far from direct pollution sources (Payer et al., 1976; Andreae and Froelich, 1984; Austin and Millward, 1986; Van der Weijden, 1990; Cutter, 1993; Guieu et al., 1993; Cutter et al., 2001).

Atmospheric emission values for antimony, as estimated by Nriagu and Pacyna (1988) and Nriagu (1989, 1990), are listed in Table 9. Although antimony natural emission values are significantly higher than in previous studies (Lantzy and Mackenzie, 1979), anthropogenic emissions to the atmosphere still exceed natural sources. Nriagu's estimations should be viewed with some caution because the original data used were taken from detailed studies carried out in the late 1970s and early 1980s and they need to be updated. For instance, (i) production of antimony was considered to be 80×10^3 metric tons/year (Nriagu and Pacyna, 1988), while in 1999, it was of 138×10^3 metric tons (see Table 2) and (ii) antimony uses have significantly changed over the last decade (see Section 2).

Antimony compounds are rather volatile and they are released into the atmosphere during the incineration

Table 9

Global emissions (10^3 metric tons/year) of antimony to the atmosphere (Nriagu and Pacyna, 1988; Nriagu, 1989, 1990; Maeda, 1994)^a

| Anthropogenic source | Natural source | | |
|--------------------------------|------------------|------------------------------|------------------|
| Energy production ^b | 1.3 | Wind-borne dust ^c | 0.8 |
| Mining | 0.1 | Sea salt spray | 0.6 |
| Smelting and refining | 1.4 | Volcanic activity | 0.7 |
| Waste incineration | 0.7 | Forest fires | 0.2 |
| | | Biogenic sources | 0.3 |
| Total | 3.5 ^d | Total | 2.6 ^c |

^aData based on a world antimony production of 80×10^3 metric tons/year (Nriagu and Pacyna, 1988). Antimony production in 1999 was 138×10^3 metric tons (see Table 2).

^bEnergy production includes coal, oil and gas.

^cIncludes industrial sources of dust.

^dA completely different estimation was published by Lantzy and Mackenzie (1979). They estimated natural and anthropogenic emissions of antimony to the atmosphere as 9.8 and 380×10^8 g/year, respectively. These values have been often cited by other authors (Salomons and Förstner, 1984; Benjamin and Honeyman, 1992).

of waste, fossil combustion, and during the smelting of metals. Antimony is one of the elements that show higher enrichments in aerosols over the concentrations expected from sea salt and from crustal sources (Peirson et al., 1973; Duce et al., 1976; Austin and Millward, 1986; Steinnes, 1990; Kersten et al., 1991; Cutter, 1993; Arimoto et al., 1995). Typical antimony concentrations in aerosols range from < 0.1 ng/m³ in the atmosphere over remote oceans (Duce et al., 1976; Buat-Menard and Chesselet, 1979; Austin and Millward, 1986; Arimoto et al., 1995) to several ng/m³ over industrialised areas (Brar et al., 1970; Dams et al., 1970). Antimony concentrations are about one order of magnitude lower over the open ocean than in a coastal environment (Peirson et al., 1974; Creclius, 1980; Andreae and Froelich, 1984; Austin and Millward, 1986; Kersten et al., 1991; Grousset et al., 1995).

The species of antimony actually present in the atmosphere may be of importance in antimony cycling. Again, not much information is available. Antimony is mainly emitted as its oxides from smelting operations (Bloch et al., 1983). Antimony emitted by combustion of coal and refuse incineration is associated with the fine particulate fraction of stack

emissions (Kowalczyk et al., 1978; Gladney et al., 1978; Coles et al., 1979). Elements that concentrate on the smaller size range are efficiently removed during precipitation events. This is confirmed by atmospheric fluxes of antimony being dominated by wet deposition (Peirson et al., 1973; Cutter, 1993; Arimoto et al., 1995).

Antimony oxides have very low solubilities (Gayer and Garrett, 1952) and this may strongly affect antimony fate in natural waters and soils. Crecelius (1980) determined antimony solubility from marine aerosol particles and found that only 40% dissolved after 24 h. This value was used by Takayanagi et al. (1996) in a box-model of antimony in Western Mediterranean Sea. Other values have been reported by Austin and Millward (1986) for the solubility in seawater of antimony contained in urban particulates (27%, 2-h leaching) and by Kersten et al. (1991) for the solubility in seawater of antimony present in polluted North Sea coastal aerosol (83%, 100-h leaching). The few existing data seems to point to a strong dependence of antimony leaching with time.

10. Conclusions

This extensive review on the occurrence of antimony in the environment presents most of the information available on the distribution and speciation of antimony in aquatic systems in a condensed format. More importantly, it has identified several important biogeochemical aspects of the element for which further research is still needed, namely:

- speciation of antimony in natural waters and its partition among dissolved and solid phases in both oxic and anoxic systems,
- kinetics of oxidation for Sb(III) under oxic conditions and of reduction for Sb(V) under anoxic ones,
- role of biota in antimony speciation, particularly, the production of Sb(III) in oxic systems and of methylated species and the identification of organisms responsible for them,
- solubility of antimony oxide under conditions relevant to freshwater and marine systems.

More research on the above points would certainly shed light on the missing information on the

processes controlling the transformation and transport of antimony species in natural systems.

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