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Atmospheric Deposition of Heavy Metals in Thrace Studied by Analysis of Moss (*Hypnum cupressiforme*)

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This work is the first systematic study of atmospheric heavy metal deposition in the Thrace region of Turkey. This region, which is the part of Turkey closest to Europe, is important for supplying agricultural products for Turkey. At the same time it is under the influence of pollution from big cities such as Istanbul and Tekirdağ. Using the moss biomonitoring technique impacts of local pollution sources as well as possible transboundary contributions were studied in this most heavily industrialized and densely populated region of Turkey. The moss biomonitoring technique has several advantages compared to traditional techniques to study atmospheric deposition of heavy metals. It is simple, cheap, and allows a great number of samples to be studied simultaneously. Because of these advantages the moss biomonitoring technique has been used for over 30 years for this purpose (Ruhling and Tyler, 1971; Steinnes, 1977; Schaug et al., 1990). Recently the moss technique has been introduced for large scale studies of atmospheric deposition of metals in a number of new countries (*e.g.* Lucaciu et al., 1999; Ceburnis et al., 1999; Grodzinska et al., 1999; Galsomies et al., 1999; Gerdol et al., 2000; Faus-Kessler et al., 2001) and the results are summarized in the European Atlas edited under the auspices of the UNECE ICP Vegetation (Buse et al.). In Turkey however this approach has not been used before, apart from some local studies along roadsides and in the vicinity of industrial facilities (Ölmez et al., 1985; Eğilli et al., 2003).

The aim of this work was threefold (i) to determine the geographical distribution of atmospheric heavy metal pollution in the Thrace; (ii) to identify the type and sources of pollutants; (iii) to determine the possible relationship between altitude and heavy metal deposition.

MATERIALS AND METHODS

The surface area of the Turkish part of the Thrace region is 23 764 km^2. This territory was divided into a 20x20 km grid and moss samples, 67 in all, were collected randomly within each square (Figure 1). All samples were collected within a 50x50 m area at each site, and all sites were selected at least 300 m away from highways and 100 m from other roads. *Hypnum cupressiforme* was chosen as

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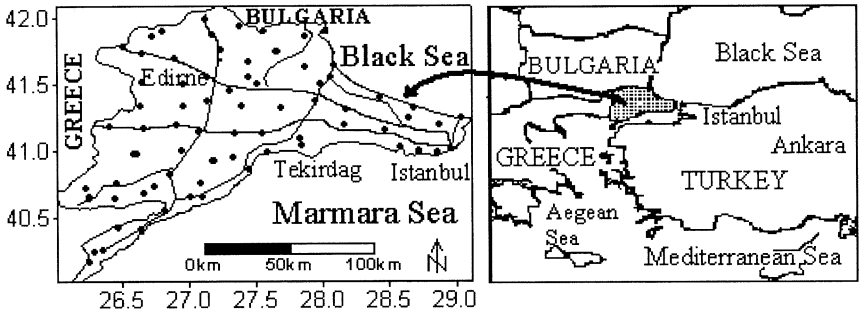

Figure 1. Sampling sites in the Thrace region.

target species since it is abundant in this region. The moss was collected at least 5 m away from big trees to avoid canopy effects and stored in plastic bags. The sampling took place in September 2001, and geographic coordinates and altitude were registered at each sampling site.

Samples were cleaned from extraneous material, then dried in oven at 40^0C to constant weight, and kept at dry laboratory conditions until chemical analysis. The green and yellowish green part of the moss was used for analysis. The manual separation of moss from other material resulted in a certain mixing of the samples, and further homogenisation was not deemed necessary. A microwave digestion system (Perkin Elmer, Microwave Sample Preparation System) was used for the decomposition of samples in 14.5M HNO_3 (65%, Merck). 0.4g dry sample was put into a Teflon® tube, 4 ml HNO_3 were added and the mixture was digested at 230^0C for 35 minutes. After cooling the digested samples were filtered through S&S black ribbon filter, and made up to volume with distilled water to make a 2.3M HNO_3 solution. The concentrations of Cu, Zn, and Ni in the extract were determined by flame atomic absorption spectrometry (Perkin Elmer 1100B). Concentrations of As, Cd and Pb were determined using graphite furnace atomic absorption spectrometry (Perkin Elmer AA-600). A $NH_4H_2PO_4$+$Mg(NO_3)_2$ mixture was used as matrix modifier for the determination of Cd and Pb, and $PdNO_3$ for the determination of As. Accuracy was checked by analysis of reference material from National Institute of Standards and Technology (NIST 1575 Pine needles). Blanks (one for every 5 samples) were prepared at the same time and same conditions as the samples to control possible contamination during the preparation of sample extracts. About 20% of the samples were analysed in duplicate for the control of total variation in sampling, decomposition, and analysis. Good agreement between results of duplicates was observed. Observed correlation coefficients between duplicates for Cd, Pb, Cu, Zn, As, Ni and Mn were 0.80, 0.99, 0.95, 0.95, 0.95, 0.97 and 0.90 respectively ($p< 0.01$). Concentrations in sample solutions were measured in triplicate. The relative deviation (RSD) between the three parallel measurements was less than 5%. The concentrations of additional 34 elements were determined by neutron activation

analysis (NAA) at the IBR-2 reactor in Dubna, Russia. Moss samples of about 0.3 g were irradiated in a Cd-screened channel in order to determine elements associated with long lived isotopes and in a thermal channel to determine elements associated with short lived isotopes. Data processing was performed using standard methods. The details of analysis are described elsewhere (Frontasyeva et al., 1994). SPSS 11.0 for Windows was used for the data analysis. Geographic Information System technology was used for constructing maps of the distribution of element concentration over the investigated area. This technology is increasingly used in environmental pollution studies especially for the determination of non-point sources of contamination (Facchinelli et al., 2001)

RESULTS AND DISCUSSION

Descriptive statistics and correlation coefficients for the elements (Table 1) and results from principal component analysis of the data (Table 2) are presented, with high values in bold. Geographical distributions of Pb, Cu, Zn, Cd, As, Ni, Sb and W in the Thrace region are shown in Figure 2. The highest values of Pb, Cu, Zn, Cd, Sb and W were observed in the vicinity of the big cities Istanbul and Tekirdag. Maximum concentrations of these elements are 239, 84, 133, 1.3, 4.0 and 16.9 $mg \cdot kg^{-1}$ dry weight, respectively, which are the highest observed in the whole series. Away from the cities the concentrations of these elements gradually decrease to background values. As and Ni show distribution patterns different from those of the above elements. It seems that there are other factors or sources that affect the distribution of these elements.

Table 1. Descriptive statistic and correlation coefficient for some elements (number of samples, n=67).

	Cu	Zn	Ni	Cd	Sb	Pb	As	W
Cu	1							
Zn	0.82	1.00						
Ni	0.21	0.30	1.00					
Cd	0.77	0.60	-0.05	1.00				
Sb	0.65	0.76	0.25	0.36	1.00			
Pb	0.94	0.74	0.08	0.81	0.49	1.00		
As	0.07	0.14	0.23	-0.02	0.35	0.00	1.00	
W	0.77	0.52	0.09	0.67	0.37	0.80	0.12	1.00
Median	7.76	30.97	6.61	0.19	0.20	9.71	1.29	1.22
Minimum	4.54	17.26	2.56	0.10	0.10	3.50	0.51	0.46
Maximum	83.82	133.01	37.75	1.31	4.03	239.41	42.05	16.94

Distribution patterns of Pb, Cu, Zn, Cd, Sb and W are nearly the same but Cu shows a difference near to the Bulgarian border. It is known that there are no major pollution sources for Cu on the Turkish side of the border, and sources of this pollution are therefore probably on the Bulgarian side.

Table 2. VARIMAX rotated principal components of *Hypnum cupressiforme* samples.

Rotated Component Matrix	Components					
	1	2	3	4	5	6
% of Variance	% 44.5	% 11.2	%7.3	%6.9	%6.3	%4.4
Al	**0.816**	-0.027	0.234	0.329	-	-0.043
As	-0.019	-0.037	-	0.081	**0.888**	-0.040
Ba	**0.834**	-0.022	0.134	-	0.054	-0.018
Br	0.413	0.260	**0.689**	0.073	0.081	0.110
Ca	0.265	0.173	**0.613**	0.333	0.119	-0.342
Cd	-0.107	**0.868**	0.009	-	-	0.124
Ce	**0.965**	-0.051	0.049	-	-	0.021
Cl	-0.151	0.252	**0.452**	-	0.039	-0.344
Co	**0.756**	0.082	0.129	**0.526**	0.136	0.126
Cr	**0.745**	-0.004	0.000	**0.494**	-	0.060
Cs	**0.825**	-0.014	0.386	0.073	0.108	0.001
Cu	0.029	**0.951**	0.137	0.085	0.135	-0.055
Eu	**0.808**	0.077	0.013	-	0.136	0.011
Fe	**0.859**	0.026	0.171	0.388	0.135	0.087
Hf	**0.909**	-0.034	0.001	0.152	-	0.094
I	0.275	0.060	**0.830**	0.057	-	0.174
K	0.433	0.132	0.211	-	0.202	-0.582
La	**0.963**	0.042	0.132	-	0.038	-0.011
Mg	**0.671**	-0.002	0.320	**0.494**	-	-0.101
Mn	0.146	-0.027	0.031	-	-	**0.826**
Mo	0.072	0.296	0.096	0.054	**0.902**	-0.124
Na	**0.883**	-0.002	-	0.266	-	-0.047
Nd	**0.888**	-0.009	0.207	0.112	0.041	0.053
Ni	0.418	0.108	0.032	**0.754**	0.216	-0.002
Pb	-0.072	**0.958**	0.045	0.038	-	-0.034
Rb	**0.816**	-0.105	0.322	-	0.084	-0.093
Sb	0.074	**0.549**	0.255	0.074	**0.576**	0.050
Sc	**0.880**	0.045	0.134	0.348	0.075	0.103
Se	0.285	0.319	0.191	-	0.187	**0.505**
Sm	**0.932**	0.058	0.032	-	0.096	0.060
Sr	**0.579**	-0.075	0.362	0.090	0.130	-0.323
Ta	**0.852**	-0.006	0.140	0.275	-	0.052
Tb	**0.930**	0.020	0.074	0.090	0.111	0.082
Th	**0.925**	-0.052	0.183	-	-	-0.117
Ti	**0.693**	-0.010	0.295	**0.482**	-	0.038
U	**0.809**	0.048	0.111	0.075	0.452	-0.045
V	0.452	0.171	0.354	0.490	0.214	-0.115
W	-0.041	0.832	-	0.034	0.040	-0.062
Yb	**0.938**	0.032	0.071	0.148	0.021	0.067
Zn	0.095	**0.771**	0.329	0.131	0.287	-0.043
Zr	**0.915**	-0.052	0.019	0.162	-	0.090

Extraction Method: Principal Component Analysis. Rotation Method: Varimax with Kaiser Normalization. Rotation converged in 8 iterations.

Interpretations of the distribution of elements and their sources in the region became clearer when correlation coefficients, PCA results and distribution maps were compared. Correlation analysis (Pearson correlation, 2-tailed) shows that

high positive correlations are evident between Cu-Cd, Cu-Pb, Cu-Zn, Cu-Sb Cu-W, Zn-Pb, Zn-Cd, Zn-Sb, Zn-W, Cd-Pb, Cd-W and Pb-W (Table 1).

This situation also can be seen in PCA results. These six elements (Cu, Cd, Pb, Zn, Sb, and W) are involved in the same factor (Factor 2) which typically represents atmospheric pollution. Factor 1 (Al, Ba, Ce, Co, Cr, Cs, Eu, Fe, Hf, La, Mg, Na, Nd, Rb, Sc, Sm, Sr, Ta, Tb, Th, Ti, U, Yb, Zr) most probably indicates soil particles trapped in the moss, whereas F3 (Br, Ca, Cl, I) indicates a marine contribution. F4 (Co, Cr, Mg, Ni, Ti) might be a second pollution factor, but it seems more likely that it is an additional soil factor from areas dominated by mafic/ultramafic rocks. F5 (As, Mo, Sb) on the other hand, is likely to represent a second pollution factor. F6 (K, Mn, Se) probably represents interference from leaching of higher plants (Steinnes, 1993). These factors are similar to those from previous studies using the moss biomonitoring technique (Schaug et al., 1990; Berg & Steinnes, 1997; Faus-Kessler et al., 2001).

The only previous data for heavy metal concentrations in moss in the Thrace region are those of Egilli et al. (2003). Their mean concentrations for Mn, Cr, Co, Zn, As, Se, and Sb are 1088, 21.7, 5.0, 189, 5.8, 2.5, and 0.6 ppm, respectively, whereas the corresponding values from the present work are 163, 17.9, 2.2, 40.3, 1.69, 2.8 and 0.3. Except for Cr and Se the levels reported by Eğilli et al are thus substantially higher than those observed in the present work. The reason for these differences may be that the sampling strategy and the number of samples were different in the two investigations. Whereas the purpose of the present work was to study the regional patterns of metal deposition and a network of 67 sites was used for this purpose, Eğilli et al. reported data only from four sites, one of which located in the urban area of Istanbul.

The concentrations of rare earth elements are very high in Thrace region moss when compared e.g. with the work of Berg & Steinnes (1997). This difference with moss samples from northern Europe has also been observed in other investigations from the Balkan region (e.g. Lucaciu et al., 1999). On the other hand, the concentrations of elements mainly of anthropogenic origin such as Cd, Pb, W, and Zn are similar to those of Berg & Steinnes (1997).

The geographic distribution maps indicate that Cu, Zn, Pb, Cd, Sb and W seem to have the same origin and same distribution patterns in the region (Figure 2). Distribution maps and PCA indicate that these pollutants have atmospheric sources, but they seem to be located in the vicinity of big cities rather than being associated with transboundary pollution. The distribution patterns of As and Ni in the region are different from that of the other elements, and may possibly be related to agricultural activities or to traffic (cf. Gerdol et al., 2000) since the southern part of Thrace has a higher traffic density and agricultural activity than the northern part which is characterized by mountains and forest. Arsenic pollution may also arise from other sources such as the use of coal for heating and

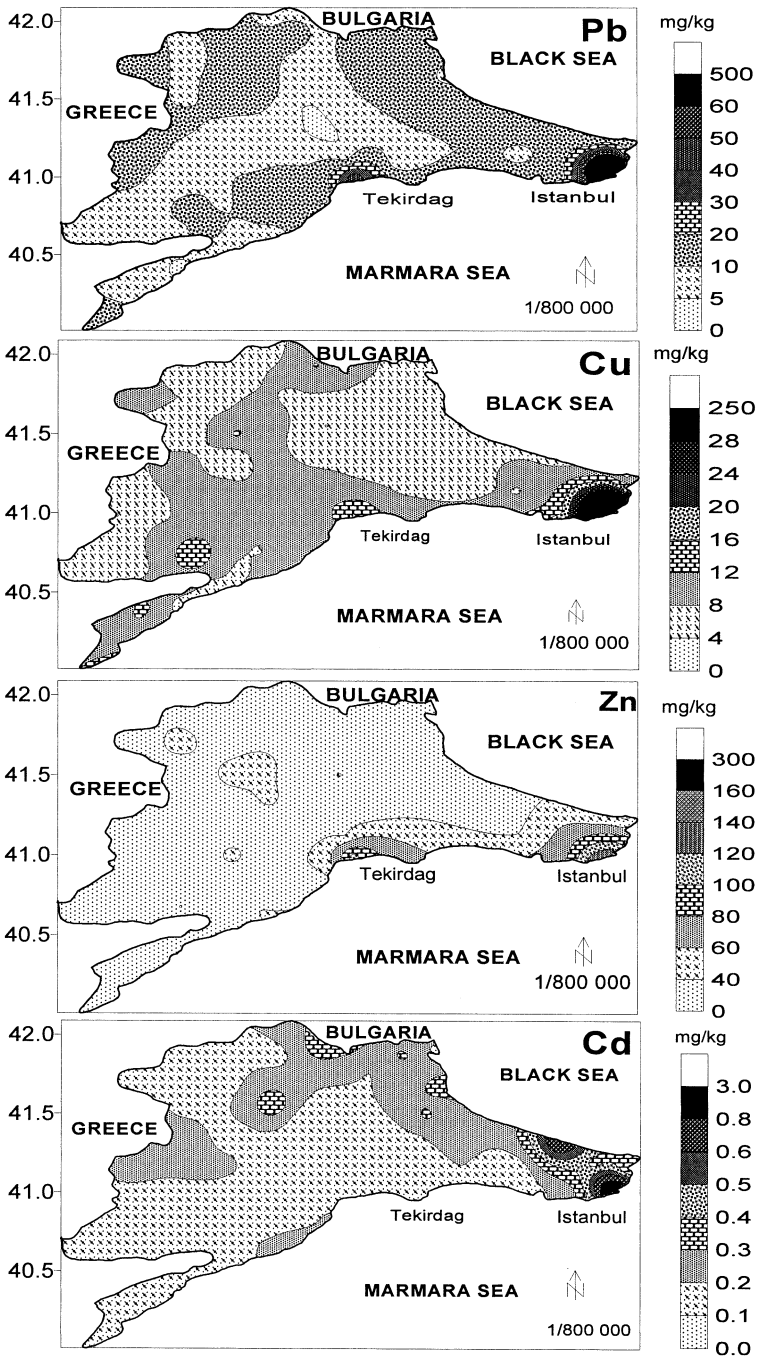

Figure 2. Geographical distribution of Pb, Cu, Zn, Cd, As, Ni, Sb and W in the Thrace region.

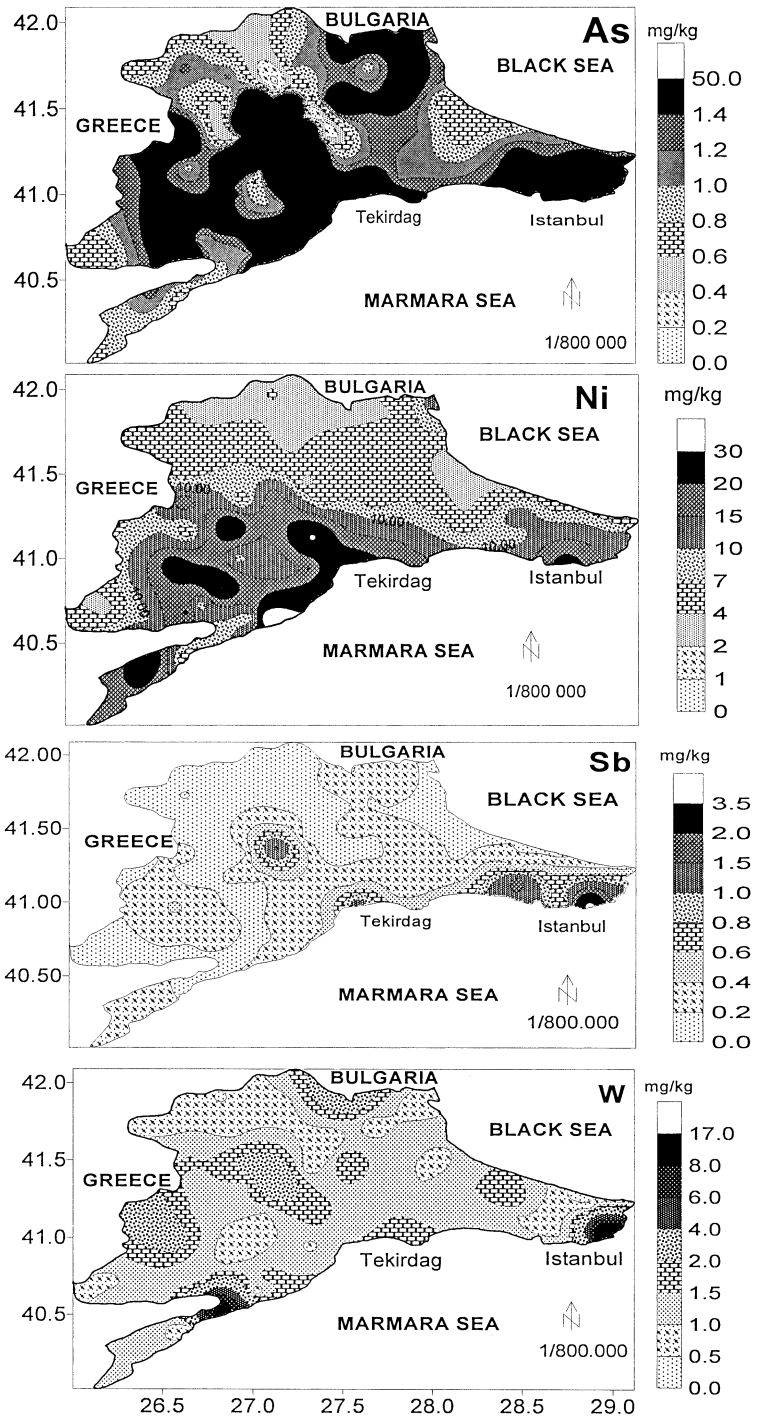

Figure 2 (Continued)

incineration plants. There are two big glass factories in the Thrace region and according to Ruhling et al. (1996) glass industry is another source of As pollution. In some investigations employing the moss monitoring technique the concentrations of some elements in moss were found to vary with altitude (Zechmeister, 1995). In this work no such relationship between moss heavy metal content and altitude was found for any element. This is in accordance with the results of Bargagli et al. (2002). The Thrace region is generally flat and the highest altitude is only 552 m, which may explain the lack of connections with altitude.

The main result of this pilot study employing the moss biomonitoring technique in Thrace appears to be that except for the metropolitan areas of Istanbul and Tekirdağ the general level of atmospheric deposition in Thrace is relatively low for most toxic metals.

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