Bull. Environ. Contam. Toxicol. (2006) 76:320–326

DOI: 10.1007/s00128-006-0924-z

Bulletin of Environmental Contamination and Toxicology

Atmospheric Deposition of Heavy Metals in Thrace Studied by Analysis of Austrian Pine (*Pinus nigra*) Needles

M. Coşkun

Canakkale Onsekiz Mart University, College for Health Services, 17100 Canakkale, Turkey

Received: 29 August 2005/Accepted: 29 November 2005

Thrace is a well-developed region in north-west Turkey where industrial and agricultural activity has led to an increase in environmental pollution. Among the various pollutants, heavy metals are of special significance because of their long residual presence in the environment and toxic effect on the biota. In order to determine the amount of pollution caused and protect the biota, a variety of monitoring methods have been developed. One of these is the biomonitoring method, used for monitoring air, soil, and water pollution. For this purpose, different biological materials such as moss, lichen, bark, and animals are used for the biomonitoring of heavy metal pollution. Some bioindicators, depending on their abundance and extent of geographical distribution, are suitable for indicating the pollution of several heavy metals in the environment.

Among plant species, the pine tree is distributed over a wide area and is more resistant to some pollutants (e.g. acid rain, heavy metals) than other species, such as moss and lichen. Due to its root system, however, it is difficult to identify whether the source of accumulated heavy metal comes from air in the atmosphere or the soil. In spite of this, parts of the tree such as the bark and needles may be used as bioindicators of atmospheric air pollution. Many studies have previously been carried out with this purpose in different parts of the world (Dmuchowski et al., 1995; Rautio et al., 1998).

The aim of this study was to assess possible atmospheric heavy metal pollution in Thrace using pine needles, and to discuss the suitability of pine needles as a bioindicator of atmospheric heavy metal pollution in this region.

MATERIALS AND METHODS

The Turkish part of Thrace has a surface area of 24.000 km^2. For the purpose of the present study, the area was divided into a 20x20 km grid and pine needle samples, 34 in all, were collected randomly within each square (Figure 1). Pine branches were collected at least 300 meters away from highways and 100 meters from other roads, and stored in plastic bags. The sampling took place in September 2001. Geographic coordinates were registered at each sampling site.

Correspondence to: M. Coşkun

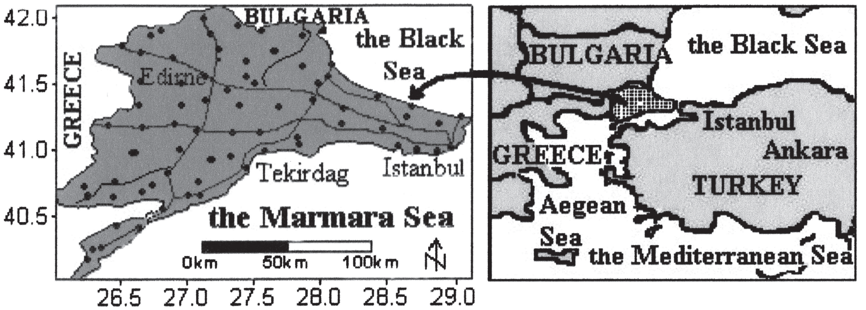

Figure 1. Sampling sites in Thrace region.

In the laboratory, new needles (the latest year) were separated from old ones and treated separately. All samples were dried in an oven at 40^0C to constant weight, and kept under dry laboratory conditions until chemical analysis. Before chemical analysis, the needle samples were crushed in plastic bags using a wooden hammer to obtain homogeneity. A microwave digestion system (Perkin Elmer, Microwave Sample Preparation System) was used for the decomposition of samples in 14.5M HNO_3 (65%, Merck). A 0.4g dry sample was put into a teflon tube, 4 ml HNO_3 was added, and the mixture was digested. After cooling, the digested samples were filtered through an 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 Mn in the extract were determined by flame atomic absorption spectrometry (Perkin Elmer 1100B). The 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 obtained from the National Institute of Standards and Technology (NIST 1575 Pine needles). Blanks (one for every 5 samples) were prepared at the same time and under the same conditions as the samples to check possible contamination during preparation of sample extracts. Approximately 20% of the samples were analyzed in duplicate to check the total variation in sampling, decomposition, and analysis. Good agreement between the results of duplicates was observed. Observed correlation coefficients between duplicates for Cd, Pb, Cu, Zn, As, and Mn were 0.98, 0.97, 0.98, 0.97, 0.97, and 0.99 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%. SPSS 11.0 for Windows was used for the data analysis. Geographic Information System technology was used to construct maps showing the distribution of element concentration over the investigated area.

Descriptive statistics and correlation coefficients for the elements are presented in Table 1. The geographical distribution of Pb, Cu, Zn, Cd, As, and Mn in the Thrace region are shown in Figure 2. The highest values of Pb, Cu, Zn, and As in new and old needles were observed near the large cities of Istanbul and Tekirdag.

Table 1. Descriptive statistic and correlation coefficient for selected elements in Austrian pine needles (*Pinus nigra*) (n=34, new needles' values in parenthesis).

	Cu	Zn	Cd	Mn	Pb	As
Mean	3.43 (3.49)	22.3 (23.1)	0.07 (0.08)	123.2 (132)	2.56 (1.60)	0.39 (0.18)
Median	2.81 (3.43)	20.9 (22.9)	0.05 (0.05)	58.0 (46.7)	1.56 (1.26)	0.32 (0.15)
Minimum	1.55 (0.50)	8.69 (11.8)	0.01 (0.02)	9.23 (15.1)	0.30 (0.22)	0.01 (0.02)
Maximum	10.2 (7.26)	54.3 (45.9)	0.24 (0.68)	628.7 (2278)	12.5 (5.27)	1.70 (0.77)
Confidence Interval (95 %)	0.63 (0.39)	3.65 (2.90)	0.02 (0.04)	51.67 (133.7)	0.87 (0.46)	0.10 (0.06)
Cu	1					
Zn	0.32(0.21)	1				
Cd	0.20(0.18)	0.02(**0.41**)	1			
Mn	0.06(0.11)	0.04(**0.48**)	**0.68**(**0.91**)	1		
Pb	**0.80**(0.21)	0.22(0.31)	0.08(0.23)	0.21(0.34)	1	
As	**0.45**(**0.47**)	0.06(0.12)	0.01(0.02)	0.29(0.03)	**0.61**(0.26)	1

RESULTS AND DISCUSSION

Away from the cities, concentration of these elements gradually decreases. Maximum concentrations of these elements are 5.27, 7.26, 45.9, 0.68, 0.77, and 2278 $mg \cdot kg^{-1}$ dry weight in new needles, and 12.5, 10.2, 54.3, 0.24, 1.70, and 682 in old needles respectively, which are the highest values observed in the whole series. The differences of mean value of metals in new and old needles, except As, are not significant statically ($p>0.05$). Similar findings were reported by other authors (Tausz et al., 2005). In another work, Rautio et al. (2003) reported that the difference between new and old needles is high in a highly polluted area, but this difference gradually decreases away from the pollution source. This result indicates that it is not possible to show the long-term change in pollution in the region using pine needles. The difference of As concentration between new and old needles is significant ($p<0.05$), except that it is not possible to say whether this difference comes from atmospheric pollution or the soil, or from the difference of metabolic activities between new and old needles. Observed correlation coefficients (Pearson correlation, 2-tailed) for the same elements, Pb, Cu, Zn, Cd, As, and Mn, in new and old needles are 0.47, 0.54, 0.71, 0.60, 0.51, and 0.63 respectively. These positive correlations indicate that new and old needles can be used for monitoring of pollution; however, Blanuša et al. (1999) reported that old needles are more suitable bioindicators than new needles. When we compare our maximum values for all elements with Gratton's (2000) results, these values match the polluted areas. However, when we compare the mean values in the current study, they match the control area (unpolluted area) values.

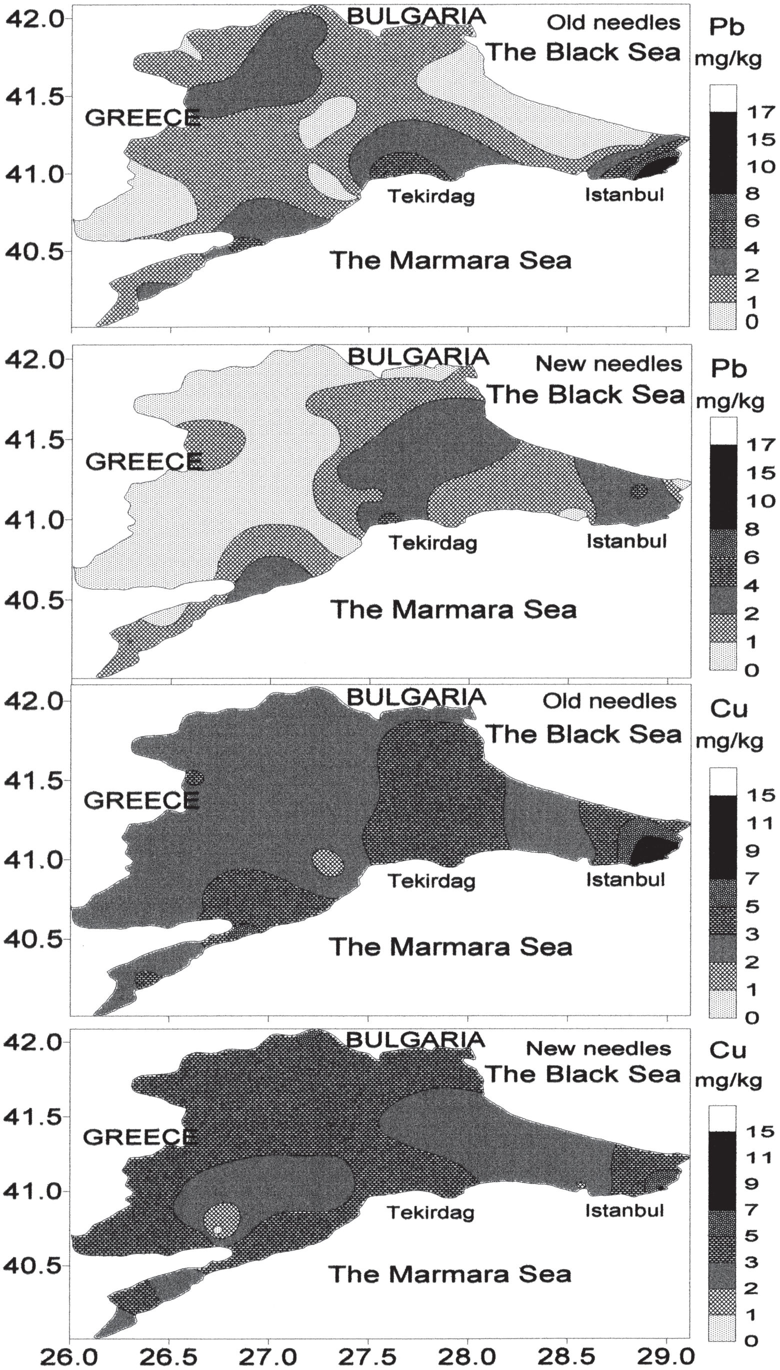

Figure 2. Geographical distribution of Pb, Cu, Zn, As, Cd, and Mn in Austrian pine needle (*Pinus nigra*) in the Thrace region.

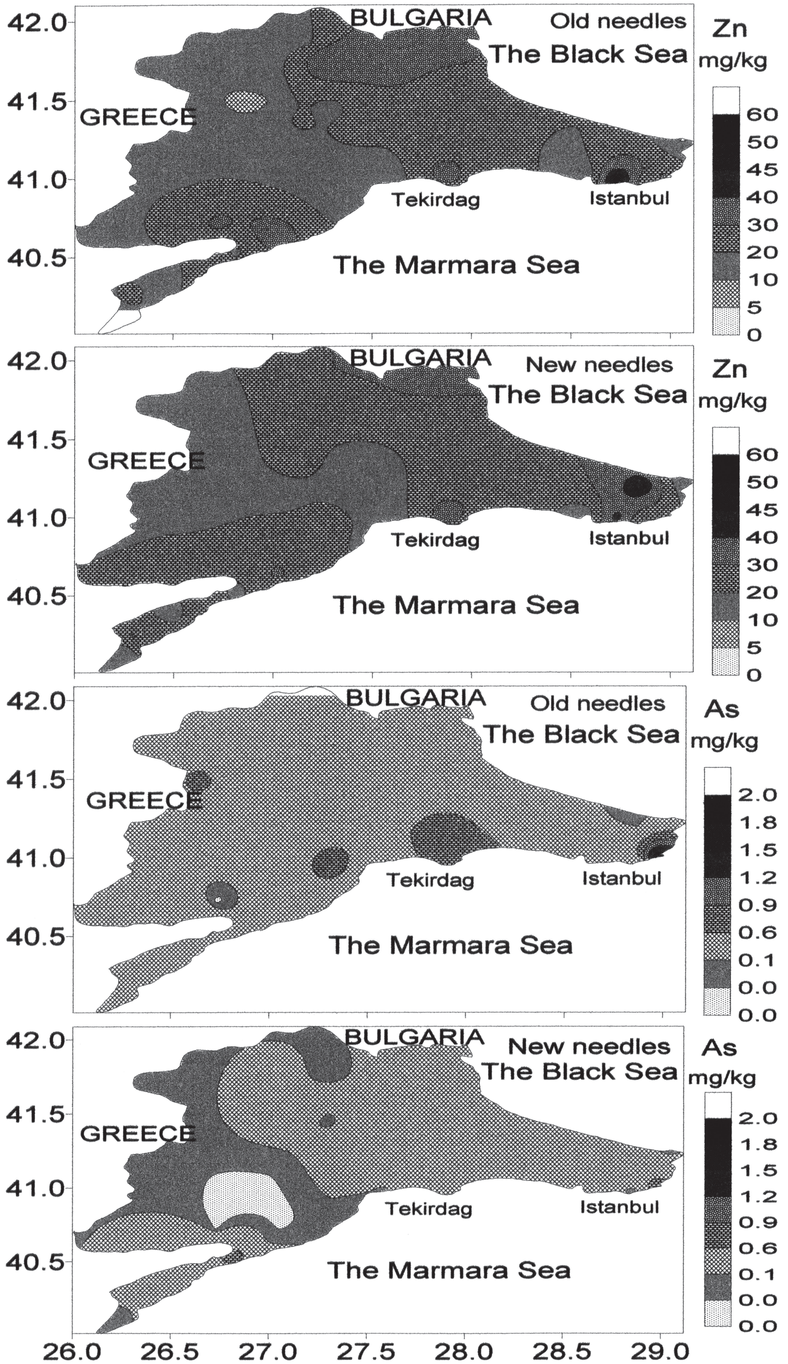

Figure 2. Continued

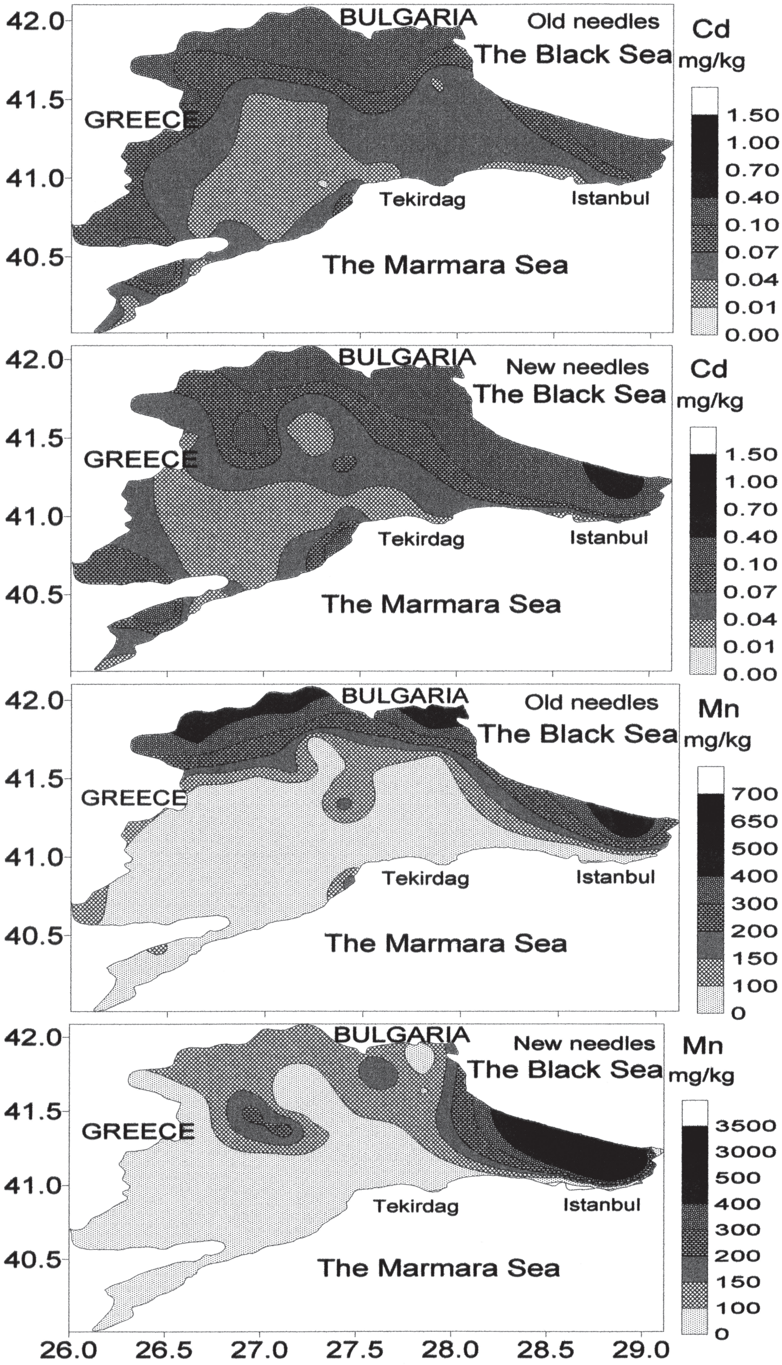

Figure 2. Continued

These results confirm that some areas have been affected by atmospheric air pollution. When the distribution map of elements found in pine needles in the region is examined, this situation can be seen clearly, especially near large cities.

Pb, Cu, Zn, and As have a similar distribution pattern while Cd and Mn show a different distribution (Figure 2). This result indicates that Pb, Cu, Zn, and As come from the same sources but Cd and Mn are from different sources, and there is also high correlation coefficient between Cd and Mn. According to Čeburnis et al. (2000), As, Pb, Cr, and V come from atmospheric pollution while Cd and Mn comes from the soil. The current results are concordant with the results of Čeburnis' study.

In conclusion, atmospheric deposition of heavy metals in the Thrace region is not high though heavy metal pollution is evident particularly near the large big cities of Istanbul and Tekirdag. These results indicate that local air pollution has taken place, and that pine needles are suitable bioindicators for determining atmospheric heavy metal deposition, though not for determining long-term changes in atmospheric pollution.

Acknowledgments. The support of the Research Council of Norway, Scientific and Technical Research Council of Turkey (TUBITAK), and Joint Institute for Nuclear Research Dubna, Moscow is gratefully acknowledged in the carrying out of this study.

REFERENCES

Blanuša M, Prester Lj, Matek M, Kucak A (1999) Trace Elements in Soil and Coniferous Needles. Bull Environ Contam Toxicol 62: 700-707.

Čeburnis D, Steinnes E (2000) Conifer needles as biomonitors of atmospheric heavy metal deposition: comparison with mosses and precipitation, role of the canopy. Atmos Environ 34: 4265-4271.

Dmuchowski W, Bytnerowicz A (1995) Monitoring Environmental Pollution in Poland in Chemical Analysis of Scots pine (*Pynus sylvestris L.*) needles. Environ Pollut 87: 87-104.

Gratton WS, Nkongolo K, Spiers GA (2000) Heavy Metal Accumulation in Soil and Jack Pine (*Pinus banksiana*) Needles in Sudbury, Ontario, Canada. Bull Environ Contam Toxicol 64: 550-557.

Rautio P, Huttunen S, Lamppu J (1998) Element concentrations in Scots pine needles on radial transects across a subarctic area. Water Air Soil Pollut 102: 389-405.

Rautio P, Huttunen S (2003) Total vs. internal element concentrations in Scots pine needles along a sulphur and metal pollution gradient. Environ Pollut 122: 273-289.

Tausz M, Trummer W, Goessler W, Wonisch A, Grill D, Naumann S, Jimėė MS, Morales D (2005) Accumulating pollutants in conifer needles on an Atlantic island-A case study with *Pinus canariensis* on Tenerife, Canary Islands. Environ Pollut 136: 397-407.