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Application of Various Methods for Assessment of Background Arsenic Concentration in Farming Soil

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The background metal concentration in soil can be assessed in many ways. The simplest methods analyze the most common values i.e. geometric or arithmetic means, and medians (Crock et al. 1992; Reaves and Berrow 1984). Background, i.e. "threshold value" is described by the equation $m + ns$, in which m is the mean, n = 1, 2 or 3, and s is the standard deviation. Nth percentiles e.g. 95^{th} or 97.5^{th}, or the upper confidence limit of the mean (95% UCL) may also be assumed as the upper limit of the background concentration (Chen et al. 2001; Crock et al. 1992). Since the contamination of soils is widespread, the assessment of background concentration is often made by employing the elimination of outliers produced by anthropogenic processes which disturb the normal distribution of metals (Matschullat et al., 2000). Background concentration may also be estimated by applying regression analysis, taking the clay, organic carbon or metal (e.g. conservative elements) concentration as predictor variables (Hanson et al. 1993; Huisman et al. 1997). The values which lie beyond the confidence interval of the regression curve are described as anthropogenically influenced.

This work aims to assess the background concentrations of arsenic in the farming soils of Suszec commune (southern Poland), applying some selected methods.

MATERIALS AND METHODS

Suszec commune is located in the southern part of Silesian Province, Pszczyna county, Poland. 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 (podzoluvisols PD, PDd Dystric Podzoluvisols) and cambisols (CM, CMe Eutric Cambisols and CMd Dystric Cambisols). In small areas, chernozems (mainly chernozems CH, CHk Calcic Chernozems) and histosols (histosols Hs, Hsi Gelic Histosols) occur.

Suszec is an agricultural and mining commune. The farming land covers 57% of its area. It is surrounded by the forest shelter belt of the Upper Silesian Industrial Region. The farming activity in the commune deals mainly with crop growing such as wheat, rye, barley as well as maize and rape. The production of decorative plants

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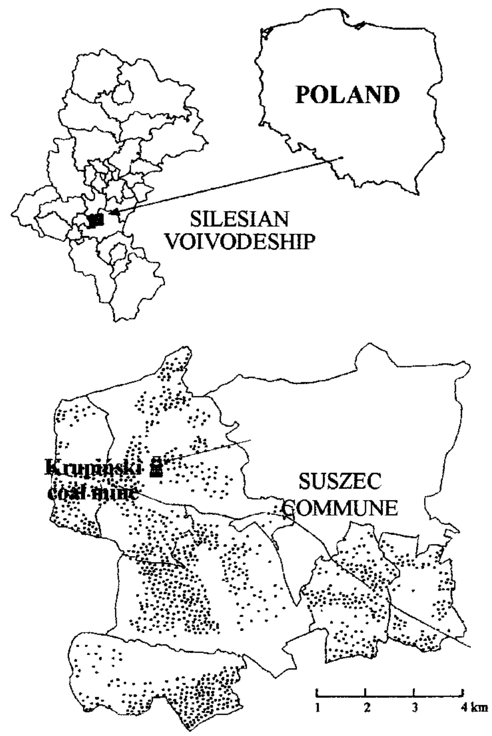

Figure 1. Location of sampling sites

and field mushrooms also plays an important role. The area is dominated by extensive agriculture. Krupiński coal mine founded in the 1980s and small vegetable processing plants are located in the area. It is affected by the contaminants emitted by the Upper Silesian Industrial Region (coal mines, non-ferrous and steel plants, chemical factories, coking plants, power stations), and the Czech Republic (Trzyniec smelter).

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. 10000 m^2 - Fig. 1. After being air dried, they were sieved through a 2 mm polyethylene sieve and dried to constant mass in a drier at 75°C. Afterwards, composite samples were mited, and subsamples were with the coning and quartering method and ground in an S-1000 Retsch centrifugal mill to a diameter of < 0.01 mm.

Soil samples 200 - 300 mg 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 nitric acid, 2 cm^3 of hydrofluoric acid and 1 cm^3 of hydrogen peroxide solution (Krachler et al. 2002). After the samples had been digested and solvent evaporated, 0.5 cm^3 of HNO_3 and 10 cm^3 of water were added, transferred into 50 cm^3 measuring flasks and filled to volume. The determination of total arsenic concentration was carried out by HGAAS, with sodium borohydride used as a reducing agent after preliminary reduction with potassium iodide. The correctness of the method was checked using the reference material IAEA-SOIL-7. The determined arsenic value was 12.8 mg/kg; the certified value was 13.4 mg/kg. The limits of detection (LOD) for As in the soil was 0.02 mg/kg.

The statistical analysis was carried out using the program Statistica ver. 5.5pl.

RESULTS AND DISCUSSION

During background assessment, it is extremely important that a given data set does not contain values in which high concentrations of particular elements result from an accidental error made during collection, preparation and determination steps, or are caused by unknown point emission sources. The detailed analysis of the data set obtained aimed to eliminate outliers prior to calculations - Fig. 2. Fig. 2 showed that the three highest values, markedly different from the others, could be outliers. However, the outlier test carried out on the data set did not allow us to omit any of those values (EPA 1998).

The histogram of the obtained results showed that distribution of arsenic was steeper and more developed on the right side compared to the normal distribution. The largest number of the obtained results fell within the ranges of 8-9 mg/kg and 7-8 mg/kg, and the arithmetic mean was higher than the median - Table 1.

In the case when a given data set does not have a normal distribution, the calculation of a range of background concentrations as the arithmetic mean ±2SD, and the calculation of other statistical parameters typical of the normal distribution which might be used to quantify background (95% UCL) are not applicable. Therefore, the geometric mean and geometric standard deviation were used to assess background. The value G+2SDG thus calculated, assumed as the upper limit of arsenic background concentration in soil, was 11.94 mg/kg. In this case, most of the results obtained (95.5%) fell within the range of the background - Fig. 3.

The right-hand development of the data set towards higher values implied that not all arsenic concentration in soil can be regarded as background values. Therefore, the application of the outlier test to the original data set seemed to be the most satisfactory solution. The iterative 2-σ technique was chosen from several tests suggested by Matschullat et al. (2000) since it allowed the most suitable background assessment (Loska et al. 2002). The iterative 2-σ technique consists in omitting all the values beyond the X ± 2SD range of the original data, and the omission procedure continues until all values fall within that range (Matschullat et al. 2000). The data subset thus obtained is used to calculate the mean and standard deviation, and the range of background concentrations, similarly to the original data, is X ± 2SD from the subset resulting from the omission process.

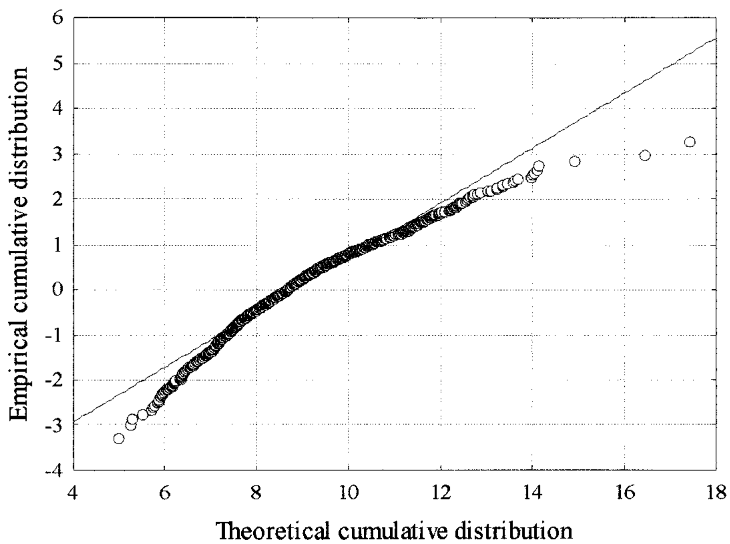

Figure 2. Probability plot for arsenic concentrations in soil

Table 1. Statistical characteristics of arsenic concentration in soil [mg/kg].

Parameter	Value
N	1230
Minimum	4.98
Maximum	17.40
Mean	8.83
Standard deviation	1.62
Lower confidence limit –95%	8.74
Upper confidence limit +95%	8.92
Geometric mean	8.69
Geometric standard deviation	1.62
Median	8.64
Percentile 95	11.83
Percentile 97.5	12.52
Skewness	0.83
Skewness log-10 transformed data	0.27
Kurtosis	1.12
Kurtosis log-10 transformed data	0.07

The application of the iterative 2-σ technique to our data set enabled us to omit 18.9% of the original data. The subset obtained had a normal distribution, and the upper limit of background concentrations was 10.19 mg/kg - Fig. 4.
The fact that the original data set did not have a normal distribution did not enable

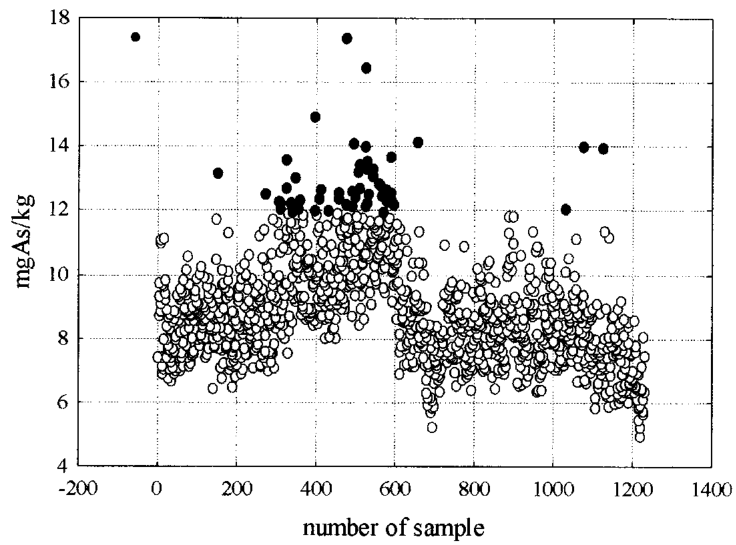

Figure 3. Results of arsenic background concentrations in soil as G+2SDG. Full marks (•) denote values higher than the upper limit of background concentrations

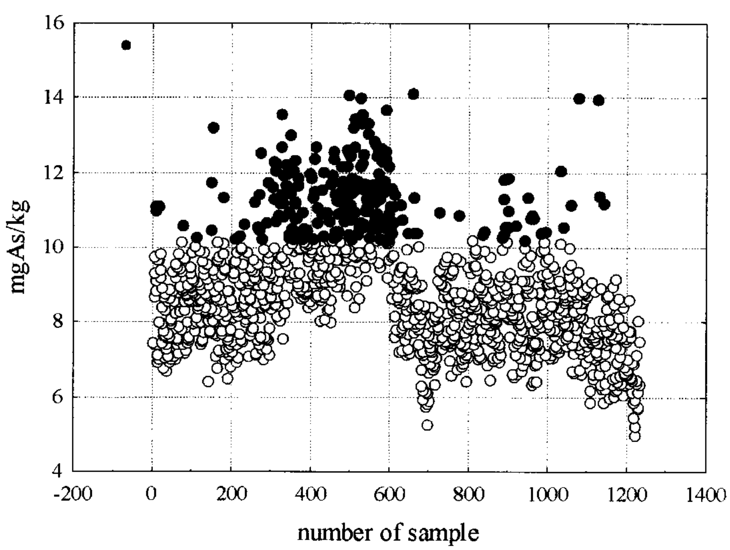

Figure 4. Results of arsenic background concentrations in soil - iterative 2-σ technique. Full marks (•) denote values higher than the upper limit of background concentrations

us to use the upper confidence limit around the mean (95% UCL) as background concentrations. In such a case, however, it is possible to use 95% UCL calculated after the log-10 transformation of original data using the following equation (Roberts and Halmes 1999):

$$UCL_{0.95} = e^{\left(\bar{x}+0.5\delta^2+\frac{\delta H}{\sqrt{n-1}}\right)} \qquad (1)$$

where:
e - constant (base of the natural log),
_- mean of the log transformed data,
α - standard deviation of the log transformed data,
H - H-statistic (Gilbert 1987),
n - number of samples.

The log-10 transformation of the data allowed us to obtain the skewness and kurtosis values of 0.27 and 0.07 respectively - Table 1. The arithmetic mean value equalled the values of the median and geometric mean. 95% UCL calculated from the equation (1) was 8.78 mg/kg. The acceptance of 95% UCL log-10 transformed data as the upper limit of the background arsenic concentration in the soil meant that as much as 45.2% of all the results were beyond the background limit - Fig. 5.
The subsequent step dealt with the assessment of the background arsenic concentration in the soil applying regression analysis. Chromium was used as a reference element. The possibility of using chromium as a reference element was confirmed in the paper by Loska et al. (2003). The concentration of chromium in the soil ranged from 13.63 mg/kg to 81.84 mg/kg, and the geometric mean was 32.28 mg/kg. Since our data set of chromium concentration was not normal, we used the log-10 transformation of the data, similarly to arsenic. The upper confidence limit around the regression curve was 8.76 mgAs/kg. This value was very similar to the value of 95% UCL log-10 transformed data and, similarly to the previous case, as much as 45.6% of the original data were higher than the value assessed as background.

The background arsenic concentration obtained in the analyzed soil by means of various methods differed considerably - Fig. 6. The highest upper limit exceeding 95th percentile was obtained by the calculation of G+2SDG from the original data. This value is 2.5 times higher than the average arsenic concentration in the non-contaminated soils of Poland (Lis and Pasieczna 1995). Also the background upper limits obtained after omitting the outliers of the original data set calculated as 95% UCL of log-10 transformed data and as a result of the regression analysis turned out to be higher than the arsenic concentration in the non-contaminated soils of Poland.

The elevated arsenic concentration in soil compared to the concentration assayed in non-contaminated soils undoubtedly result from industrial influences, both long-range atmospheric transport and local industrial plants. In conclusion, it is suggested that the background concentrations of arsenic in the soil of the area examined should

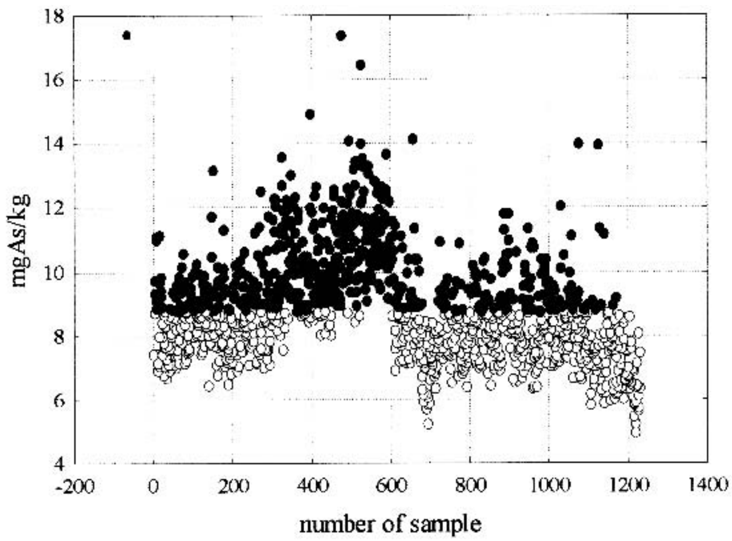

Figure 5. Results of arsenic background concentrations in soil as 95% UCL. Full marks (•) denote values higher than the upper limit of background concentrations.

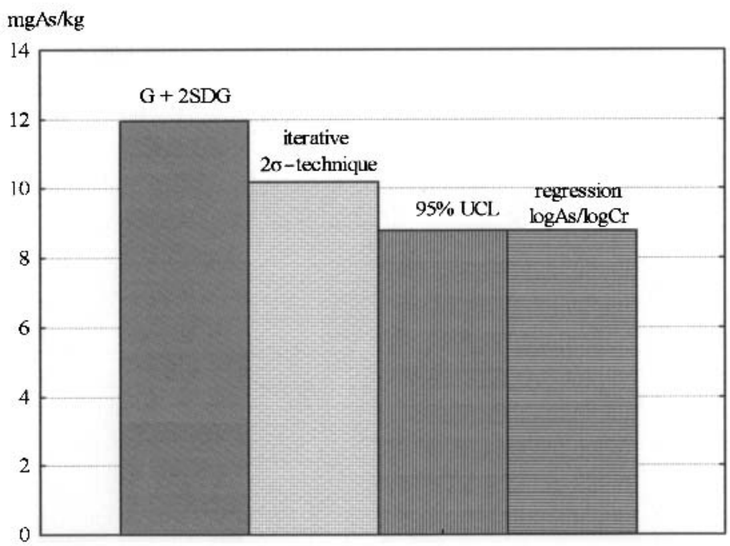

Figure 6. Results of assessment of arsenic background concentrations in soil carried out applying various methods

be accepted at the lower level of the examined values i.e. approx. 8.8 mg/kg. This value reflects most accurately the resultant impact of arsenic concentration from natural sources and human activity in Suszec commune.

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