Bull Environ Contam Toxicol (2007) 79:367–370
DOI 10.1007/s00128-007-9232-5

# Determination of Atmospheric Heavy Metal Pollution in Canakkale and Balikesir Provinces Using Lichen (*Cladonia rangiformis*) as a Bioindicator

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Received: 13 March 2007 / Accepted: 5 June 2007 / Published online: 17 July 2007


**Abstract** A regional study was conducted to assess the current level of atmospheric heavy metal pollution (Pb, Zn, Cr, Cu, Cd) in the Canakkale and Balikesir provinces of Turkey, and also to establish a baseline for future studies of atmospheric heavy metal pollution. The lichen *Cladonia rangiformis* was used for determining the distribution of heavy metals in the atmosphere. The highest concentration of all these elements was observed in the vicinity of Balikesir province where there is an abandoned lead–zinc main. On the other hand, apart from the mining area, the concentration of heavy metals was similar to the data reported for unpolluted areas. Maximum values of Pb, Zn, Cr, Cu, and Cd were 33.8, 47.6, 13.0, 5.29, and 0.69 mg/kg in dry weight, respectively. Spatial distribution of these elements, apart from Cr, was similar. Correlation coefficients between Zn–Pb, Cr–Zn, Cu–Pb, Cu–Zn, Cd–Zn, and Cd–Cr were high and positive, and indicated that they come from the same sources.

**Keywords** Heavy metal · Lichen · Atmospheric pollution · Bioindicator

Many pollutants are released into the atmosphere from different sources. These pollutants are known as nitrogenoxides, sulphuroxides, pesticides, herbicides, suspended particulates, and heavy metals. Among these, the heavy metals are emitted into the atmosphere from industrial and many other anthropogenic sources. Those pollutants threaten not only human health but also the structure of the ecosystem. Pollutants given out from one source fall either in the area immediately surrounding the source or are carried to remote areas. Biomonitoring provides valuable information about the quantity and quality of pollutants in the atmosphere. It is also an easy, inexpensive, and practical method of determining air quality when compared with conventional monitoring methods. Therefore, many studies have been devoted to show the distribution of atmospheric air pollutants (Loppi and Bonini 2000; Garty et al. 2002). For this purpose, different bioindicator organisms have been used for the monitoring of atmospheric air pollution (Steinnes 1977; Sloof 1995; Coskun 2006a, b). Among the bioindicators, moss and lichen species occupy first place as biomonitors showing local and regional variations in heavy metal pollution. They have no real root systems but accumulate heavy metal cations, supplied by dry and wet deposition (Rühling and Tyler 1971). This means lichens have to take their minerals and other nutrients from wet and dry deposition, therefore, many chemicals found in the atmosphere can be absorbed and adsorbed over the whole lichen surface. Canakkale and Balikesir are not big cities, but they have various pollutant sources in the near vicinity due to mining, agricultural activities and use of non-approved heating materials in houses. There is an abandoned lead and zinc mine containing 2 million tons of tailings located in Balikesir, a coal burning power plant near to Canakkale, and also several coal mines in the region.

The aim of this study was to obtain the first data about the heavy metal concentrations of lichen in this area, and to determine the distribution of atmospheric heavy metals in the Canakkale and Balikesir provinces.

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## Materials and Methods

Epigeic lichen samples (*Cladonia rangiformis*) were collected at ten stations in the Canakkale and Balikesir province in September 2004 (Fig. 1). Sampling sites were chosen at least 300 m away from highways and at least 100 m away from other roads and settlement areas. All samples were collected at open areas to represent atmospheric deposition. In each sampling station, one composite lichen sample, about 200–300 g, was collected in the center and diagonally opposite corners of a 50 × 50 m square area. Geographic coordinates of the sampling sites were determined using global position system (GPS) and the lichen samples were stored in plastic bags during field and laboratory studies. All samples were cleaned of residual and other waste matter in the laboratory. Thalli of lichen samples were selected and then dried in an oven at 60°C. All the cleaned and dried samples were ground and homogenized using plastic mill. Mineralization of lichen samples was carried out using a Microwave digestion system (CEM Mars X-press). For this purpose, dried 0.5 g lichen tissue was put into a Teflon vessel, 10 ml of concentrated nitric acid (Merck, 65%) was added, and the mixture was digested. After cooling, the digest was evaporated to a dry state then 10 ml of deionized water was added; afterwards the digest was filtered and diluted with deionized water up to 25 ml. The concentrations of Pb, Zn, Cr, Cu, and Cd were determined by using ICP-OES, and the detection limits of those elements were 0.170, 2.40, 0.004, 0.25 and 0.01 mg/kg, respectively. Concentrations of heavy metals in each sample were measured in triplicate and all the relative standard deviations (RSD) for replicates were less than 5%. SPSS 11.0 for Windows was used for the data analysis. Geographic information system (GIS) with Kriging algorithm was used to show the distribution pattern of heavy metals in the study area. Accuracy was checked by analysis of reference materials obtained from the National Institute of Standards and Technology (NIST 1575 Pine needles).

## Results and Discussion

The correlation coefficients (Pearson 2-tailed) between the elements are presented in Table 1. Obtained correlations between Zn–Pb, Cr–Zn, Cu–Pb, Cu–Zn, Cd–Zn, and Cd–Cr are high and show positive. This shows that they come from same source or sources. Correlations between Cr–Pb, Cu–Cr, Cd–Pb, and Cd–Cu are not high. The mean value and standard deviation of Cr are same. This similarity reveals a uniform distribution and also the natural origin of Cr.

The accuracy of measurements was checked using standard reference material (Pine needles). The difference between the certified and obtained values was insignificant and at a reasonable level. The certified, measured, and recovery values are presented in Table 2. The concentrations of elements are presented in Table 3. The highest values of Pb, Zn, Cr, Cu, and Cd are 33.8, 47.6, 13.0, 5.29, and 0.69 mg/kg in dry weight, respectively. The geographical distribution of Pb, Zn, Cr, Cu, and Cd in the study area is given in Figs. 2, 3, 4, 5 and 6.

When the geographical distribution patterns of all elements are examined, the maximum values of all five elements are observed in the vicinity of Balikesir province. Outside this area, concentrations of these elements are close to the concentrations of lichens collected in an unpolluted area in Italy (Conti et al. 2004). The highest values of Pb, Zn, Cr, Cu, and Cd from the unpolluted area were given as 3.62, 53.2, 2.81, 4.45, and 0.09 mg/kg, respectively (Conti et al. 2004) (Table 4). The maximum values of Pb, Cu, Cd and Cr obtained in this study are 33.8, 5.29, 0.69 and 13.0 mg/kg, respectively. It is evident that these values are much higher than the value given by Conti.

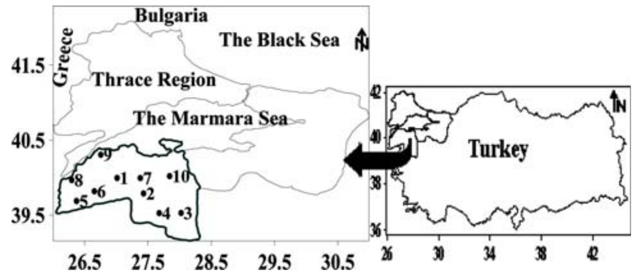


**Fig. 1** Sampling stations in Canakkale and Balikesir provinces

**Table 1** Pearson correlation (2-tailed) coefficients between measured elements in lichen

| | Cd | Cr | Cu | Pb | Zn |
|---|---|---|---|---|---|
| Cd | 1.00 | | | | |
| Cr | **0.72** | 1.00 | | | |
| Cu | 0.36 | 0.13 | 1.00 | | |
| Pb | 0.10 | 0.09 | **0.69** | 1.00 | |
| Zn | **0.70** | **0.57** | **0.67** | **0.67** | 1.00 |

$P < 0.05$

**Table 2** Certified and measured results of Cd, Cr, Cu, Pb, and Zn in Pine needles (NIST 1575) (mg/kg)

| | Certified | Measured | Recovery, % |
|---|---|---|---|
| Cd | <0.5[a] | 0.20 | na |
| Cr | 2.6 | 2.0 | 78 |
| Cu | 3.0 | 2.92 | 97 |
| Pb | 10.8 | 10.7 | 99 |
| Zn | na | 88.2 | na |

[a] Not certified

**Table 3** Heavy metal concentration in lichen samples (mg/kg in dry weight, n:10)

| Station no. | Station name | Cd | Cr | Cu | Pb | Zn |
|---|---|---|---|---|---|---|
| 1 | Can | 0.27 | 2.24 | 1.87 | 4.86 | 24.2 |
| 2 | Alancik | 0.34 | 4.82 | 5.29 | 33.8 | 47.6 |
| 3 | Esenli | 0.23 | 3.09 | 2.66 | 1.66 | 20.1 |
| 4 | Kozoren | 0.69 | 13.0 | 3.85 | 5.58 | 45 |
| 5 | Bahceli | 0.30 | 11.3 | 2.50 | 1.35 | 33.1 |
| 6 | Bayramic | 0.31 | 2.97 | 2.61 | 4.21 | 27.7 |
| 7 | Camoba | 0.24 | 3.90 | 4.01 | 1.88 | 30.4 |
| 8 | Ezine | 0.26 | 6.60 | 1.91 | 7.51 | 27.5 |
| 9 | Sahinli | 0.23 | 3.4 | 2.8 | 3.41 | 22.4 |
| 10 | Darıca | 0.26 | 3.81 | 3.41 | 5.21 | 26.7 |
|  | Mean ± SD | 0.31 ± 0.14 | 5.52 ± 3.72 | 3.09 ± 1.06 | 6.95 ± 9.63 | 30.5 ± 9.15 |

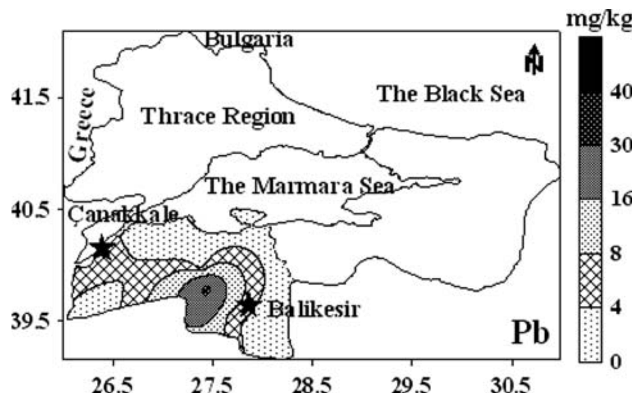


Fig. 2 Distribution of Pb

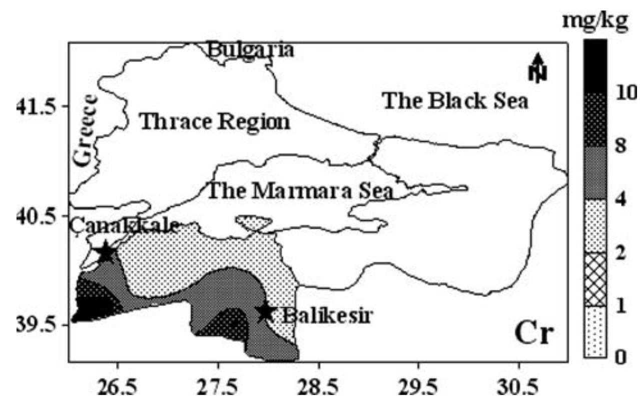


Fig. 4 Distribution of Cr

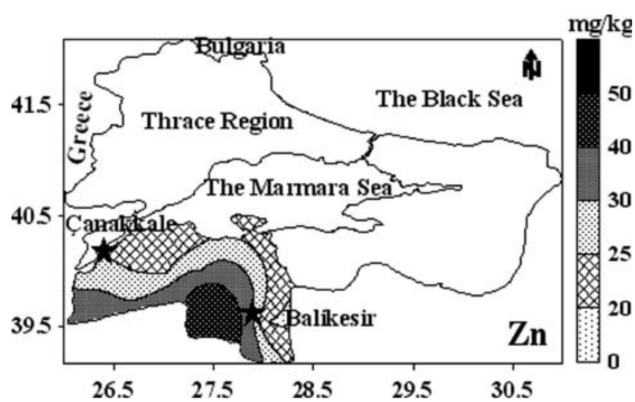


Fig. 3 Distribution of Zn

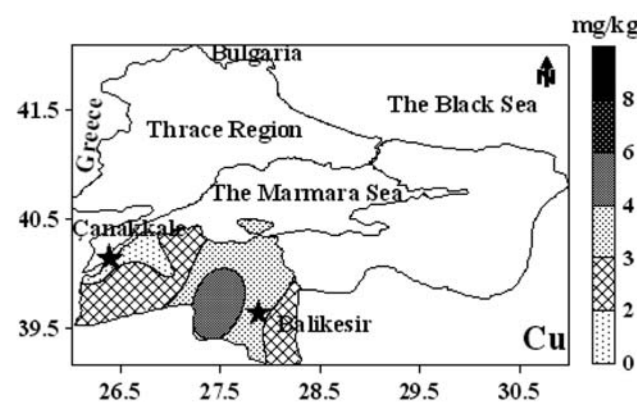


Fig. 5 Distribution of Cu

However, the mean values of these elements are more or less the same. The large difference in maximum values most likely comes from local pollution in the Balikesir province, where the highest values of all elements were obtained. The concentration levels of all elements in the remaining part of the sampling area are close to Conti's mean value. Bowen's results represent a general concentration of elements in lichen, and our results were within Bowen's range but different from Adamo's results. These variations may have arisen from different species and/or locations.

The Cu concentration as measured in the lichen samples shows an even distribution in the study area. In spite of this, the highest value of Cu was obtained to the west of Balikesir, as with the other measured elements. In this area there is an abandoned Pb–Zn mine dam with 2 million tons

**Table 4** Heavy metal concentrations in lichen species from different studies (mg/kg), (ranges in brackets)

| | *Evernia prunastri* (Conti 2004) | Lichens (Bowen 1979) | *Pseudevernia furfuracea* (Adamo 2003) | Foliose (e.g. *Parmelia*, *Hypogymnia*) (Adamo 2003) | *C. rangiformis* (This study) |
|---|---|---|---|---|---|
| Cd | 0.08 (0.05–0.09) | – | 0.46 | (<0.1–0.3) | 0.31 (0.14–0.69) |
| Cr | 1.69 (1.04–2.81) | (0.6–7.3) | 2.23 | (1–4) | 5.52 (2.24–13.0) |
| Cu | 3.35 (1.94–4.45) | (9–24) | 5.42 | (4–10) | 3.09(1.06–5.29) |
| Pb | 2.24 (1.05–3.62) | (1–78) | 23 | (1–8) | 6.90 (1.35–33.8) |
| Zn | 31.3 (20.3–53.2) | (20–60) | 99 | (20–90) | 30.5 (9.15–47.6) |

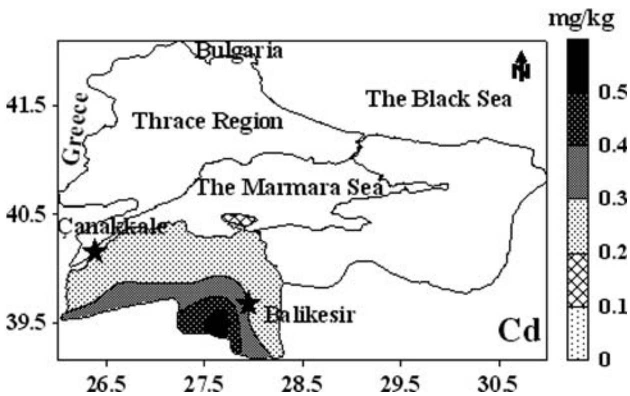


**Fig. 6** Distribution of Cd

of waste without any protective measures lying in an open area (Aykol et al. 2003). Resuspention of these elements from waste most probably enhanced the lichen element content in this area. Other than the abandoned mining area, there are no other important sources, industrial or anthropogenic, for the mentioned elements.

When the distributions maps of all elements are examined, Pb, Cu, Cd, and Zn show a similar distribution pattern and the west of Balikesir is affected by atmospheric air pollution. In another study, the same high values were obtained for Pb, As, Sb in the west of Balikesir city (Yenisoy-Karakaş and Tuncel 2004).

The Cr distribution is slightly different from other elements in the region. Its maximum value was also measured in west of Balikesir province and near to Canakkale. It would appear that a certain amount of Cr comes from lithogenic sources.

As a result, we can conclude that lichen samples in the study area, apart from the western part of Balikesir province, contain low levels of heavy metals. These levels in lichen were considered to be the natural level by Bowen and Conti (Bowen 1979; Conti et al. 2004). However, extreme values of the heavy metals were found around the abandoned mine area near to Balikesir, showing that abandoned mining is the main source of atmospheric air pollution in this part of the region. These data will be a base for further studies on this subject and will contribute to showing the spatial and temporal changes in distribution of atmospheric heavy metals in the area studied.

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