Trends in antimony pollution near exposed traffic nodes: comparison with arsenic

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ABSTRACT: The significant part of antimony (Sb) contamination can be associated with extremely loaded traffic areas, where braking vehicles produce the abrasion dust containing up to 5% wt. of Sb₂S₃. Heavy loaded cross-roads from three different regions of the Czech Republic (Central Europe) were monitored for Sb content in road dusts, topsoils and reference soils during the two-year season (2015–2017). The concentration of antimony exceeded up to 60 times the background values and varied from 5 to 70 µg g⁻¹ in topsoils, and from 70 to 160 µg g⁻¹ in road dusts with the preferable binding to fine particle fraction (<0.1 mm).

1 INTRODUCTION

Antimony (Sb) is a global environmental contaminant and one of the elements of increasing environmental significance. While arsenic (As) represents a historical toxic substance monitored in the long term, antimony is a typical emerging contaminant that has been classified as a serious problem for future generations (CEC, 1998). The significant part of Sb contamination can be associated with extremely loaded traffic areas, where braking vehicles produce the abrasion dust containing up to 5% wt. of Sb₂S₃. Antimony released during braking process is mostly bound in fine atmospheric particulate matter, i.e. in PM₁₀ (ca 32 µg Sb/braking/car) and PM_{2.5} (ca 22 µg Sb/braking/car) (Iijima *et al.*, 2008), a minor part remains in non-exhaust traffic emissions (road dust). Roadside topsoils accumulate large amounts of vehicle emissions, so the concentrations of antimony in them can reach more than 60 times of background value. As with arsenic, the soil pH/Eh importantly determine antimony species in soils. Arsenic has been found as pentavalent arsenate, AsO₄³⁻ in the oxidic surface zone (0–3 cm) and as trivalent arsenite, AsO₃³⁻ under slightly reducing conditions (9–12 cm) (Wilson *et al.*, 2010), while antimony as pentavalent hydrated antimonate, Sb(OH)₆⁻ represents the major oxidation state over a wide Eh range (Mitsunobu *et al.*, 2008).

The binding of both As and Sb oxyanions in soils has been mostly controlled by the complexation with iron (Fe^{III}), whereas Sb exhibits significantly higher affinity to natural organic matter (NOM) compare to As (Mitsunobu *et al.*, 2008).

The aim of this study was to monitor heavy loaded cross-roads from three different regions of the Czech Republic (Central, South and East Bohemia) for antimony content in road dusts and topsoils during the

two-year season (2015–2017). The same samples were tested for As content to the evaluation of current contamination trends in exposed urban areas.

2 EXPERIMENTAL

2.1 Sampling

Road dusts and urban topsoils (0–5 cm) were collected periodically (4 sampling data during 2015–2017) at busy cross-roads in three big cities in the Czech Republic (Prague (P) in middle Bohemia, České Budějovice (CB) in southern Bohemia and industrial Ostrava (O) in eastern Bohemia) and kept in PVC packages. Topsoils were taken as three sub-samples from the area of 20 × 20 cm, mixed together, quartered, dried and sieved to <0.315–0.1 mm and <0.1 mm fractions, respectively. Road dusts were collected close to roads exposed to heavy traffic circulation, mixed together, dried and sieved to <0.315–0.1 mm and <0.1 mm fractions, respectively.

2.2 Sample processing

The fractions of solid samples were analysed for major components by XRF (Rigaku NEX QC), for the specific surface area as S_{BET} (Micromeritics ASAP 2020) and for TOC using elementary analysis (Fisons 1108). Finally, all samples were mineralized by microwave digestion (Berghof MWS-2 speedwave) with HCl and HNO₃ (1:3).

The concentration of Sb in aqueous solutions was determined by HG-AFS using PSA 10.055 Millennium Excalibur. The samples were pre-treated with a solution of HCl (36% v/w) and KI (50%) with ascorbic acid (10%). The declared detection limit was 0.05 ppm

Table 1. Average Sb concentration ($\mu\text{g g}^{-1}$) in topsoil and road dust fractions.

Locality	Urban soils		Road dust	
	<0.1 ^{*)}	0.1–0.315	<0.1	0.1–0.315
P	13.6	5.5	45.3	29.9
CB	53.7	23.1	164.6	89.1
O	5.6	2.5	12.8	6.5

^{*)} particle size in mm

and the standard deviation was experimentally determined as 2.5%.

3 RESULTS AND DISCUSSION

3.1 Antimony content in topsoils and road dust

The data in Table 1 illustrate a major binding of Sb in fine particles (more than double the concentrations compare to the coarser fraction), and a significantly higher content of Sb in road dust compare to soils. While the concentration ranged from units to tens of $\mu\text{g g}^{-1}$, in road dust it reached up to tens to hundreds of $\mu\text{g g}^{-1}$ in topsoils. Evident local variability in Sb contamination (CB >> P > O) can be explained by the different traffic intensity at the sampling sites.

3.2 Antimony correlation with Fe and OM

In all aspects, antimony demonstrated better correlation with organic matter than with Fe. Very good Sb/C_{org} correlation ($R^2 = 0.893$) was found in topsoils, less apparent correlation factor ($R^2 = 0.702$) could be assigned to Sb/C_{org} in road dust. Unlike arsenic, that exhibited high positive correlation with Fe in different natural solids (Dousova *et al.*, 2012), Sb/Fe correlation in topsoils was worse ($R^2 = 0.594$) and even none Sb/Fe correlation was found in road dust.

3.3 Important trends in Sb and As pollution in urban areas

The contamination impact of brake abrasion (Fig. 1) illustrated decreasing trend in Sb content from source brake abrasion over the road dust and topsoils to the reference soils, which were collected in places without transport, as close as possible to the sampling sites. Nevertheless, the minimum Sb concentration measured in the reference soils exceeded the declared background value ($0.1\text{--}1.9 \mu\text{g g}^{-1}$) markedly.

Thanks to brake pads abrasion and growing usage of PET bottles the world antimony production sharply increased over the last 40 years (USGS, 2017). Conversely, in most of European countries arsenic emissions declined by 70–85% following the considerable decrease of atmospheric emissions in Central Europe from 1985–2000. Over the 20-year time span As concentrations in vertical atmospheric deposition decreased 8 times, those in interception deposition decreased 16 times (Doušová *et al.*, 2007).

Figure 1. Contamination effect of source brake abrasion.

4 CONCLUSIONS

Brake abrasion dust represents one of the major sources of antimony pollution. In exposed localities antimony concentration exceeded up to 60 times the background value and decreased in the order: brake abrasion ($\approx 10^3 \mu\text{g g}^{-1}$) > road dust ($\approx 10^2 \mu\text{g g}^{-1}$) > topsoils ($\approx 10^1 \mu\text{g g}^{-1}$) >> reference soils ($< 1 \mu\text{g g}^{-1}$) being mostly accumulated in fine particles. Contrary to arsenic, antimony correlated better with OM than with Fe in topsoils, its straight correlation with Fe/OM in road dust was not observed. While arsenic contamination has recently decreased thanks to a massive decline of arsenic emissions, antimony contamination indicates a dangerous progress due to growing automotive traffic.

ACKNOWLEDGEMENTS

This work was part of projects 16-13778S (Grant Agency of Czech Republic).

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