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Antimony Concentration in Farming Soil of Southern Poland

K. Loska,[1] D. Wiechuła,[2] I. Korus[1]

[1] Silesian Technical University, Institute of Engineering of Water and Wastewater, ul. Konarskiego 18, 44-100 Gliwice, Poland
[2] Silesian University of Medicine, Department of Toxicology, ul. Jagiellońska 4, 41-200 Sosnowiec, Poland

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Antimony concentration in the Earth's crust is estimated to be 0.2 - 0.3 mg/kg (Fowler and Goering 1991; Taylor and McLennan 1995), and its background concentration in the world soils is < 1 - 8.8 mg/kg, 0.48 mg/kg on average (Shacklette and Boerngen 1984). Antimony concentration in soil increases as a result of human activity; vehicle emissions (Dietl et al. 1996; Huang et al. 1994), emissions of smelters (Fowler and Goering 1991; Pacyna 1984) and coal combustion (Nriagu and Pacyna 1988) being especially effective. Antimony accumulates primarily in the surface layers of soil which indicates that antimony contamination results mainly from air deposition (Kabata-Pendias and Pendias 1985). The global input of antimony into soil with wastewater is estimated to be 4.7 - $47*10^6$ kg/year (Nriagu and Pacyna 1988). As a result of contamination, antimony concentration in soil may increase to 260 mg/kg (Ragaini et al. 1977), and even 857 mg/kg (Trnovsky et al. 1988).

Antimony concentrations in soil may affect the quality of crops in a given area. It is an element which is readily taken up by plants, although it is not indispensable to them. Investigations revealed that its presence in plants originates from surface deposition and its concentration correlates with the concentrations of its available forms in soil (ATSDR 1992).

In this work, antimony concentration was assayed in the surface layer of farming soils, at the same time being affected by long-range atmospheric transport from the Upper Silesian Industrial Region and local sources (coal mine).

MATERIALS AND METHODS

Suszec commune is located in the southern part of Silesian Province, Pszczyna county. The dominant formations in the area are Carboniferous deposits with layers from the Tertiary and Quaternary periods. The predominant types of soils in the commune are podzoluvisols and cambisols. In small areas, chernozems and histosols occur.

Suszec is an agricultural and mining commune. The farmland covers 57% of its area. It is surrounded by the forest shelter belt of the Upper Silesian Industrial Region.

Correspondence to: D. Wiechuła

Krupiński coal mine founded in the 1980s and small vegetable processing plants are located in the commune. The commune consists of 6 villages: Suszec, Rudziczka, Kryry, Mizerów, Kobielice and Radostowice. The landscape of the last four villages is typically agricultural, only Suszec and Rudziczka is partially dominated by the local industry.

The samples were collected in October 2001. The surface soil layer to a depth of 20 cm (ploughing layer) was sampled. Each sample was a composite of 30 - 40 subsamples from within an area approx. 0.02 km^2 - Fig. 1. 1230 samples weighing approx. 1 kg were taken to the laboratory. After being air dried, the samples were sieved through a 2 mm polyethylene sieve and dried to constant mass in a drier at 75°C.

Figure 1. Location of sampling sites

pH was determined applying the potentiometric method in 1 M potassium chloride in 1 : 5 suspension following the standard PN-ISO 10390, dated December 1997. The measurement was performed with a CX 721 multifunctional apparatus.

In order to assay antimony, the dried samples were averaged applying the coning and quartering method, and ground in an S-1000 Retsch centrifugal mill to a diameter of < 0.01 mm. 250 mg ± 20% samples of the soil were digested applying a microwave sample preparation system MLS-1200 MEGA equipped with a MDR-300/S rotor and a microwave system for concentration and evaporation of acids FAM-40 equipped with a MCR-6/E rotor manufactured by Milestone. The digestion was carried out with a mixture of 3 cm^3 of HNO_3, 2 cm^3 of HF and 1 cm^3 of H_2O_2. After the acids had been digested and evaporated, 0.5 cm^3 of HNO_3 and 10 cm^3 of water was added, transferred into 50 cm^3 measuring flasks and filled to volume. The determination of total antimony concentration was carried out applying hydrid generation AAS, sodium borohydride being used as a reducing agent after preliminary reduction with potassium iodide. The correctness of the methods was validated on the basis of the reference material IAEA-SOIL-7 containing 1.7 mgSb/kg (value determined - 1.62 mgSb/kg).

RESULTS AND DISCUSSION

Antimony concentration in the soil ranged from 0.34 mg/kg to 2.26 mg/kg - Table 1. The largest number of results fell within the range of 0.60 - 1.00 mg/kg, and individual values over 1.2 mg/kg formed a characteristic right-hand side of the distribution of the results obtained. Since the distribution was not normal, our analysis of antimony concentrations in the soil employed non-parameter statistics.

Table 1. Antimony concentration in the soil of Suszec commune [mg/kg]

Parameter		Value
Range		0.34 – 2.26
Mean ± SD		0.81 ± 0.16
Confidence interval	–95%	0.80
	+95%	0.82
Median		0.80
Quartile	lower	0.70
	upper	0.90
Skewness		1.62
Kurtosis		11.19

A strong correlation was observed between antimony and humus concentrations in the soil of interest - Fig. 2. It was described by a positive correlation coefficient of r = 0.25 consistent with the literature data showing that over 90% of antimony released during aeration binds to organic matter and Fe, Mn oxides (Hammel et al. 2000; Kabata-Pendias and Pendias 1999).

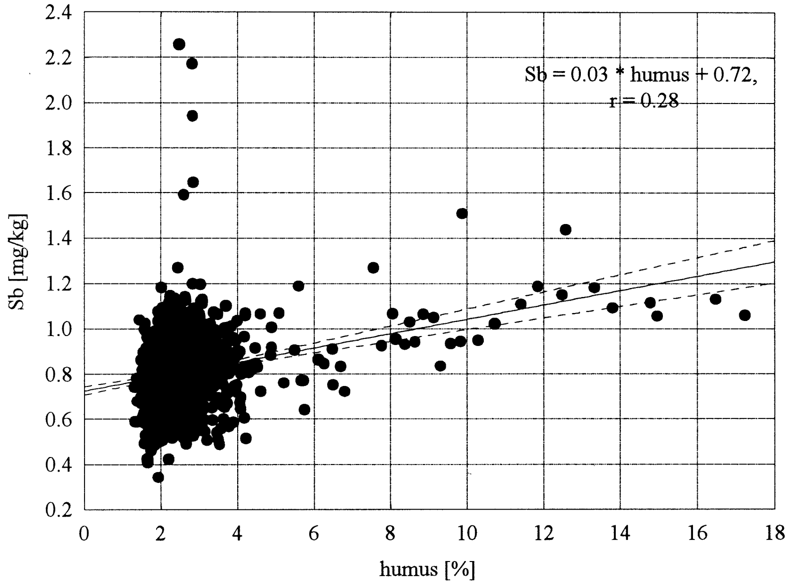

Figure 2. Correlation between antimony concentrations and humus content in soil

In the soil investigated, an increase in humus content resulted in an increase in antimony concentrations. For example, the median value in the soil containing up to 2% of humus was 0.74 mgSb/kg, 2 - 3% - 0.81 mgSb/kg, 3 - 4% - 0.82 mgSb/kg, and over 4% - 0.92 mgSb/kg.

No correlation between antimony concentration and soil pH was found. Its concentration in the very acid soils (pH < 4.5) was 0.80 mg/kg, while in the neutral ones (pH = 6.6 - 7.2) it reached - 0.82 mg/kg. A decrease in soil pH did not affect the mobility of antimony in the soil, which was consistent with the data presented by Li and Thornton (1993).

The value of the median for antimony was 0.80 mg/kg. Similar antimony concentration of 0.88 mg/kg was assayed in the surface layers of Norwegian soils (Steinnes et al. 1997). However, antimony concentration determined in Suszec commune was two times higher in comparison to the world soils (Shacklette and Boerngen 1984).

Antimony concentration in the soil was not associated with the local industry. Analysis of its concentrations in the soils of particular villages revealed that although its maximum values occurred in the most industrial village of Suszec, its average values were not higher than the ones assayed in the other villages of the commune - Fig. 3. The highest mean antimony concentration was found in Kryry, a typical agricultural village, with prevailing peat soils in which humus content exceeded 16%. It might be assumed that antimony concentrations in the soil of Suszec commune is closely connected with the emission from the Upper Silesian Industrial Region and the Czech Republic. The contribution of long-range atmospheric transport to antimony contamination had also been emphasized by Steinnes (1980; 1997).

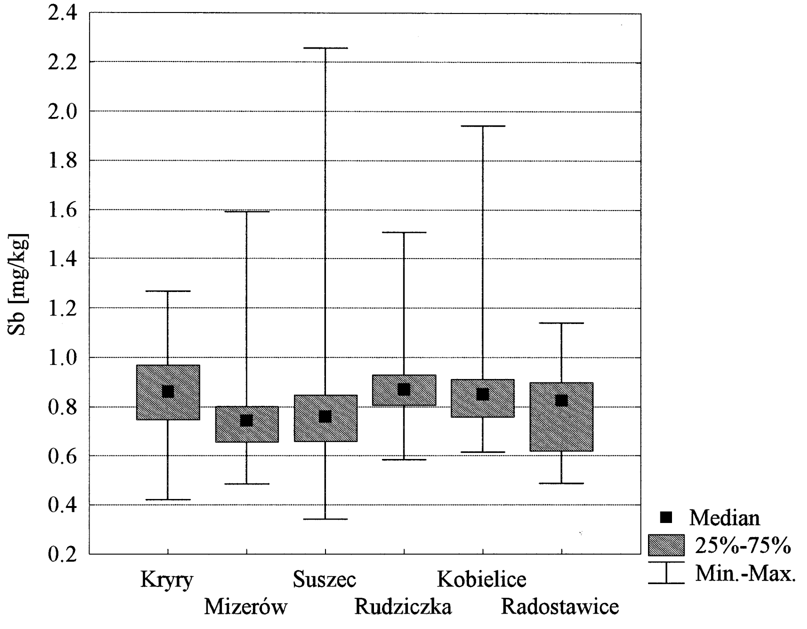

Figure 3. Antimony concentrations in particular villages of Suszec commune

The value of 0.82 mg/kg may be assumed as the background antimony concentration since it corresponds to the upper limit of confidence interval for the arithmetic mean (95% UCL). According to numerous authors, the application of 95% UCL may serve as a good and relatively easy way of assessing an average concentration of an element in a given area (Chen et al. 2001).

95% UCL was computed for the log 10-transformed data, because the distribution of original data was not normal (Roberts and Halmes 1999). The assumption of 95% UCL as the boundary antimony concentration in the soil resulted in a situation in which over half of the results exceeded the value and pointed to antimony contamination of the soils - Fig. 4.

The extent of antimony contamination of the soil was determined on the basis of geoccumulation index (I_{geo}) (Müller 1969) and enrichment factor (EF) (Buat-Menard 1979). In the formula

$$I_{geo} = \log_2 \frac{C_n}{1.5 \cdot B_n}$$

C_n - denoted successive antimony concentration determined in the soil,
B_n - antimony concentration in the Earth's crust of 0.2 mg/kg (Taylor and McLennan 1995).

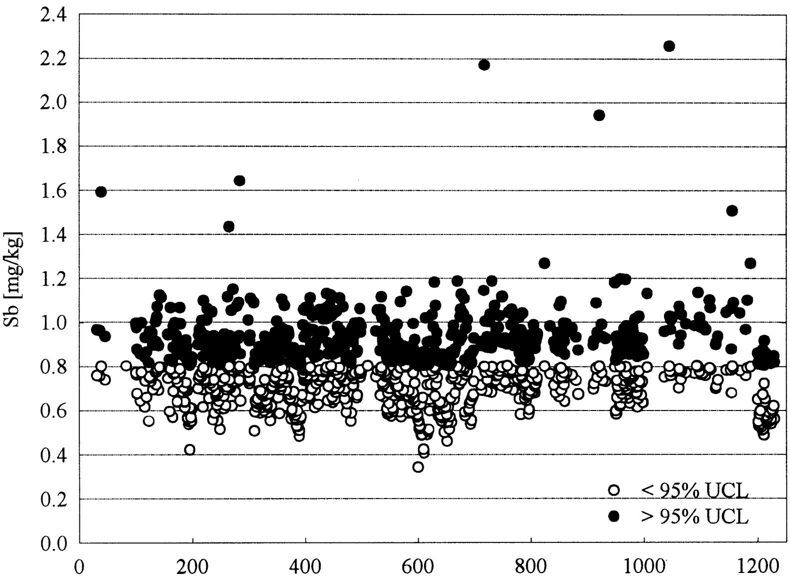

Figure 4. Assessment of antimony background concentrations in soil as a 95% UCL

The enrichment factor was calculated using the formula:

$$EF = \frac{C_n}{C_{ref}} \Big/ \frac{B_n}{B_{ref}}$$

where

C_n - antimony concentration in the soil tested,

C_{ref} - antimony concentration in the Earth's crust (Taylor and McLennan 1995),

B_n - concentration of normalizing element in the soil tested,

B_{ref} - concentration of normalizing element in the Earth's crust.

Calcium concentration in the soil of interest, and its concentration in the Earth's crust of 3% were assumed as a normalizing agent (Taylor and McLennan 1995).

The geoccumulation indexes and enrichment factors for antimony in the soil are given in Fig. 5. The index of geoccumulation ranged from 0.18 to 2.91 (1.40 on average). Thus, the soils tested may be classified as moderately contaminated by antimony because of the average antimony concentration, while the maximum concentrations indicated considerable contamination of the soil.

The results concerning the degree of antimony contamination of the soil were identical applying the enrichment factor. Its values ranged from 2.33 to 15.07, the average value being 4.89. According to the interpretation of the enrichment factor, the values from the range of 2 - 5 indicate moderate contamination of the soil, while the range of 5 - 20 points to considerable contamination.

Despite the elevated antimony concentration in the soil against the Earth's crust,

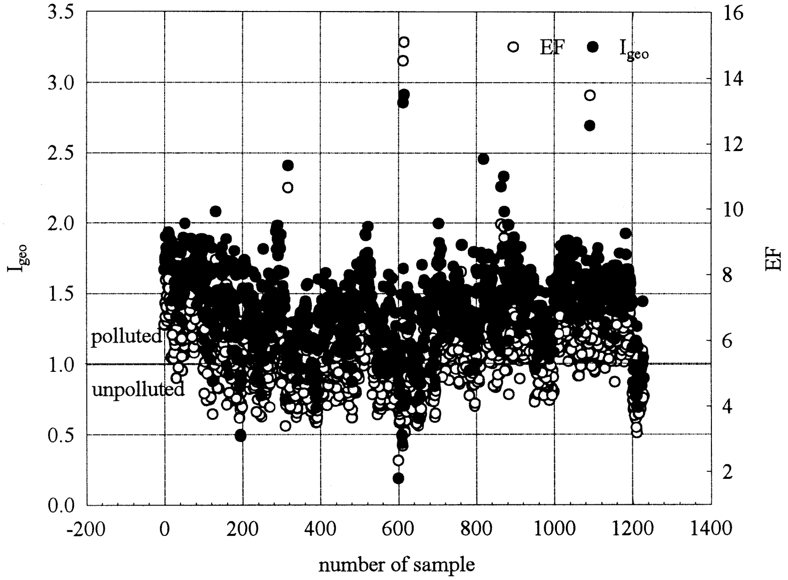

Figure 5. Assessment of soil contamination applying index of geoaccumulation and enrichment factor

it does not pose any hazard to plant life. According to the data by Eikmann and Kloke (1993), the value of 5 mg/kg is reported as tolerable content.

The investigations showed that antimony concentration in the soil of Suszec commune of 0.8 mg/kg was higher that the value found for non-contaminated world soils. In the soils with very high humus content, antimony concentration showed a strong increasing tendency, whereas soil pH did not affect antimony concentration in the soil. The application of geoccumulation index and enrichment factor to the assessment of antimony contamination in the soil showed that the farming soils in Suszec commune were moderately contaminated. Similar concentrations of antimony in both typically agricultural and industrial villages indicated that contamination of the soil was associated with the long-range transport rather than local emission sources.

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