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HEAVY METAL POLLUTION OF SURFACE SOIL IN THRACE REGION (TURKEY)

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Загрязнение тяжелыми металлами поверхностных почв
района Трэйс (Турция)

В работе представлены результаты анализа поверхностных почв, отобранных в 73 точках на территории района Трэйс в северо-западной части Турции. При использовании двух взаимодополняющих методов — эпитеплового нейтронного активационного анализа (ЭНАА) и атомной абсорбционной спектроскопии с пламенной атомизацией (ААС) и атомизацией в графитовой печи (ГФ ААС) установлены концентрации 37 элементов. Содержание Cu, Zn, Ni, Cd, Mn, Co, Pb и As определяли с использованием ААС и ГФ ААС, остальные 29 элементов были определены при помощи ЭНАА. Впервые публикуются данные о содержании As, Ba, Br, Ca, Cd, Ce, Cr, Cs, Eu, Fe, Hf, I, In, K, La, Mn, Mo, Na, Nd, Rb, Sb, Sc, Sm, Sr, Ta, Tb, Th, Ti, U и V в почвах данного региона. Результаты показывают, что исследуемые почвы минимально подвержены влиянию промышленности или какой-либо другой антропогенной деятельности. Распределение элементов в почвах, вероятнее всего, объясняется литогенными вариациями химического состава материнских пород, за исключением, очевидно, повышенных концентраций Pb, Cu, Cd и Zn в почвах в районе Стамбула. Пространственное распределение содержания Cu, Zn, Ni, Cd, Cr, Pb и As на исследуемой территории картировано с использованием ГИС-технологий.

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Heavy Metal Pollution of Surface Soil in Thrace Region (Turkey)

Samples of surface soil were collected at 73 sites in the Thrace region, northwest part of Turkey. Two complementary analytical techniques, epithermal neutron activation analysis (ENAA) and atomic absorption spectrometry (AAS) with flame and graphite furnace atomization were used to determine 37 elements in the soil samples. Concentrations of Cu, Zn, Ni, Cd, Mn, Co, Pb, and As were determined using AAS and GF AAS and ENAA was used for the remaining 29 elements. Results for As, Ba, Br, Ca, Cd, Ce, Cr, Cs, Eu, Fe, Hf, I, In, K, La, Mn, Mo, Na, Nd, Rb, Sb, Sc, Sm, Sr, Ta, Tb, Th, Ti, U, and V are reported for the first time for soils from this region. The results show that concentrations of the most elements were little affected by the industrial and other anthropogenic activities performed in the region. Except for distinctly higher levels of Pb, Cu, Cd, and Zn in Istanbul district than the median values for the Thrace region, the observed distributions seem to be mainly associated with lithogenic variations. Spatial distributions of Cu, Zn, Ni, Cd, Cr, Pb, and As were plotted in relation to the concentration values in soil using Geographic Information System (GIS) technology.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR, at the Department of Chemistry, Norwegian University of Science and Technology (Trondheim, Norway) and at the Çanakkale Onsekiz Mart Üniversitesi Sağlık Hizmetleri Meslek Yüksekokulu (Turkey).

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INTRODUCTION

The soil, a main part of the terrestrial ecosystem, is a habitat for a great number of organisms but at the same time, it is perhaps the most endangered component of our environment, open to influence from a variety of different pollutants arising from human activities (industrial, agricultural, etc.) [1, 2]. Prevention of soil pollution and its harmful effects however requires some basic knowledge about the soil. The soil has a very complex structure and exhibits greatly different properties from place to place. On each site, the soil has different features and it is not always easy to decide if a part of an area is polluted or not. However, if some basic knowledge (geochemical properties, human activities, and atmospheric contamination, etc.) is available for the area of interest it may be easier to determine the degree of pollution for that area.

Among pollutants, heavy metals have been the subject of particular attention because of their long-standing toxicity when exceeding specific thresholds. Among the key issues in the environmental research on heavy metals is their mobility in the ecosystems and transfer in the food chains [3, 4, 5, 6, 7, 8]. Uncontrolled development in industry, agriculture and urbanization accelerates the input of heavy metals into the environment in many parts of the world. Many scientific activities have been devoted to the determination of sources, types, and degree of heavy metal pollution in soil [9, 10, 11]. An important background for this kind of work is knowledge of geochemical baseline concentrations of elements. Frequently erroneous conclusions are drawn about soil pollution with metals because the baseline information does not exist.

In the Thrace region, situated in the northwestern part of Turkey, geochemical baseline concentrations in soil are lacking not only for most of the commonly discussed heavy metals but also for most other trace elements. This region is one of the most important agricultural areas of Turkey and has very fertile soils. The organic matter content of the topsoil is normally low. Intensive use of the region for agriculture, strong increase of the population in connection with industrialization, and opening the farmlands to urbanization means a high risk of polluting the soil with heavy metals and other harmful substances. The region also has highways with dense automobile traffic, and many industrial enterprises are located in this region. Lack of strict application of environmental protection legislation, need for better control of the pollution situation and absence of basic data about heavy metal pollution in the region was the background for the present work. The work is intended to be a base for future investigations of activities leading to temporary changes in concentrations of elements in Thrace region soil.

Distribution maps produced will help to clarify the situation in the region with respect to heavy metal level.

EXPERIMENTAL

The region, which has an area of 24 000 km², was divided into 20 × 20 km square grids and topsoil (the uppermost 10 cm) was collected within each square at 73 sites in September 2001 (Fig. 1). All samples were collected at least 300 meters away from highways and 50 meters away from the other roads.

Open, uncultivated and flat areas of land were chosen. The region has three main types of soil (GDRS data): these are eutric vertisol (covers the greatest part of the region), mollic fulvisol, and rendzic leptosol (Fig. 2) [12].

Fig. 1. Sampling region and sampling sites

Samples were collected using plastic tools and stored in plastic bags. All samples were dried and passed through a 2-mm sieve. Aliquots of about 0.4 g were digested with 5 ml 65% HNO₃ in a microwave digestion system for the determination of the HNO₃-soluble fraction of heavy metals.

The concentrations of Pb, As, and Cd were determined by means of a graphite furnace atomic absorption spectrometry (Perkin Elmer AA-600) with an automatic sample changer (AS-800). A NH₄H₂PO₄ + Mg₂O₃ mixture for the determination of Cd and Pb, and PdNO₃ for the determination of As were used as matrix modifiers. Cu, Zn, and Ni were determined using flame atomic absorption spectrometry (Perkin Elmer 1100B). Accuracy was checked by analysis of reference material from National Institute of Standards and Technology (NIST 2709 San Joaquin Soil). In the case of As, Pb and Cd, the reference material SpS-Sw2 Batch 108 (Spectra pure Standards AS) was used in addition to the soil reference material. Running of blanks was done to check possible contamination of sample extracts. All blanks, one for every five sample, were prepared at the same time and the same conditions as for the samples. About 20% of the samples were analyzed in replicate for the control of total variation in sampling, analysis, and extraction

of the sample. Good agreements between results of replicates were observed ($p < 0.01$). Sample solutions were run in triplicate. The relative deviation (RSD) between the three parallel measurements was normally less than 5%. Contents of the other 29 elements were determined using Epithermal Neutron Activation Analysis (ENAA) as described elsewhere [12].

SPSS 10 for Windows was used for principal component analysis. Geographic Information System (GIS) technology was used for constructing the distribution maps of elements concentration over the area. Surfer 6.0 software with kriging algorithm was used to interpolate the data.

Fig. 2. Soil composition of Thrace region (from GDRS)

RESULTS AND DISCUSSION

Descriptive statistics for some elements were given in Table 1, along with World median values for the same elements estimated by Bowen [14]. In Table 2, the present results for Cu, Zn, Ni, Cd, Cr, Pb, and As were compared with international reference values for soils [15]. Results from VARIMAX principal component analysis (PCA) were listed in Table 3. Spatial distributions of elements were plotted according to their concentrations (Fig. 3).

The present maximum values of all elements in Table 2 except Pb, Cd and Cu are lower than the maximum value of normal range values of natural soils cited by the EEA report. However, the same values of As, Cd, Cr, Cu, Ni, Pb and Zn exceed the Dutch standard values (normal level in good soil) for these elements. On the other hand, median values of all these elements are below the Dutch standard values for good soil but the maximum values of Cr, Cu, Ni and Pb are higher than the maximum allowable levels of Dutch standard values. These

Table 1. Descriptive statistics for heavy metals studied in this work (mg/kg)

	Mean	Median	Range	World median*
As	8	7	1.9–51	6
Ba	550	490	240–1160	500
Br	8	6	0.1–30	10
Ca	30700	16100	1750–164700	15000
Cd	0.2	0.1	0.03–1.7	0.35
Ce	69	64	30–150	50
Co	11	10	1.5–27	8
Cr	173	93	20–830	70
Cs	4.0	3.4	1.4–12.8	4
Cu	20	16	1.8–167	30
Eu	0.8	0.8	0.2–1.6	1
Fe	26900	27100	5800–55400	40000
Hf	5.4	5.0	2.2–10	6
I	8.5	8.0	2.2–22	5
In	0.4	0.4	0.09–0.7	1
K	20100	19100	8700–46700	14000
La	26	25	11.5–59.7	40
Mn	600	467	62–3760	1000
Mo	0.6	0.5	0.08–4.6	1.2
Na	7800	7700	1400–21700	5000
Nd	24	23	12–5	035
Ni	50	36	2.6–249	50
Pb	33	19	4.8–968	35 (12**)
Rb	93	89	35.5–186	150
Sb	0.9	0.6	0.2–6.7	1
Sc	10	10	3.5–20	7
Sm	5.6	5.4	2–13	4.5
Sr	178	149	44–543	250
Ta	1.2	1.0	0.4–2.2	2
Tb	0.8	0.7	0.3–1.4	0.7
Th	9	9	4–24	9
Ti	3700	3800	1500–6800	5000
U	2.6	2.3	1.3–5.5	2
V	78	80	18.6–170	90
Zn	45	45	6–165	90
*Values from Bowen (1979).				
**Prior to global contamination.				

results showed that there had been pollution of these elements in some sampling points where the maximum values obtained were more than the Dutch maximum allowable values.

Table 2. Normal range of heavy metals in natural soil and Dutch value for good soil quality (mg/kg) from EEA 1999 report [15]

	Range in natural soil*	Normal level in good soil (Dutch standard)*	B value (maximum allowable level)**	C value (needs soil decontamination measures)**	Present study (range)	Present study (median value)
As	1–50	29			1.9–51	7
Cd	0.01–0.70	0.8	5	20	0.03–1.7	0.1
Cr	1–1000	100	250	800	20–830	93
Cu	2–100	36	100	500	1.8–167	16
Ni	7–4.280	35	100	500	2.6–249	36
Pb	2–200	85	150	600	4.8–968	19
Zn	10–300	140	500	3000	6–165	45
*Source: International Ash Working Group, 1997; Lame and Leenaers, 1998.						
**From Dutch standard-1988, quoted by Ewers, 1991 and Lacatusu, 1998 [16].						

The results obtained in this work are also compared with similar data for Izmit Gulf surface soil [17]. The two sets of data show good agreement for rural soil. Yilmaz et al.'s mean values for Cu, Zn and Pb were 21, 56 and 16 ppm, respectively, whereas our median values for Cu, Zn and Pb are 16.2, 44.5 and 18.9, respectively. The present median values also show close agreement in most cases with world median values for soil (Bowen, 1979). The highest values of the metals shown in Table 2 were observed in areas near to Istanbul. The lead maximum value is nearly five times higher than EEA maximum value of normal range for natural soil and eleven times higher than Dutch value for good soil. The chief sources are presumably intensive vehicle traffic and various industrial activities in the Istanbul region. The above results show that there are some areas in Thrace region that are polluted with heavy metals to undesirable levels. In the following the observed results for the above seven elements are discussed in relations to the distribution maps in Fig. 3.

As

The highest values of As are observed in samples from the Istanbul district and from areas near the Bulgarian border. However, the obtained concentrations of As are between the limitation values of EEA for natural soil value (Table 2).

Cd

The greater part of Thrace region seems not to be polluted with Cd, except in the vicinity of Istanbul and near the Bulgarian border, where Cd concentrations are the highest.

Table 3. Results of principal component analysis

Rotated Matrix Component					
% of Variance	1	2	3	4	5
	21.7 %	19.1 %	12.0 %	8.3 %	6.3 %
As	0.153	0.088	0.861	0.132	-0.103
Ba	0.141	-0.209	-0.249	-0.321	0.767
Br	0.448	0.173	0.198	0.601	-0.039
Ca	-0.144	0.293	0.539	0.248	0.182
Cd	0.497	-0.052	0.499	0.306	-0.072
Ce	0.917	0.163	0.091	0.118	0.100
Co	0.304	0.759	0.056	0.305	-0.090
Cr	-0.142	0.576	-0.261	0.317	0.015
Cs	0.469	0.542	0.215	0.113	0.158
Cu	-0.111	0.294	0.846	0.152	0.039
Eu	0.687	0.387	-0.063	0.142	0.173
Fe	0.321	0.848	0.156	0.188	0.034
Hf	0.364	-0.290	-0.353	-0.064	0.021
I	0.318	0.220	0.164	0.670	0.016
In	0.054	-0.112	0.279	-0.036	0.430
K	0.081	-0.158	-0.141	-0.707	0.504
La	0.927	0.141	0.092	-0.029	-0.027
Mn	0.617	0.217	0.145	0.026	-0.004
Mo	0.292	0.086	0.455	-0.159	-0.058
Na	-0.180	0.143	-0.349	-0.665	0.098
Nd	0.791	0.234	0.020	0.234	0.148
Ni	-0.133	0.793	-0.049	0.270	-0.083
Pb	-0.215	-0.039	0.676	0.127	0.161
Rb	0.422	-0.008	-0.103	-0.252	0.755
Sb	0.208	0.011	0.863	0.080	-0.104
Sc	0.338	0.893	0.110	0.013	0.036
Sm	0.882	0.245	0.052	-0.055	-0.038
Sr	-0.191	0.206	0.010	0.222	0.561
Ta	0.747	0.121	-0.030	-0.044	-0.089
Tb	0.737	0.460	-0.009	0.218	0.084
Th	0.713	0.221	0.013	0.144	0.392
Ti	0.382	0.786	0.102	-0.048	-0.223
U	0.650	0.092	0.184	-0.509	-0.011
V	0.291	0.815	0.239	0.015	-0.187
Zn	0.416	0.568	0.463	0.280	0.082
Extraction Method: Principal Component Analysis. Rotation Method: VARIMAX with Kaiser Normalization. Rotation converged in 12 iterations.

Fig. 3, a

Fig. 3, b

Fig. 3, c

Fig. 3, d

Fig. 3, *e*

Fig. 3, *f*

Fig. 3, g. Spatial distribution of heavy metals in Thrace region (*a* — As; *b* — Cd; *c* — Cr; *d* — Cu; *e* — Ni; *f* — Pb; *g* — Zn)

Cr

Cr concentrations in the northern part of the region are lower than in the southern part and all obtained values are not outstanding than given values for world average. This difference may be explained by the fact that the two regions have different soil types. The south part is mainly covered by eutric vertisol (Fig. 2) and the distributions of Cr and this soil type match each other.

Cu

The greater part of the region has low levels of Cu, except the Istanbul area and the area near to the Bulgarian border. The highest single value is observed in Istanbul area, probably due to polluting activities in the metropolitan area. Another high value near the Bulgarian border is difficult to explain by any activity on the Turkish side, and may originate from transboundary pollution.

Pb

Severe pollution is observed near to Istanbul and at two local points near the borders to Bulgaria and Greece. The greater part of the region however appears not to be appreciably polluted. The highest value of Pb is evident in samples from Istanbul, nearly five times higher than the accepted maximum value for natural soil (Table 2).

Ni

The southwest part of the region shows higher levels than the northern part. The distribution pattern of Ni is similar to those of Cr and eutric vertisol soils, and it seems that it is mainly of natural origin.

Zn

Slight Zn pollution is evident in the vicinity of Istanbul and near the Bulgarian border. The greater part of the region appears not to be polluted. The PCA defines a component matrix consisting of five different factors, which are interpreted as follows: F1 (Ce, Eu, La, Mn, Nd, Sm, Ta, Tb, Th, and U) represents one lithogenic component. The distribution pattern of F1 shows no relation with settlement areas. F2 (Co, Cr, Cs, Fe, Ni, Ti, Zn) could reflect a combination of industrial pollution and a lithogenic component, but may as well be entirely lithogenic.

All elements associated with F3 (As, Ca, Cd, Cu, Pb, Sb) indicate pollution from industries and other anthropogenic activities. F4 (Br, I, K, Na) may indicate contribution to the soils from the atmospheric deposition of marine salts. F5 (Ba, Rb, Sr) is interpreted as an additional lithogenic component. These results are similar to corresponding interpretations of top-soil heavy metal data from the literature [10, 18].

It should be emphasized that there is a lack of data for the natural concentrations of most of these elements in the bedrock and underground soils in Thrace. It is therefore fully possible that values that would be defined as pollution in other regions simply represent the natural background. As indicated above that could clearly be possible in the cases of Cr and Ni, where there are no particular air pollution sources that could explain the apparently high values in the south. That however does not eliminate the need for further studies in order to see if the high levels of the metals in question are yielding similarly high levels in agricultural crops. Even if the reason for the high levels encountered is natural, it may be that crops absorb these metals to high levels.

CONCLUSIONS

The PCA and the measured results show that surface soils in the Thrace region are polluted to a certain extent with several of the metals studied in this work. This situation is also obvious from the distribution maps shown for some of the elements. The heavy metal pollution is particularly pronounced in areas near Istanbul, but we are not aware of any scientific studies so far showing harmful effects of this pollution on the human population or other biological species. However, large amounts of crops, especially vegetables, are harvested from gardens and farmlands near to Istanbul and served to people living in the

city. Because of this, it is necessary to determine the levels of heavy metals in soil and apply strict rules regulating the use of soils for agriculture and other purposes. The degree of soil pollution around the city of Istanbul may indicate a risk for human health also in connection with pollution of fresh watersources supplying the city with drinking water. Further studies should be carried out in all areas where excessive levels are shown in the surface soils, even if the reason is a high natural content, in order to see to what extent agricultural crops growing on these soils have metal concentrations within acceptable levels.

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