



Biomonitoring of antimony in environmental matrices from terrestrial and limnic ecosystems

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Environmental Specimen Bank of Germany which have been collected over 14 years. The analytical procedure is based on an open vessel acid digestion of freeze-dried biological samples and the subsequent quantification of Sb in the digests by flow injection hydride generation atomic absorption spectrometry. Strict quality control schemes were applied to the entire procedure to guarantee accurate and precise results. No long-term changes of the Sb concentrations were found in spruce shoots or poplar leaves from different sampling sites. However, spruce shoots from a semi-natural region showed concentrations of Sb ($\sim 22 \text{ ng g}^{-1}$; range: $17\text{--}29 \text{ ng g}^{-1}$) that were approximately four times lower than in corresponding samples from an urban-industrialized area. The analysis of virgin and washed elder leaves revealed that approximately 20–30% of the Sb is present on the leaf surface. Sb levels in elder leaves ranged from $5.2 \pm 0.3 \text{ ng g}^{-1}$ in samples from Argentina to $589 \pm 30 \text{ ng g}^{-1}$ in leaves collected directly beside a motorway in Germany. Similarly, poplar leaves from Argentina and Chile showed about 4 ng Sb g^{-1} , whereas 150 ng Sb g^{-1} was found in poplar leaves from Germany. The lowest concentrations of Sb were determined in digests of pigeon eggs ($\sim 2 \text{ ng g}^{-1}$), bream liver ($\sim 4 \text{ ng g}^{-1}$) and deer liver ($\sim 6 \text{ ng g}^{-1}$). A similar pattern of Sb concentrations in spruce shoots, leaves or liver samples from an industrialized area and an agrarian ecosystem in Germany was established. Concentrations of Sb in elder leaves were closely associated with car traffic, giving maximum concentrations of 589 ng g^{-1} directly beside a motorway, 207 ng g^{-1} 50 m from the motorway and 153 ng g^{-1} in a close residential area.

Aim of the investigation

During recent years, the environmental concern about antimony (Sb) has grown considerably because anthropogenic emission has resulted in an increasing concentration of Sb in the environment. However, the knowledge about the potential harmful effects of this metal on plants and animals is still scarce and needs to be further elucidated.

The estimated concentration of Sb in the Earth's crust is between 0.2 and $0.3 \mu\text{g g}^{-1}$. Antimony is present in the aquatic environment as a result of rock weathering, soil runoff and through effluents from mining and smelting.¹ The main pathways are the atmospheric input and the water cycle. Currently, there are some indications in marine ecosystems that Sb is accumulated in biological matrices.^{2,3} Inhalation of Sb compounds may lead to pneumonitis, fibrosis, bone marrow damage and carcinomas.⁴ Commercial uses of the metal include storage batteries, flame retardants, pigments and explosives. Antimony-bearing ores such as stibnite (Sb_2S_3) are commonly associated with those of lead, zinc, copper and tin and contamination by antimony is associated with the mining and smelting of these metals. The annual production of Sb is estimated to be about 70 000 tons. Antimony may also reach soils *via* emissions from incineration and fossil fuel combustion and by the addition of soil amendments such as fertilizers, sewage sludge and fly-ash. As a result of concerns about its environmental impact and harmful effects on organisms, Sb and its compounds are listed as priority pollutants by the US Environmental Protection Agency (EPA) and the German Research Community (DFG).^{5,6}

The concentrations of Sb in many biological samples are in the low ng g^{-1} range, frequently even lower.^{7–9} Environmental monitoring of concentrations of Sb in matrices from unexposed areas requires analytical instrumentation with detection limits as low as possible. Currently, inductively coupled plasma mass spectrometry (ICP-MS) provides such low detection limits.⁷ However, ICP-MS instruments are relatively expensive and also the running costs of ICP-MS are greater than those of other analytical devices. An instrumental set-up consisting of hydride generation coupled to an atomic absorption spectrometer (HG-AAS) is significantly cheaper and offers low detection limits similar to ICP-MS.^{10–12}

An Environmental Specimen Bank (ESB) provides the unique opportunity to analyse samples retrospectively, as subsamples of all specimens that have been collected over the years are stored above liquid nitrogen to preserve their chemical composition. This study was also aimed at supplying accurate and precise concentrations of Sb of representative environmental samples from the Federal ESB of Germany.¹³ These data are needed to assess long-term trends as well as to predict future trends regarding concentrations of Sb in environmentally relevant samples and thus to reveal the concern about Sb.

Experimental

Apparatus

All plant and liver samples were mineralized in digestion vessels made from glassy carbon (20 ml, Perkin Elmer,

Norwalk, CT, USA) in an aluminium heating block (Gebrüder Liebisch, Bielefeld, Germany). A flow injection system (FIAS 400, Perkin Elmer), equipped with an autosampler (AS 90, Perkin Elmer) was coupled to an atomic absorption spectrometer (AAS 4100, Perkin Elmer), for the quantification of Sb in the digests.^{11,12}

Chemicals and standards

High-purity water (18.2 MΩ cm, Millipore, Milford, MA, USA) was used for the preparation of all solutions. Acids for mineralizations were sulfuric acid (96%, suprapur[®], Merck, Darmstadt, Germany), hydrofluoric acid (40%, suprapur[®], Merck), perchloric acid (70%, suprapur[®], Merck) and nitric acid (65%, p.a., Merck). For the flow injection system, the carrier solution was prepared from hydrochloric acid (32%, Riedel-de-Haen, Seelze, Germany). NaBH₄ solutions were prepared daily by dissolving appropriate amounts of powdered NaBH₄ (analytical-reagent grade, Riedel-de-Haen) in 0.04% (w/v) NaOH (30%, suprapur[®], Merck) in high-purity water. Sb(v) was reduced to Sb(III) with aqueous solutions containing 30% (w/v) KI (suprapur[®], Merck) and 5% (w/v) ascorbic acid (p.a., Merck).

Calibration solutions (0.1–3 μg l⁻¹) for Sb were prepared daily by diluting adequate aliquots of stock standard Sb solutions containing 1000 mg SbCl₃ l⁻¹ in 5 mol l⁻¹ HCl (Merck) to the appropriate concentrations with 10% HCl.

Procedure

The following mineralization procedure was applied to all samples: 200–300 mg of powdered samples were weighed into the digestion vessels and, subsequently, 3 ml of nitric acid and 0.5 ml of HF were added to the dry powders; the vessels were gently shaken to mix the contents and allowed to stand overnight; next morning, 0.3 ml of HClO₄ and 0.5 ml of H₂SO₄ were added to the vessels and, finally, the vessels were heated in an aluminium block, as described in detail earlier.^{11,12} No hydrofluoric acid was used for the mineralization of liver samples and the volume of perchloric acid was increased to 0.5 ml. After reaching room temperature again, the contents of the vessels were quantitatively transferred into 10 ml calibrated flasks. The completely clear solutions were filled to the mark with 10% HCl.

Specimens and reference materials

For validation of the developed method, several reference materials with certified Sb concentrations were analysed. All reference materials were used as bottled. Results were corrected for the humidity content in the reference materials as determined on aliquots of each material by a moisture analyser (LP 16, Mettler-Toledo, Greifensee, Switzerland). The following reference materials were employed: CRM 281 Rye Grass and CRM 186 Pig Kidney, BCR, Belgium; GBW 07604 Poplar Leaves, GBW 07602 Bush Branches and Leaves, GBW 07605 Tea, all from the Institute of Geophysical and Geochemical Exploration, Langfang, The People's Republic of China; SRM 1572 Citrus Leaves, SRM 1515 Apple Leaves, SRM 1575 Pine Needles and SRM 1577a Bovine Liver, all from NIST, Gaithersburg, MD, USA.

Elder leaves were collected near Juelich directly beside a highly frequented motorway at two different locations in autumn 1998 (A and B in Table 1, see later). Additionally, elder leaves from bushes approximately 50 m away from sampling site A were collected. Two height fractions (80–200 cm and >200 cm) of elder leaves were obtained at location B. Moreover, elder leaves from two residential areas in Juelich and from an urban area in the city of Bariloche, Argentina were investigated.

Poplar leaves from Argentina (city of Bariloche: samples

from the city centre and from a lakeside at the outskirts; height fraction 1.8–2.5 m) and Chile (Andes, height fraction 1.8–3.0 m) were investigated. After harvesting, all samples were immediately (within 15 min) stored in the gaseous phase above liquid nitrogen and subsequently dried to constant weight in a drying oven held at 60 °C overnight, before they were ground in a blender (Krupps, Germany) at room temperature.

To make a rough estimation as regards the amount of Sb present in particles on the leaf surfaces (and not in the leaves), some fractions of elder leaves were also rinsed with high-purity water before mineralization.

To assess the long-term trends of the concentrations of Sb in plant species from distinct geographical regions, spruce shoots and poplar leaves of the Federal Environmental Specimen Bank (FESB) of Germany, collected during the past 14 years in Germany, were investigated. All samples from the FESB were collected and processed under well defined and reproducible conditions according to standard operating procedures.¹⁴ Thus, every precaution was taken to obtain representative samples of the same quality each year. Spruce shoots were available from an urban–industrialized area (Saarland) and from a semi-natural region (National Park of Berchtesgaden). Poplar leaves were obtained from two urban–industrialized areas (city of Leipzig and the urban–industrialized region of the Saarland). These specimens were stored as fresh homogenized powder samples above liquid nitrogen. Before mineralization, they were freeze-dried, revealing a water content between 49 and 67% for plant materials. Similarly, pigeon eggs, deer liver and bream liver samples were treated before aliquots (~250–300 mg) of the dried powders were mineralized and subsequently analysed for Sb by HG-AAS. As freeze-drying does not remove all water from the powders, results were corrected for their moisture content as mentioned above.

Determination of antimony

Antimony(v) in 4 ml aliquots (10 ml aliquots for liver samples) of digestion solution was spontaneously reduced to Sb(III) with 1 ml of a solution containing 30% KI and 5% ascorbic acid. Stibines were generated using 0.2% (w/v) NaBH₄ solution (0.3% for liver samples), stabilized with 0.04% (w/v) NaOH, in 10% (w/v) HCl as carrier with the flow injection system. The gaseous hydrides were transported from the gas–liquid separator to the temperature-controlled quartz tube atomizer of the atomic absorption spectrometer. A hollow cathode lamp (HCL) for Sb was used throughout the experiments. The detailed operating conditions of the flow injection hydride generation AAS system were reported previously.^{11,12} The concentrations of As and Se in spruce shoots were determined as described earlier.¹⁵

Results and discussion

The monitoring strategy applied here is directed towards the sampling of fresh materials from different ecosystems. Special procedures guarantee that almost no changes occurred in the chemical composition of the collected bioindicators.^{13,14} The application of reproducible and well documented procedures allows long-term environmental monitoring of representative samples. Therefore, one can obtain data about the concentrations in various samples, and it is also possible to transform such analytical numbers into environmental information, *i.e.* the establishment of long-term trends, regional comparisons and ecosystem-related statements. The supplementary activity of specimen banking allows the retrospective analysis of samples from the past with respect to new compounds of environmental interest. The following results on antimony

represent a good example because the ultratrace determination of this element in biological matrices was not possible 15 years ago. Specimen banking increases the level of quality assurance of environmental data because part of the original material is always stored for later checks of the analytical results, providing traceability to the original material.¹⁶

Quality control

To ensure the accuracy and precision of the developed analytical procedure (mineralization/dilution/HG-AAS), eight commercial reference materials were analysed. Generally, experimental concentrations were in good agreement with certified or indicative values, whenever available. The following concentrations of Sb, reported as ng g^{-1} , were found (certified) in these reference materials: Bush Branches and Leaves, 73 ± 12 (78 ± 15); Poplar Leaves, 44 ± 4 (45 ± 5); Tea, 53 ± 5 (50 ± 5); Rye Grass, 45 ± 4 (47 ± 5); Apple Leaves, 10 ± 1 (13=indicative value); Pine Needles, 163 ± 11 (200=indicative value); Bovine Liver, 2.1 ± 0.4 (3=indicative value); Pig Kidney, 1.9 ± 0.1 (no indicative value available). Digests of Bovine Liver and Pig Kidney were additionally spiked with appropriate amounts of Sb to obtain recovery data, yielding adequate results.¹²

To check whether or not the freeze-drying process results in a loss of analyte, fresh powder aliquots (~ 300 mg) of spruce shoots and beech leaves were digested and analysed for Sb. These investigations revealed that no detectable change in the concentrations between fresh and freeze-dried materials can be observed.¹¹

Time course of Sb in spruce shoots and poplar leaves

Concentrations of Sb found in spruce shoots collected during 1985 and 1998 at two different locations in Germany are summarized in Fig. 1. Generally, no definite long-term changes of the Sb concentrations in spruce shoots could be established. However, spruce shoots from the semi-natural area (National Park of Berchtesgaden) showed concentrations of Sb ($\sim 22 \text{ ng g}^{-1}$; range: $17\text{--}29 \text{ ng g}^{-1}$) that were approximately four times lower than those in corresponding samples from the urban-industrialized area of the Saarland. The concentrations of Sb in these spruce shoots ranged from 51 to 112 ng g^{-1} dry material.

Poplar leaves from two urban-industrialized areas (city of Leipzig and Saartal) were available from 1991 to 1998. Sampling campaigns were not performed every year and therefore no continuous annual data points could be generated

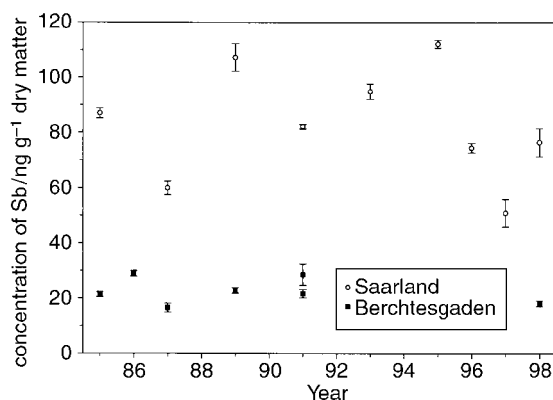


Fig. 1 Time trends of Sb in spruce shoots from a semi-natural region (National Park of Berchtesgaden) and from an urban-industrialized area (Saarland) in Germany. Means and standard deviations are the results from at least three independent digestions. Shoots from Berchtesgaden were collected at Hirschbichtal (1985 to 1991) and then continued at Wimbachtal (1991: upper point).

for Fig. 2. Similar to the spruce shoots investigated, no long-term trends in the Sb concentration in poplar leaves could be established. A relatively low concentration of Sb was found in poplar leaves from the Saartal in 1991 ($58 \pm 3 \text{ ng g}^{-1}$) whose origin is currently unknown. The concentrations of Sb in the other poplar leaves ranged from 92 to 155 ng g^{-1} . In contrast to the spruce shoots analysed, no differences in the Sb concentration related to the sampling site could be found in these poplar leaves.

Comparison of long-term trends of Sb, As and Se

Spruce shoots from the Saarland, representing an urban-industrialized area, were chosen to compare the time course changes of concentrations of As and Se with that of Sb (Fig. 3). Concentrations of As steadily fell from 382 ng g^{-1} in 1985 to 96 ng g^{-1} in 1998. The origin of As in such ecosystems is often related to activities of heavy industry. The structural changes of this industry during the last 15 years and improvements in filtering technology have led to reduced emissions. Consequently, the biomonitor 'spruce shoots' reflects the improved atmospheric situation of this region. However, concentrations of Sb, an element said to be closely related to As, did not show such a clear trend. Concentrations of Sb in these spruce shoots fluctuated year by year, ranging from 51 to 112 ng g^{-1} . The same holds true for concentrations of Se with values from 20 to 46 ng g^{-1} (Fig. 3). The origin of the extremely high Sb concentration (348 ng g^{-1}) found in the

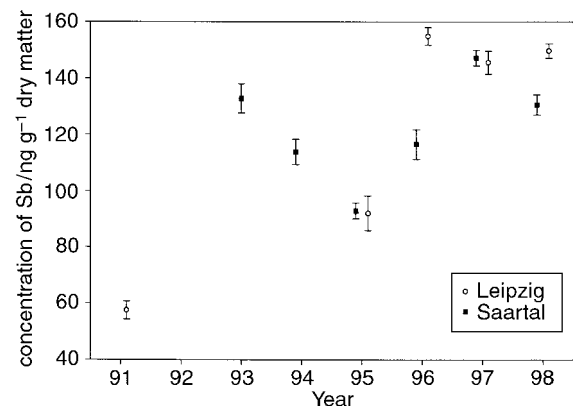


Fig. 2 Time course of Sb in poplar leaves from the highly urban-industrialized area of Leipzig and from the urban-industrialized area of the Saartal with lower population and traffic density. Means and standard deviations are the results from at least three independent digestions.

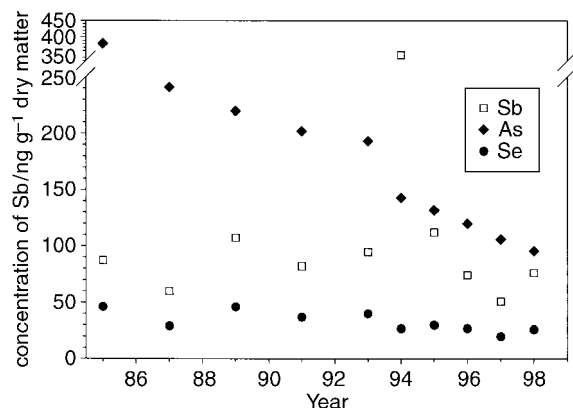


Fig. 3 Comparison of long-term changes of concentrations of As, Se and Sb in spruce shoots from the urban-industrialized area of the Saarland during the last 14 years. Means and standard deviations are the results from at least three independent digestions.

spruce shoots from 1994 is presently not known. Several subsamples from different bottles were analysed for Sb, always yielding the same high values. Therefore, contamination due to sample pretreatment or during analysis can be excluded. In order to maintain a clear distinction of data sets, this high concentration of Sb from 1994 is not reported in Fig. 1.

Influence of sample pretreatment on the concentration of Sb

For any risk assessment, it is vital to know whether or not the entire amount of Sb found in a sample is exclusively present in or also partly on the sample surface (dust particles). Therefore, elder leaves collected in a residential area and beside a well-frequented motorway were used to make a rough estimation between virgin leaves and leaves that had been briefly rinsed with high-purity water. As can be clearly seen in Fig. 4, concentrations of Sb from washed specimens were always lower than from non-washed leaves. However, it must be stated that the leaves were transferred to the gaseous phase above liquid nitrogen immediately after harvesting and, upon arrival in the laboratory, samples were stored frozen in a refrigerator at -20°C until mineralization. Therefore, fresh leaves were not used for the comparison of the effect of washing on the concentrations of Sb, but defrosted leaves. The cell structures of these frozen leaves might have been partially destroyed due to freezing, leading to a potentially higher release of antimony compared to fresh leaves washed with high-purity water. Approximately 20% less Sb was found in washed elder leaves collected beside the motorway, whereas washed leaves from the residential area had about 30% lower concentrations of Sb compared to the corresponding fractions of virgin elder leaves (Fig. 4).

Concentrations of Sb in elder leaves from different locations

To investigate the variation of the concentration of Sb in the same kind of bioindicator, elder leaves collected at different locations in Germany and Argentina were analysed (Table 1). A strong association of the concentration of Sb in elder leaves with traffic was established. The highest concentrations of Sb were found in leaves directly beside motorways ($\sim 590 \text{ ng g}^{-1}$, A and B). Samples collected approximately 50 m from motorway A showed only about 35% of the Sb concentrations determined in leaves taken directly beside the motorway (Table 1). The concentrations of Sb determined in leaves from different height fractions revealed that the fraction above 200 cm showed approximately 80% of the concentrations established in the fraction between 80 and 200 cm. Even lower concentrations were found in elder leaves collected in two residential areas in Juelich. Because antimony is used as an additive in the vulcanization process of tyres and as a fire

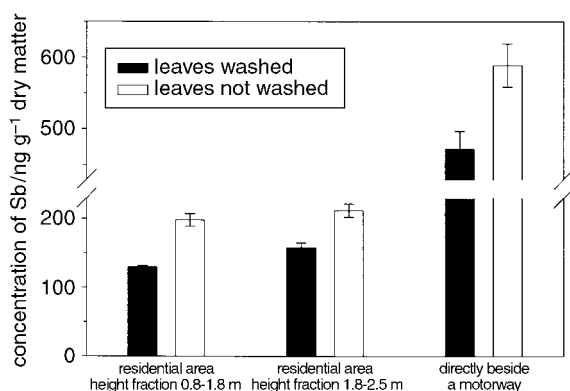


Fig. 4 Concentrations of Sb in virgin and washed elder leaves of different origin. Means and standard deviations are the results from at least three independent digestions.

Table 1 Concentrations (ng g^{-1} dry mass) of Sb in virgin elder leaves collected in autumn 1998 at different locations

Location	N^a	Concentration $\pm \sigma$	RSD (%)
Directly beside motorway A	4	589 ± 30	5.1
50 m from motorway A	3	207 ± 13	6.3
Directly beside motorway B, height fraction 80–200 cm	4	591 ± 26	4.4
Directly beside motorway B, height fraction >200 cm	5	468 ± 19	4.1
Residential area 1 (Juelich)	4	198 ± 9	4.5
Residential area 2 (Juelich)	4	153 ± 5	3.3
Argentina, urban area	9	5.2 ± 0.3	5.8

^aNumber of subsamples analysed.

Table 2 Concentrations (ng g^{-1} dry mass) of Sb in virgin poplar leaves collected in autumn 1998 at different locations

Location	N^a	Concentration $\pm \sigma$	RSD (%)
Chile, Andes	3	3.9 ± 0.4	10
Argentina, lakeside	9	4.3 ± 1.3	30
Argentina, urban area	4	19.6 ± 2.3	12
Germany, Saartal	4	131 ± 4	3.1
Germany, Leipzig	3	150 ± 3	2.0

^aNumber of subsamples analysed.

Table 3 Spectrum of concentrations (ng g^{-1} dry mass) of Sb in various environmental samples collected during 1997 at an urban-industrialized and an agrarian location in Germany

Type of sample	N^a	Concentration $\pm \sigma$	RSD (%)
<i>Urban-industrialized region of the Saarland</i>			
Spruce shoots	3	51 ± 5	9.8
Poplar leaves	6	147 ± 3	2.0
Pigeon eggs	3	2.1 ± 0.2	9.5
Deer liver, 1-year-old roe deer	5	8.3 ± 1.2	14
Bream liver	4	3.8 ± 0.7	18
<i>Agrarian region of the Bornhöved lake district</i>			
Spruce shoots	6	64 ± 1	1.5
Beech leaves	4	39 ± 2	5.1
Deer liver, 1-year-old roe deer	3	5.9 ± 0.5	8.5
Deer liver, 2–3-month-old fawns	3	6.4 ± 0.3	4.7

^aNumber of subsamples analysed.

retardant in brake linings, car traffic contributes significantly to an increase of Sb in the environment.¹⁷ Interestingly, concentrations of Sb in elder leaves from an urban area in Argentina (city of Bariloche) had by far the lowest values (Table 1). Compared to the Sb levels beside the motorways in Germany, the concentrations of Sb found in Argentina were approximately 100 times lower.

Concentrations of Sb in poplar leaves from different locations

Similar to elder leaves, concentrations of Sb in poplar leaves from Argentina, Chile and Germany were also investigated. Again, samples from South America showed much lower concentrations of Sb compared to corresponding specimens from Germany (Table 2). These low concentrations of Sb ($\sim 4 \text{ ng g}^{-1}$) found in leaves from Argentina and Chile might be regarded as the natural background levels of Sb. Although significantly elevated concentrations of Sb were found in samples from an urban area (city of Bariloche) in Argentina, these Sb levels were still approximately seven times lower than the Sb levels in poplar leaves collected in Germany. Concentrations of Sb in leaves from the densely populated urban-industrialized area of the city of Leipzig in Germany were approximately 13% higher than in leaves from another urban-industrialized region with a distinctly lower population

and traffic density (Saartal), thus indicating again the impact of traffic on the increase of Sb in the environment.

Levels of Sb in samples from urban-industrialized and agrarian ecosystems

Various bioindicators from two ecosystems (urban-industrialized region of the Saarland and agrarian region of the Bornhöved lake district) were compared in order to elucidate the different Sb pattern in these specimens (Table 3). In addition to shoots and leaves, egg and liver samples from these two areas were analysed for Sb. Distinct differences in the Sb concentrations were found in comparable samples from both ecosystems. Spruce shoots from the Saarland showed only about 80% of the concentrations of Sb of shoots from the Bornhöved lake district (Table 3). On the contrary, Sb levels in beech leaves from the agrarian sampling site were approximately three times lower than those in poplar leaves from the urban-industrialized area. One must consider the divergent possibilities of accumulation of Sb of the two plant species due to the different geometry and surface properties of their leaves. This might lead to a slightly changed uptake of Sb. Nevertheless, a three times increase of Sb in poplar leaves from the urban-industrialized area of the Saarland indicates a distinct accumulation of Sb in these leaves. Much lower concentrations of Sb than found in plant samples were determined in digests of deer liver, with higher concentrations found in liver samples from the urban-industrialized region. The lowest Sb concentrations were detected in bream liver ($\sim 4 \text{ ng g}^{-1}$) and pigeon eggs ($\sim 2 \text{ ng g}^{-1}$).

Conclusion

Concentrations of Sb determined in limnic and terrestrial samples varied by a factor of approximately 280. The lowest concentrations were found in pigeon eggs ($\sim 2 \text{ ng g}^{-1}$), whereas elder leaves collected directly beside a motorway in Germany showed the highest concentrations of Sb (591 ng g^{-1}). A close association of Sb levels with car traffic could be established, supporting the recent local findings of Dietl *et al.*¹⁷ Interestingly, poplar leaves and elder leaves from Argentina and Chile showed significantly lower concentrations of Sb than corresponding samples from Germany.

For a sound risk assessment as regards concentrations of Sb in the environment, more information about the toxicity and levels of Sb in representative samples from different trophic levels is required. Moreover, the identification and quantification of Sb compounds in such samples, *i.e.* speciation, will help to shed more light on the role of Sb in environmental processes.

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