

# Antimony in Urban Roadside Surface Soils: Concentration, Source and Mode of Occurrence

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**Abstract:** Antimony (Sb) is one of the elements of increasing environmental significance. In this study, concentrations of Sb were measured on 21 roadside topsoil samples collected from a medium-size city, Xuzhou (China), in order to assess the magnitude of contamination and to identify the possible contamination sources. The mode of occurrence of Sb and the effect of particle size fractions on Sb concentration distributions were also investigated from two specific soil samples. Median of Sb concentrations of the investigated urban surface soils is  $0.96 \text{ mg kg}^{-1}$ . The Sb in the Xuzhou topsoils is mainly attributed to the inputs of coal combustion and almost independent of the particle size fractions. The most common mode of occurrence of Sb is in association with organically-bound fraction.

**Keywords:** Antimony, Source, Urban soils.

## 1. INTRODUCTION

Antimony is a global environmental contaminant. Compared to Hg, Pb, Cd or As, there have been remarkably few studies with respect to the predominant sources, biogeochemical behavior and ultimate fate of Sb in the environment [1]. Antimony has been determined in rocks, soils, fossils, volcanic gases and waters, as well as in plant and animal tissues. Antimony has low concentrations in the earth's crust ( $0.2\text{-}1.0 \text{ mg kg}^{-1}$ ) [2]. The anthropogenic inputs are significant in many areas in comparison to the natural ones. Previous studies have shown that up to  $3.5 \text{ t yr}^{-1}$  are emitted to the atmosphere from human activities and up to 18 000 and 26 000  $\text{t yr}^{-1}$  are estimated as inputs to the aquatic ecosystems and soils, respectively [2]. The human contributions of Sb are 100- to 200- fold higher than the atmospheric Sb emissions from natural sources (*ca.*  $2600 \text{ t yr}^{-1}$ ) [3]. Antimony anthropogenic sources mainly include both domestic and industrial coal and fuel combustion, pyrometallurgical non-ferrous Cu-Ni-based metal production, incinerators and road traffic [2, 4-8]. In addition, a large number of other industrial processes like the manufacture of paints, semiconductors, computer chips, plastics, compact discs, bactericides, etc., involve the use of Sb compounds. Due to these wastes and emissions into the environment, Sb constitutes a very important subject for environmental and health-related studies [9-11].

Urban roadside topsoils are the "recipients" of large amounts of pollutants from a variety of sources including industrial wastes, vehicle emissions, coal burning waste as well as other activities. Accordingly, roadside topsoils have become an increasingly important environmental sampling medium for assessing anthropogenic pollutant levels in the

urban environment [12, 13]. Despite the clear impact of Sb in the environment, so far few studies have focused on measuring Sb in urban soils. Moreover, the toxicity of antimony is not only dependent upon the total concentration but also its chemical form in the environment. Therefore, it is also important to know the mode of occurrence of Sb in urban soils. The concentrations of most heavy metals in soil are usually controlled by the particle size because finer particles, due to their high specific area (surface area per unit volume), may adsorb more heavy metals. Thus, the effects of particle size fractions on concentration distributions of Sb is of importance for transport of soil-bound Sb and pollution control by various remedial options. In this study, concentrations of antimony in urban roadside topsoils were determined and the mode of occurrence of Sb investigated. The predominant anthropogenic sources of Sb and the effects of particle size fractions on concentration distributions were also elucidated.

## 2. MATERIALS AND METHODS

### 2.1. Studying Area and Sampling

Xuzhou, ( $33^{\circ}43' - 34^{\circ}58' \text{N}$ ,  $116^{\circ}22' - 118^{\circ}40' \text{E}$ ), is in the northwestern part of Jiangsu, one of the provinces of China. Xuzhou (China) is an important centre of historic and modern day industrial activities where coal provided the fuel for manufacturing. A total of 21 roadside topsoil samples (0 - 10 cm depth) were collected within the city of Xuzhou. At each sampling point, three sub-samples, with a  $20 \times 20 \text{ cm}$  surface, were taken and then mixed to obtain a bulk sample. Such a sampling strategy was adopted in order to reduce the possibility of random influence of urban waste not clearly visible. All the samples were collected with a stainless steel spatula and kept in PVC packages. The soils samples were air-dried and sieved through a 2-mm nylon sieve.

In addition, two sampling sites (sample # 1 and sample # 11) were selected to investigate the effect of particle size on Sb concentration distribution and the mode of occurrence.

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These two sites were chosen to reflect differences in land use within an urban setting. The first (sample # 1) is in the area close to the Xuzhou Steel-iron Plant and the second site (sample #11) is close to the city centre in an area with mostly automobile traffic.

## 2.2. Determination of Sb Concentrations

The Sb concentrations in 21 soil samples were dissolved with HF-HNO<sub>3</sub>-HCl acid mixture and determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, X-Series, Thermo Electro Co. USA) [14]. The conditions of analytical determination for Sb are described in Table 1.

Caution was taken in preparing and analyzing samples to minimize contamination from air, glassware and reagents, which were all of superior quality. Replicated measures of standard reference materials provided by China Environmental Monitoring General Station, reagent blanks and duplicated soil samples randomly selected from the set of available samples were used to assess accuracy and precision.

**Table 1. The Parameters of ICP-MS Used for Sb Determination**

Parameters	Values
Forward power	1200W
Nebuliser flow rate	0.80 L/min
Auxiliary flow rate	0.75 L/min
Cool flow rate	13.50 L/min
Internal standards	Rh, Re

## 2.3. Chemical Fractionation Method for the Determination of the Mode of Occurrence of Sb

Two samples (Sample # 1 and # 11) were characterized by the three-step "BCR" extraction scheme. A detailed description of the BCR-protocol is presented by Quevauviller *et al.* [15]. Briefly, the sequential extraction was performed by sequentially extracting 0.5 grams of the soil samples in a 50 ml centrifuge tube at room temperature using a mechanical shaker with:

Fraction 1: acid extractable species. The sample was extracted with 20 ml 0.11 mol l<sup>-1</sup> acetic acid (16 h shaking period);

Fraction 2: bound to Fe-Mn oxide species. The residue was extracted with 20 ml 0.1 mol l<sup>-1</sup> hydroxylamine hydrochloride (16 h shaking period);

Fraction 3: bound to organic species. The residue was extracted with a two-fold 5 ml 8.8 mol l<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> (pH 2-3) digestion at 85 °C and subsequently with 25 ml 1 mol l<sup>-1</sup> ammonium acetate (16 h shaking period);

Fraction 4: bound to silicate species. The residue was extracted with HF-HNO<sub>3</sub>-HCl acid mixture (This step is not a speciation of the BCR protocol).

After shaking, the soil suspension was each time centrifuged at 3000 rpm and the supernatant solution was decanted, filtered through a Millipore filter (pore size 0.45 µm)

and set aside for analysis. After each of the steps, the soil residue was washed every time with 10 ml H<sub>2</sub>O (15 min). After centrifuging, the washing solution was carefully decanted and discarded. The Sb concentrations in leachate were determined by ICP-MS. Each ICP-MS measurement was repeated twice. Relative standard deviations remained 5%. Accuracy was checked by measuring one of the standard solutions as unknown sample.

## 2.4. Effect of Particle Sizes on Sb Concentration Distributions

The effect of particle sizes on enrichments of Sb was also obtained from the two representative soil samples (#1 and # 11). These two samples were initially sieved through a 1000 µm nylon sieve to remove coarse sand and then divided by particle diameter into five physical size fractions, 500-250, 250-125, 125-74, 74-45 and < 45 µm. The soil samples in various particle size fractions were dissolved with HF-HNO<sub>3</sub>-HCl acid mixture and the Sb concentrations were measured by ICP-MS.

## 2.5. Statistical Analysis

Statistical analysis of data was performed with SPSS Ver. 14.0 for windows software.

## 3. RESULTS AND DISCUSSION

### 3.1. Total Concentrations and Predominant Sources of Sb

The Sb concentrations of surface soil samples ranged from 0.79 to 53 mg kg<sup>-1</sup>, with a median of 0.96 mg kg<sup>-1</sup> (Table 2). The highest Sb concentration (53 mg kg<sup>-1</sup>) was found in sample # 2 and almost 65 times of the regional background value. The sampling site (Sample # 2) is close to Xuzhou Mechanical Plant. The reason why the Sb concentration is so high is still not clear. The Sb concentrations in Xuzhou urban roadside topsoils are comparable to those reported in Table 3.

Certain trace metals have been successfully used to identify natural or anthropogenic sources for the urban environment. Ely *et al.* [17] used metals such as Cu, Zn and Pb to evaluate the contribution of traffic to the surrounding urban environment. The correlations between metals (e.g. Ga, Al and Ti) and clays in the soil samples have also been used to indicate the natural origin of these metals [13, 18]. Previous studies have shown that toxic elements Hg and As are principally derived from coal combustion in Xuzhou urban surface soils [13]. The significant positive correlations (P < 0.01) between Sb and Hg or As (Table 4) indicate that the Sb in Xuzhou surface soils is probably mainly ascribed to inputs of coal combustion (though traffic emissions cannot be totally disregarded in any urban environment).

It is well documented that the Cu/Sb ratio is commonly used to identify the Sb contamination source. Sternbeck *et al.* [19] proposed diagnostic criteria for brake wear particles that included a ratio of 4.6 ±2.3 for Cu/Sb. Adachik *et al.* [20] reported the ratio of Cu/Sb of 2.5 in street dust, which was within the diagnostic criteria for brake wear particles. Hjortenkrans *et al.* [15] found in roadside soils the Cu/Sb ratio of between 3.6 and 150, with a mean of 20±19. The wide interval was attributed to the contribution from both



