Polish Journal of Environmental Studies Vol. 12, No. 2 (2003), 187-192

Assessment of Arsenic Enrichment of Cultivated Soils in Southern Poland

K. Loska[1]*, D. Wiechuła[2], B. Barska[3], E. Cebula[4], A. Chojnecka[5]

[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
[3]PRInż. SA Holding, Pl. Grunwaldzki 8/10, 40-950 Katowice, Poland
[4]Silesian Technical University, Inorganic Chemistry and Technology Institute,
ul. Krzywoustego 6, 44-100 Gliwice, Poland
[5]Candela Ltd., ul. Czarnieckiego 72, 01-541 Warsaw, Poland

Received: 28 October, 2002
Accepted: 27 December, 2002

Abstract

Arsenic content in the cultivated soils of an area affected by long-range atmospheric transport from the Upper Silesian Industrial Region (southern Poland) and point emission sources (coal mine) was 8.7 mg/kg on average. The calculated index of geoaccumulation pointed to moderate arsenic contamination of the soil. The enrichment factor calculated as a ratio between arsenic content in the soil and arsenic content in the earth crust applying the logarithmic values of reference elements (i.e. chromium and calcium) also classified the soil as moderately contaminated with arsenic.

Keywords: arsenic, soil, index of geoaccumulation, enrichment factor

Introduction

Arsenic is one of the most common elements occurring in the environment. It is estimated that about 60% of arsenic present in the environment is of anthropogenic origin [1]. The main industrial sources of its contamination are mining activities, copper production and use of low quality coal, cattle dips, smelters and pesticides [2-7].

Arsenic occurs in all soils of the world. Its average content in non-contaminated soils is approx. 5 mg/kg [8-10]. In the contaminated soils, its content may reach 14000 mg/kg [5], or even 27000 mg/kg [11]. Other authors suggest 2500 mg/kg as a value which indicates the existence of contamination [12-15].

Arsenic present in soils is easily taken in by plants but despite their high tolerance to its elevated concentrations, an excess of arsenic can hinder their growth. The presence of arsenic in soil may also be harmful to people, both through plant consumption from contaminated areas as well as inhalation and absorption through skin [11]. Thus, the assessment of arsenic enrichment of soil in farming areas, notably the ones affected by industrial contamination, is of great importance.

The assessment of soil enrichment with elements can be carried out in many ways. The most common ones are the index of geoccumulation and enrichment factors.

The index of geoaccumulation (I_{geo}) has been used as a measure of bottom sediment contamination since the 1970s [16], and numerous research has employed it to assess the contamination of soils [17-18]. It determines contamination by comparing current metal contents with pre-industrial levels [19]. The content accepted as background is multiplied each time by the constant 1.5 in order to take into account natural fluctuations of a given

*Corresponding author

substance in the environment as well as very small anthropogenic influences. The value of the geoaccumulation index is described by the following equation:

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

where:
C_n - arsenic content in tested soil,
B_n - background content; here the average arsenic content in the earth crust of 1.5 mg/kg [20].

The interpretation of the obtained results is as follows: $I_{geo} \leq 0$ practically uncontaminated, $0 < I_{geo} < 1$ uncontaminated to moderately contaminated, $1 < I_{geo} < 2$ moderately contaminated, $2 < I_{geo} < 3$ moderately to heavily contaminated, $3 < I_{geo} < 4$ heavily contaminated, $4 < I_{geo} < 5$ heavily to very heavily contaminated and $I_{geo} \geq 5$ very heavily contaminated.

The use of the enrichment factor (EF) for the assessment of bottom sediment contamination with metals has been suggested by Buat-Menard [21]. Its version adapted to assess the contamination of various environmental media is as follows:

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

where:
C_n - content of the examined element in the examined environment,
C_{ref} - content of the examined element in the reference environment,
B_n - content of the reference element in the examined environment,
B_{ref} - content of the reference element in the reference environment.

An element is regarded as a reference element if it is of low occurrence variability and is present in the environment in trace amounts. It is also possible to apply an element of geochemical nature whose substantial amounts occur in the environment but has no characteristic effects i.e. synergism or antagonism towards an examined element. The most common reference elements are Sc, Mn, Al and Fe [22].

Five contamination categories are recognized on the basis of the enrichment factor:

EF < 2 – depletion to minimal enrichment,
EF = 2-5 – moderate enrichment,
EF = 5-20 – significant enrichment,
EF = 20-40 – very high enrichment,
EF > 40 – extremely high enrichment [23].

Despite certain shortcomings [24], the enrichment factor, due to its universal formula, is a relatively simple and easy tool for assessing enrichment degree and comparing the contamination of different environmental media.

In this work, the index of geoaccumulation and enrichment factor have been applied to assess arsenic contamination of farming soils located in the southern part of Silesian Voivodeship (a province in southern Poland).

Experimental Procedures

Location of the Research

Suszec commune is located in the southern part of Silesian Voivodeship, Pszczyna county (Fig. 1). The dominant formations in the area are Carboniferous deposits with layers from the Tertiary and Quaternary periods. According to soil-agricultural maps the area of the commune is dominated by podsolic soils which occur in flat areas where the flow of surface water is very slow, and brown soils formed in the areas with good conditions for the flow of surface water. Lowmoor peat formed in the hollows of the land.

Suszec is an agricultural and mining commune where Krupiński coal mine founded in the 1980s and small vegetable processing plants are located. It is surrounded by the forest shelter belt of the Upper Silesian Industrial Region. The farming land covers 4,344 ha in total, which is 57% of the commune's area. The commune consists of 6 villages: Suszec, Rudziczka, Kryry, Mizerów, Kobielice and Radostowice.

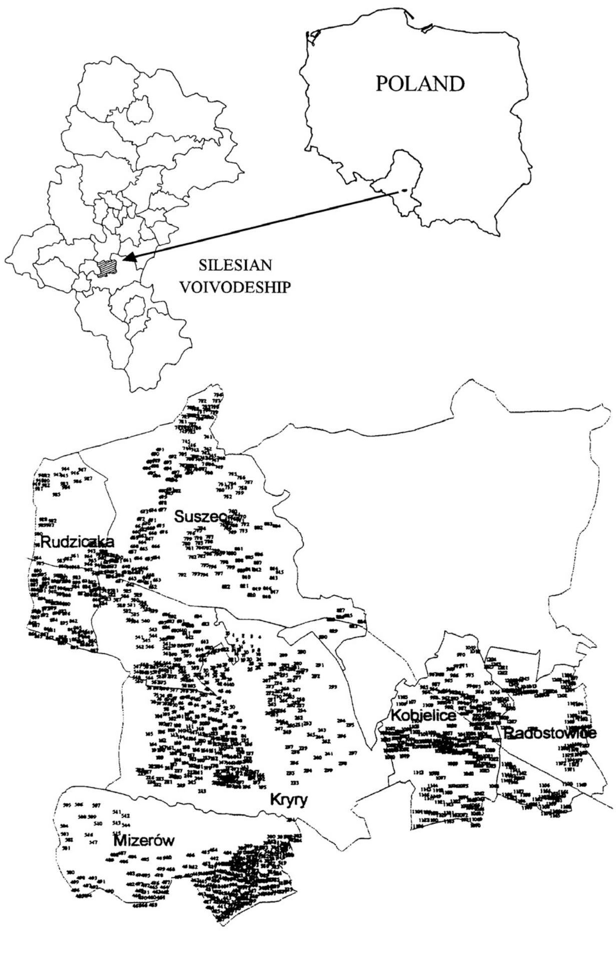

Fig. 1. Location of soil sample collection stations in the vicinity of Suszec commune.

Sample Collection and Analytical Procedure

Samples of the soil were taken in October 2001. In total, our research covered the area of 2461 ha of farming land from Suszec commune. Sample collection sites covered the area of 2 ha of farmland each and were scattered in a regular pattern (Fig. 1). Samples of 0-20 cm surface layer of the soil were taken with an Egner's Soil Sampler. Approximately 30-40 single samples which constituted a 1kg cumulative sample were collected from an area of 2 ha and then transferred to the laboratory. A total of 1221 cumulative samples were collected.

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. Afterwards they 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 mineralized by means of the microwave method applying a microwave mineralization 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 mineralization 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. After the acids had been minerlized 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 arsenic content was carried out applying hydride generation, sodium borohydryde being used as a reducing agent after preliminary reduction with potassium iodide. The correctness of the methods was checked on the basis of reference material IAEA-SOIL-7 (measured value 12.8±0.9 mg/kg, certified value 13.4 mg/kg).

Statistical analysis was carried out using the program Statistica for Windows ver. 5.5. The normality of the data set distribution was analyzed applying the test by Kołgomorow-Smirnow. The significance of the differences between the groups was examined by means of ANOVA variance.

Results

Statistical characteristics of arsenic content in the soil of particular villages of Suszec commune are given in Table 1. The distribution of arsenic content in particular villages was similar to the normal one. Arsenic contents in the surface layer of the soil in particular villages differed significantly (ANOVA variance analysis, $p < 0.05$). Mean content of arsenic was the highest in Mizerów, which is located in the south of the commune. Its maximum content was found in Suszec, the biggest agglomeration of industrial plants in the area (e.g. coal mine). The minimum content and the lowest mean arsenic content in soil were found in Radostowice.

Fig. 2 illustrates the values of geoaccumulation index. Applying the classification by Müller [18], the tested soils may be described as moderately polluted due to mean arsenic contents (excepting Mizerów - moderately to strongly polluted).

When calculating the enrichment factor, chromium and calcium were used as reference elements. The contents of reference elements assayed in the soil of the villages from Suszec commune were collated in Table 2. Arsenic content in the earth's crust of 1.5 mg/kg [20] was accepted as a reference value in the tested environment. The mean contents of Cr and Ca in the earth crust of 185 mg/kg and 30,000 mg/kg respectively [20] were accepted as reference values.

The factors of soil enrichment with arsenic are shown in Figs. 3 and 4. When calcium was used as a reference element, the obtained values were extremely high. In the case of chromium as a reference element, the mean values of enrichment factor lay within the range of < 20, indicating a significant enrichment of soil.

Discussion of Results

A comparison of the results of assessment of soil enrichment with arsenic obtained by all the methods demonstrates that indexes of geoaccumulation indicate much lower soil contamination (moderate) than the enrichment factors (significant - Cr and extremely high contamination - Ca).

The big difference between the indexes of geoaccumulation and enrichment factors raises a question as to the real soil enrichment with arsenic in the tested area.

Table 1. Arsenic content in the soil from Suszec commune [mg/kg].

Village	N	Range	Arithmetic mean	Standard deviation	Geometric mean	Lower quartile	Median	Upper quartile
Kryry	299	6.44 - 13.20	8.55	1.10	8.48	7.63	8.54	9.22
Mizerów	213	7.56 - 14.11	10.22	1.31	10.13	9.20	9.97	11.24
Suszec	311	5.27 - 16.45	9.10	1.80	8.93	7.74	8.73	10.39
Rudziczka	125	6.46 - 11.85	8.52	1.16	8.44	7.70	8.35	9.11
Kobielice	176	5.86 - 14.01	8.24	1.23	8.16	7.40	8.00	8.80
Radostawice	97	4.98 - 11.20	7.11	1.00	7.04	6.37	6.94	7.78
Total	1221	4.98 - 16.45	8.82	1.59	8.68	7.63	8.63	9.71

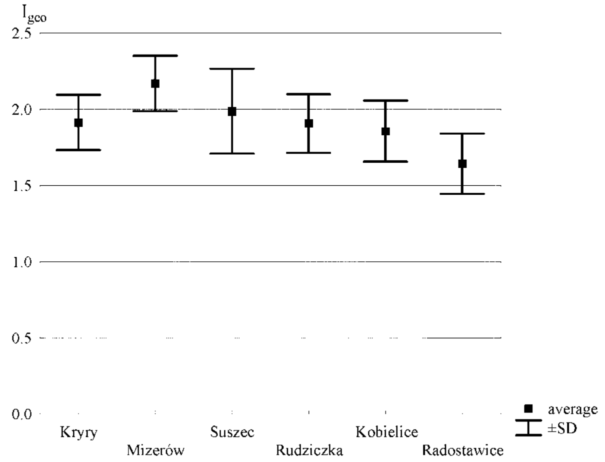

Fig. 2. Index of geoccumulation of arsenic in soil.

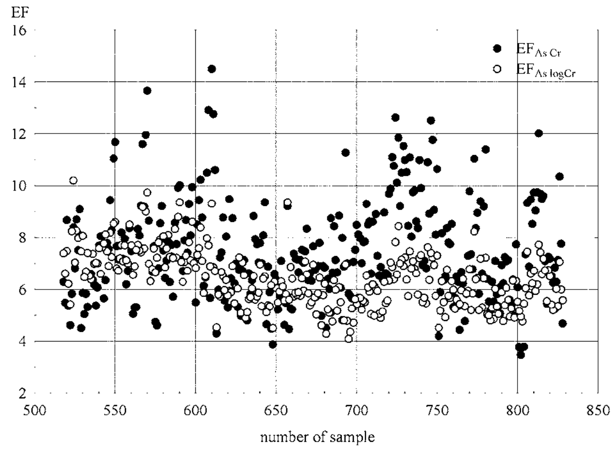

Fig. 5. Comparison of $EF_{As/Cr}$ and $EF_{As/logCr}$ in the soil of Suszec village.

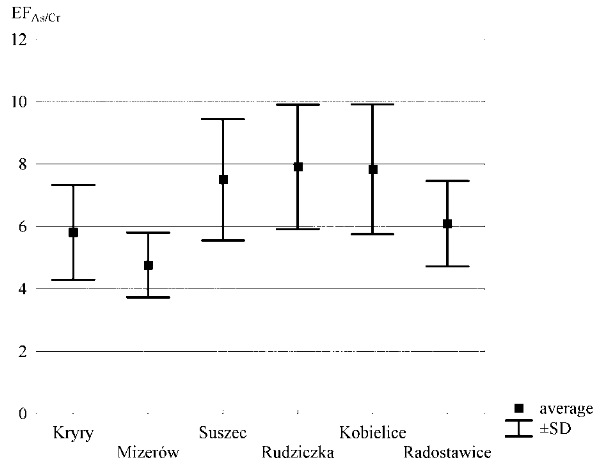

Fig. 3. Enrichment factor As/Cr.

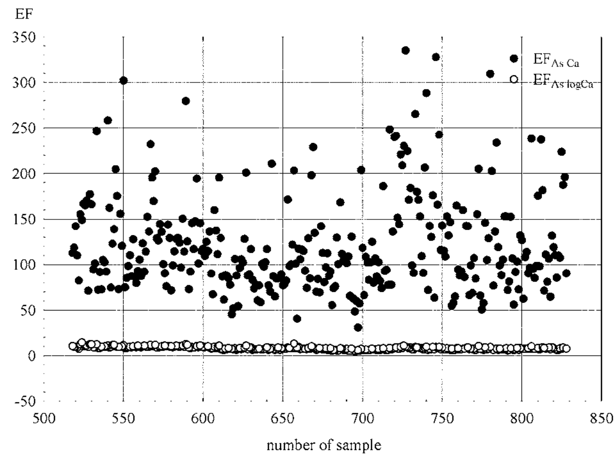

Fig. 6. Comparison of $EF_{As/Ca}$ and $EF_{As/logCa}$ in the soil of Suszec village.

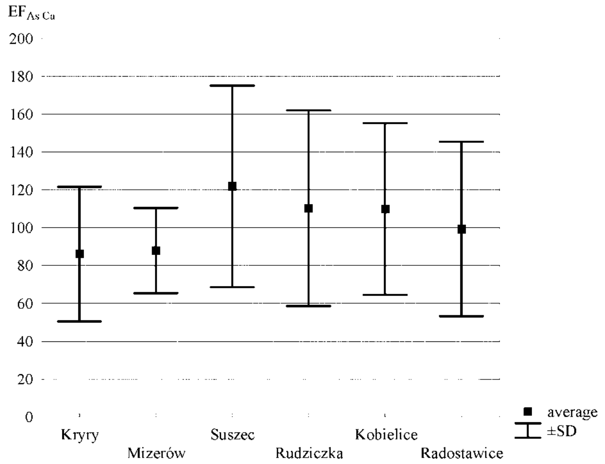

Fig. 4. Enrichment factor As/Ca.

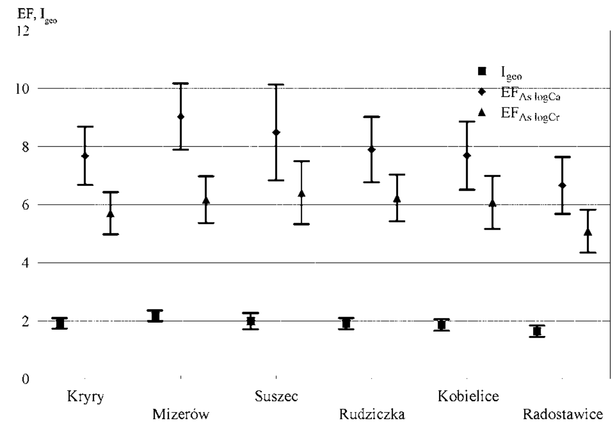

Fig. 7. Compilation of I_{geo} and enrichment factor calculated for logarithmized data sets.

Table 2. Calcium and chromium contents in the soil from Suszec commune [mg/kg].

Village	N	Range	Average mean ± SD
Ca			
Kryry	299	701 - 10343	2311 ± 1032
Mizerów	213	1024 - 4112	2437 ± 559
Suszec	311	532 - 5581	1716 ± 677
Rudziczka	125	565 - 9726	1871 ± 1003
Kobielice	176	468 - 4304	1698 ± 581
Radostawice	97	446 - 5937	1694 ± 736
Cr			
Kryry	299	17.38 - 81.84	36.49 ± 10.21
Mizerów	213	28.44 - 77.87	51.71 ± 9.72
Suszec	311	13.95 - 68.93	30.04 ± 9.48
Rudziczka	125	13.91 - 62.07	26.94 ± 8.62
Kobielice	176	13.63 - 59.46	26.07 ± 7.24
Radostawice	97	18.96 - 69.60	28.29 ± 6.80

The index of geoaccumulation seems to be a more objective tool for assessing contamination. The values of enrichment factor in this particular case did not reveal the real arsenic content in soil (e.g. the soil in Mizerów where mean arsenic content was the highest displayed) lower enrichment factors than the soil in Radostowice, where the lowest arsenic content was found (Figs. 3 and 4).

A discussion about enrichment factors should start with an analysis of the selection of proper reference elements. Chromium has already been used as a reference element in other works [25]. Also, calcium seems to fulfil the conditions required of a reference element - its content in the soil was high but it resulted mainly from the geochemistry of the area and not anthropogenic influence. An analysis of the obtained data sets concerning chromium and calcium content in soil showed their wide scatter - variability coefficient for calcium reached 40%, for chromium 30%, whereas for arsenic it was 12%. In all the villages tested, the distributions of the obtained sets of reference elements differed markedly from normal.

Finding the logarithm of the initial data sets on chromium and calcium contents in soil enabled us to obtain a normal distribution of results in all the villages tested. Figs. 5 and 6 show the enrichment factors calculated for Suszec village applying chromium as a reference element (initial data) and logCr (logarithmized data), as well as calcium (initial data) and logCa (logarithmized data). It is clearly seen that the application of logarithmized data set caused a decrease in the calculated enrichment factors and much smaller scatter of the obtained values compared to the initial data.

The enrichment factor calculated by means of logCr and logCa was compared to the index of geoaccumulation (Fig. 7). It can be easily noticed that the application of logarithmized initial data on the contents of reference elements diminished the differences in the values of the parameters used to assess soil contamination. The application of logarithmized data to the calculation of enrichment factors gives more realistic evaluation of soil contamination with arsenic in particular villages - the enrichment factor was the highest in Mizerów and Suszec, which displayed the highest mean arsenic content in soil; Radostowice had the lowest value.

Conclusions

Our investigations revealed a moderate to strong arsenic contamination of the soil in Suszec commune. The level of contamination is affected by close proximity of the Upper Silesian Industrial Region, long-range atmospheric transport from the Czech Republic and point emission sources (coal mine). The best results illustrating the degree of soil contamination with arsenic are achieved applying the index of geoaccumulation and enrichment factors calculated using logarithmized contents of reference elements - chromium and calcium. The lack of normality of the initial data set concerning the contents of reference elements imposes serious limitations to their use in calculations.

References

1. NRIAGU J.O. A global assessment of natural sources of atmospheric trace metals. Nature **338**, 47, **1989**.
2. TEMPLE P.J., LINZON S.N., CHAI B.L. Contamination of vegetation and soil by arsenic emission from secondary lead smelters. Environ. Pollut. **12**, 311, **1977**.
3. BRIGHT D.A., COEDY B., DUSHENKO W.T., REIMER K.J. Arsenic transport in a watershed receiving gold mine effluent near Yellowknife, Northwest Territories, Canada. Sci. Total Environ. **155**, 237, **1994**.
4. HUNT L.E., HOWARD A.G. Arsenic speciation and distribution in the Carnon estuary following the acute discharge on contaminated water from a disused mine. Marine Pollut. Bull. **28**, 33, **1994**.
5. McLAREN R.G., NAIDU R., TILLER K.G. Fractionation of arsenic in soils contaminated by cattle dip. 1st International Conference: Contaminants and the Soil Environment, Adelaide, Australia, 177, **1996**.
6. AZCUE J.M., MURDOCH A., ROSA F., HALL G.E.M. Effects of abandoned gold mine tailings on the arsenic concentrations in water and sediments of Jack of Clubs Lake, BC. Environ. Technol. **15**, 669, **1994**.
7. WALSH L.M., KEENEY D.R. Behavior and phytotoxicity of inorganic arsenic in soils. ACS Symp. Ser., **7**, 35, **1975**.
8. GOLDSCHMIDT V.M. Geochemistry. Ed.: Muir A., Oxford, Oxford University Press, pp. 468, **1958**.
9. ATSDR (Agency for Toxic Substances and Disease Registry). Toxicological Profile for Arsenic. **2000**.
10. LIS J., PASIECZNA A. Geochemical atlas of Poland 1: 2500000. PIG, Warszawa, **1995**.

11. EPA. Exposure and risk assessment for arsenic. Washington, DC: U.S. Environmental Protection Agency. Code of Federal Regulation. PB 85-221711. EPA 440/4-85-005. 1.1-4.68, **1982**.
12. LAMB I.A., HUGHES M.J., HUGHES C.E. Dispersion of arsenic in soil and water of the Ballarat Goldfield, Victoria". 1st International Conference: Contaminants and the Soil Environment, Adelaide, Australia, 275-276, **1996**.
13. WHO. Environmental Health Criteria, No. 18: Arsenic. Geneva, World Health Organization, **1981**.
14. DIAZ-BARRIGA F., SANTOS M.A., MEJIA J.J., BATRES L., YANEZ L., CARRIZALES L., VERA E., DEL RAZO L.M., CEBRIAN M.E. Arsenic and cadmium exposure in children living near a smelter complex in San Luis Potosi, Mexico. Environ. Res. **62**, 242, **1993**.
15. IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans, Some metals and metallic compounds. Lyon, International Agency for Research on Cancer **234c**, 39, **1980**.
16. MÜLLER G. Index of geoaccumulation in sediments of the Rhine River. Geojournal **2**, 108, **1969**.
17. MIKO S., PEH Z., BUKOVEC D., PROHIC E., KASTMÜLLER Z. Geochemical baseline mapping and Pb pollution assessment of soils in the karst in Western Croatia. Nat. Croat., **9** (1), 41, **2000**.
18. KWAPULIŃSKI J., MIROSŁAWSKI J., WIECHUŁA D., ROCHEL R., BURCZYK J., SOWADA B., IWANEK K. The use of ecotoxicological parameters for estimation of the quality of medicinal plant yielding areas. Bromat. Chem. Toksykol. **XXIX** (3), 243, **1996** (in Polish).
19. MÜLLER G. Die Schwermetallbelastung der Sedimenten des Neckars und Seiner Nebenflüsse. Chemiker-Zeitung **6**, 157, **1981**.
20. TAYLOR S.R., McLENNAN S.M. The geochemical evolution of the continental crust. Reviews in Geophysics **33**, 241, **1995**.
21. BUAT-MENARD P. Influence de la retombée atmosphérique sur la chimie des métaux en trace dans la matičre en suspension de l'Atlantique Nord. Thesis, Univ. Paris VI, p. 434, **1979**.
22. LOSKA K., CEBULA J., PELCZAR J., WIECHUŁA D., KWAPULIŃSKI J. Use of enrichment, and contamination factors together with geoaccumulation indexes to evaluate the content of Cd, Cu, and Ni in the Rybnik Water Reservoir in Poland. Water, Air, Soil Pollut. **93**, 347, **1997**.
23. SUTHERLAND R.A. Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii. Environ. Geol. **39** (6), 611, **2000**.
24. REIMANN C., DE CARITAT P. Intrinsic flaws of element enrichment factors (EFs) in environmental geochemistry. Environ. Sci. Technol. **34**, 5084, **2000**.
25. McMURTRY G.M., WILTSHIRE J.C., KAUAHIKAUA J.P. Heavy metal anomalies in coastal sediments of Oahu, Hawaii. Pac. Sci. **49**, 452, **1995**.