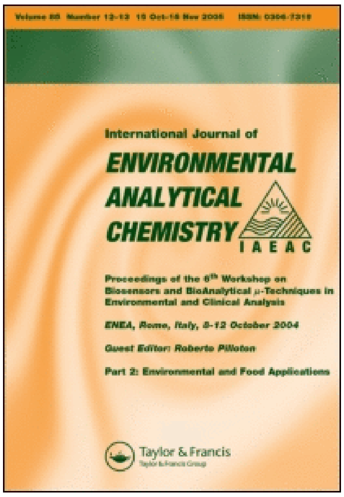

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Assessment of Heavy Metals Air Pollution in Urban and Industrial Environments Using OAK Leaves as Bionindicators

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To cite this Article Vassileva, Emilia , Velev, Veltcho , Daiev, Christo , Stoichev, Teddor , Martin, Michel , Robin, Dominique and Haerdi, Werner(2000) 'Assessment of Heavy Metals Air Pollution in Urban and Industrial Environments Using OAK Leaves as Bionindicators', International Journal of Environmental Analytical Chemistry, 78: 2, 159 — 173
To link to this Article: DOI: 10.1080/03067310008044408
URL: http://dx.doi.org/10.1080/03067310008044408

Intern. J. Environ. Anal. Chem., Vol. 78(2), pp. 159-173
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ASSESSMENT OF HEAVY METALS AIR POLLUTION IN URBAN AND INDUSTRIAL ENVIRONMENTS USING OAK LEAVES AS BIOINDICATORS

EMILIA VASSILEVA[a*], VELTCHO VELEV[a], CHRISTO DAIEV, TEDDOR STOICHEV[a], MICHEL MARTIN[b], DOMINIQUE ROBIN[b] and WERNER HAERDI[b]

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(Received 15 November 1999; In final form 26 May 2000)

In recent investigation the leaves of *Quercus cecciliflora* are applied as bioindicator for evaluation of heavy metal air pollution (Cd, Pb, and Zn) in urban and industrial districts of Sofia and Sofia Field (Bulgaria). Except dry oak leaves, the rainwater was collected to survey the heavy metals deposition. The dependency between the mean heavy metal fallout and the metal concentration in oak leaves have been investigated. The results were compared with corresponding results from an incineration plant situated in the vicinity of Geneva, which were also collected for a similar study. A heavy metal fallout maps indicating the sites which are most exposed to pollution have been drawn.

Keywords: Quercus cecciliflora; bioindicator; heavy metal fallouts; atmospheric pollution; oak leaves; rain water

INTRODUCTION

The global distribution of heavy metals by various emitters like traffic, industries, home hold, energy supplies, agriculture etc. is well-known problem of the environment. The input of elements, among them heavy metals, into ecosystems due to human activity has become an increasing burden during the last centuries. Trace elements, even if deposited constantly in small rates over long periods of time, accumulate in the environment and will probably pose an increasing hazard in the future.

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A main task of environmental monitoring is to get information covering whole regions or countries about the order of magnitude and the spatial distribution of heavy metal pollution. Their effects on vegetation and individual plants are differently pronounced and it is already a useful approach to gain important information on the heavy metal contamination by selection of suitable bioindicator systems. The traditional bioindicatos like mosses and lichen are rare in urban areas and the trees appear to be a major plant type for biomonitoring [1–7]. There are considerable data regarding the retention and bioaccumulation of heavy metal from tree leaves and the biological affect caused from the toxicity of these metals [8–15]. Despite a growing tend in several industrialized countries to use unleaded petrol, automobile exhaust fumes are still a major source of lead emissions. Distribution of lead and cadmium were often investigated, probably because of their toxicity and ubignitous occurrence in polluted ecosystems. Lead can be used as an indicator of pollution by automobile exhaust fumes, whereas cadmium may be taken as a rough measure of the general antropogenic pollution of the environment [1,16]. This assumption may be true in urban areas, but this is a too far reaching generalization, since in many places particular elements other than cadmium are polluting the environment.

Martin et al. [17–20] have shown that exposed to atmospheric pollution dry oak leaves exhibit the property of accumulating heavy metals such as cadmium, lead, zinc. The analysis of heavy metals in oak leaves exposed to heavy metals fall out from an incineration plant situated in the vicinity allow these leaves to serve as bioindicator of air pollution. Their results proving the ability of the plant to reflect adequately environmental pollution encouraged us to apply continue these investigations.

The current paper aims to present part of a study on heavy metal air pollution in urban and industrial districts of Sofia and Sofia Field (Bulgaria), carried out by using *Quercus cecciliflora* as a bioindicator.

EXPERIMENTAL

Sampling procedures

20 sampling sites were selected in Sofia, surrounding suburbs and in the Sofia Field (Figure 1). They are situated as follow:

- 11 sampling sites (2,5–7, 9–13, 16 and 20) in Sofia and surrounding suburbs;
- 6 sampling sites (1, 3, 8, 14, 15 and 18) in Sofia Field in the vicinity of metallurgical plant;
- 3 referent sites (4, 17 and 19) in clear region.

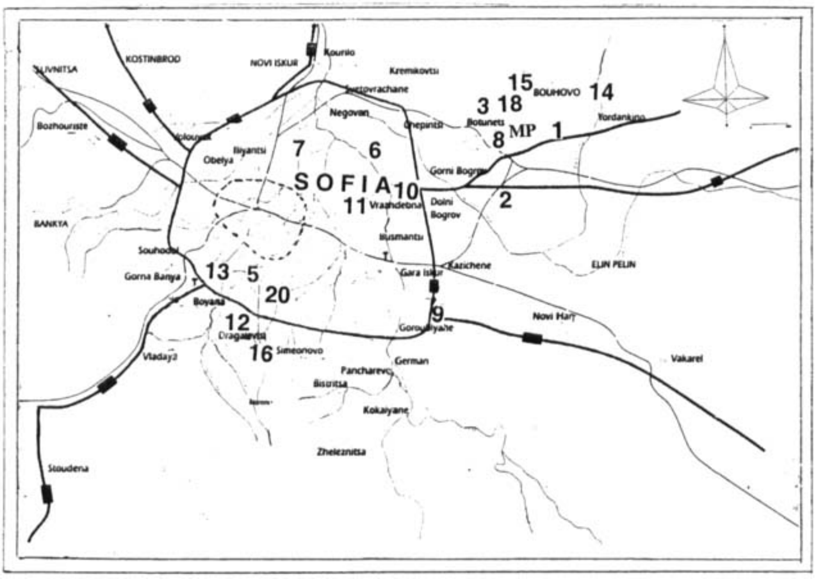


FIGURE 1 Sampling map and the Rose of Winds for Sofia and Sofia Field. MP-location of the Metallurgical plant. Scale 1:5 000 000. With dotted line is indicated the area corresponding to Figure 5

Metallurgical plant is situated at 25 km distance from Sofia. The selected clear region is located at 100 km away from Sofia (Balkan Mountain). In every site leaves from one tree were collected. Three factors were taken into account during the plant site selection: industrialization, traffic road and meteorological data. Table I describes sampling sites together with the expected type of pollution. Figure 1 represents the location of the sample sampling sites as well as the dominant winds in the studied area. The sampling was performed monthly from 15 October to 31 March in 1996 –1997, 1997 –1998 and 1998 – 1999 years (the period when the oak leaves are dry). The green oak leaves were collected from the same sampling sites in the Middle of September. 45 – 50 leaves were taken uniformly from around the trees at a trunk height of about 1.5–2 m above the ground. Samples (leaves) were thoroughly cleaned with dry air (pressure 0.4–0.5 atm) to remove dust particles and then lyophilised. After drying the leaves from each sample site were placed in separated polyethylene containers and stored at the room temperature. For each sampled tree specimens of the soil are also taken at a depth of 30 cm in order to evaluate ground variability and its possible effect on elemental contents in the leaves.

TABLE I Description of the Sampling Sites, selected for the collection of oak leaves

N.	*Location Field*	*Antropogenic Influence*	*Sample Sites*
1.	Sofia field – Iron Metallurgy	Mixed Industrial Pollution	1, 3, 8, 14, 15 18
2.	Sofia – Industrial Zone	Mixed Industrial Pollution	5, 20
3.	Sofia – Different Living Quarters	Urban Pollution	7, 16
4.	Sofia – Park Zone	Urban Pollution	6, 10, 12
5.	Sofia – Urban Roadside	Roadside Pollution	11, 13
6.	Sofia – Highway	Roadside Pollution	2, 9
7.	Balkan Mountain	Background	4, 17, 19

Treatment of samples. Mineralization

Before analysis samples were ground in the liquid nitrogen. For each single sample set approximately 10g (dry weigh) samples have been obtained. 0.2 g subsamples of the homogenised material were placed in a 10 ml polypropylene tube and treated with 1 ml conc. HNO_3. After 2 hours heating at 100°C for evaporation of nitrogen oxides 0.5 ml H_2O_2 were added and heating continued about 2 hours yet. 1 ml 50 ppm tantalum (V) and drop of Triton X-100 were introduced before centrifuge. Each final solution was diluted in 10 ml with Millie Q water and analyzed for lead (Pb), cadmium (Cd) and zinc (Zn).

Metal deposition rates were measured using conventional total deposit gauges. Eleven sampling points with different type of antropogenic influence were selected for collecting the rainwater – sites 1, 4, 5, 7, 8, 10, 12, 13, 16, 17 and 19. The gauges were positioned 1.5–2 m above ground on oak leaves and left for 27–28 days (over tree sampling periods during). To prevent contamination, deposit bottles were soaked in10 % HNO_3 for 24 h prior to use. After collection, the volume contents of each total deposit bottle were measured and transferred to a conical flask. The empty bottle was rinsed twice with 1 % HNO_3 and the washings poured into the conical flask. Finally 2 ml concentrated HNO_3 was added. The total depositions were then calculated by taking into account the funnel area and number of days, when the gauges had been in the field.

Apparatus and analysis

A Perkin-Elmer ICP-AES (Plasma 1000) coupled to an ultrasonic nebulizer Cetac U-500 AT was used. The analytical wavelengths were set at λ=228.810 nm for Cd, λ=220.347 nm for Pb and λ=205.558 nm for Zn.

Tantalum (V) at λ=226.230 nm was used as an internal standard. The blank solution contains MillieQ water, 1ml conc. HNO_3 and 0.5 ml H_2O_2 and has been treated in the same way as dry oak leaves samples. Working standard solution were prepared by appropriate dilution with MillieQ water from multielemental stock ICP-AES standard solution (Merck). The method of calibration curve was applied. The analyses were performed in three replicates of the same digest. The accuracy and precision of the method have been validated by analysis of two standards (National Bureau of Standards, NBS, Canada) with numbers 1573 (tomato leaves) and 1575 (pine needles). The obtained recoveries were 96.5% for Cd, 97.5% for Zn and 97.8 for Pb.

RESULTS AND DISCUSSION

The oak leaves remain on the trees during winter (till the end of March), whereas the other trees lose their leaves in the winter season. During this period the leaves are dry and accumulate metals from atmospheric contamination. Special advantages of *Quercus cecciliflora* as an accumulation indicator are its wide distribution and frequent occurrence in many industrialised and urban regions in Bulgaria. 20 samples from different regions with antropogenic influence were collected and analyzed monthly during 3 years. The results obtained from the analysis of the oak leaves exposed to heavy metal fallouts until end of March for tree years are shown in Tables II. The detected difference in heavy metal concentration is a good demonstration of the sensitivity of *Quercus cecciliflora* as a bioindicator, because the emitters in the investigated regions are of different types and logically the major pollutants should be in different levels. Table III shows the main values of the determined elements for the same sampling sites and years for the still green leaves in the middle of September. The variation for all elements in oak leaves from sampling sites with different antropogenic input is quite lower – in the range between 8–21%. This results support the assumption that significant pollution changes at these sampling sites, generally don't lead to considerable differences in heavy metal levels in green oak leaves. In previous studies Martin et all, [17,18] found also that dry oak leaves show consistently higher metal levels than green leaves, which is connected with their structure (no cuticule) and their high accumulation capacity for substances derived as wet deposition from the atmosphere. The absence of grow rate for oak leaves in the winter period is further priority that must be taken into account. The mechanism of trace element uptake and retention by dry oak leaves has been also investigated [21,22].

TABLE II The mean concentration (X ± SD) of cadmium, lead and zinc in dry oak leaves in the end of March from sampling sites 1–20 (mean values in μg/g dry weight; n=3). Sampling sites are described in Table I

Sample Site	*1997*			*1998*			*1999*		
No.	***Cd***	***Pb***	***Zn***	***Cd***	***Pb***	***Zn***	***Cd***	***Pb***	***Zn***
1.	1.62 ± 0.06	119 ± 4	175 ± 5	1.40 ± 0.06	112 ± 4	183 ± 5	1.26 ± 0.09	107 ± 4	163 ± 3
2.	1.11 ± 0.05	78.9 ± 3.1	174 ± 5	0.95 ± 0.05	63.1 ± 3.3	162 ± 3	1.24 ± 0.11	49.1 ± 2.3	142 ± 5
3.	1.00 ± 0.03	59.2 ± 2.5	78.8 ± 4.7	0.87 ± 0.03	61.1 ± 2.2	79.6 ± 4.0	1.11 ± 0.1	55.1 ± 2.0	67.1 ± 0.9
4.	0.07 ± 0.01	1.4 ± 0.1	26.7 ± 1.1	0.05 ± 0.01	1.3 ± 0.1	29.4 ± 1.2	0.09 ± 0.01	1.0 ± 0.1	22.9 ± 2.6
5.	0.68 ± 0.04	47.2 ± 1.5	137 ± 3	0.67 ± 0.05	56.4 ± 1.9	127 ± 4	0.62+0.09	50.6 ± 11.6	123 ± 2
6.	0.28 ± 0.01	8.1 ± 0.8	68.5 ± 1.4	0.36 ± 0.01	7.9 ± 0.2	52.2 ± 1.4	0.21 ± 0.01	9.2 ± 0.3	48.1 ± 1.7
7.	0.45 ± 0.02	37.1+2.3	125 ± 3	0.38 ± 0.03	31.1 ± 1.9	111 ± 4	0.37 ± 0.02	27.5 ± 1.1	119 ± 4
8.	0.94 ± 0.05	96.1 ± 4.9	151 ± 4	1.12+0.11	93.5 ± 5.8	146 ± 5	0.87 ± 0.05	94.0 ± 3.7	119 ± 5
9.	0.54 ± 0.02	39.1 ± 3.1	130 ± 4	0.70 ± 0.06	43.1 ± 3.1	145 ± 5	0.43 ± 0.01	26.5 ± 1.3	120 ± 3
10.	0.22 ± 0.02	11.6 ± 1.3	102 ± 4	0.26 ± 0.02	9.6 ± 0.9	96.1 ± 0.9	0.26 ± 0.03	10.2 ± 0.6	99.6 ± 1.9
11.	0.46 ± 0.04	17.3 ± 0.5	123 ± 6	0.49 ± 0.06	19.8 ± 1.8	113 ± 3	0.55 ± 0.03	19.4 ± 1.1	119 ± 2
12.	0.35 ± 0.03	7.6 ± 10.3	89.0 ± 3.8	0.29 ± 0.01	6.4 ± 0.4	83.1 ± 2.8	0.29 ± 0.02	12.2 ± 0.4	69.6 ± 1.5
13.	0.26 ± 0.03	34.3 ± 2.1	82.1 ± 3.2	0.29 ± 0.01	28.2 ± 1.3	104 ± 2	0.33 ± 0.01	24.3 ± 1.7	111 ± 3
14.	0.67 ± 0.03	50.4 ± 1.1	137 ± 4	0.86 ± 0.08	59.9 ± 2.3	151 ± 3	0.56 ± 0.03	50.8 ± 2.4	73.1 ± 1.2
15.	1.32 ± 0.04	78.9 ± 3.1	142 ± 5	1.21 ± 0.05	83.4 ± 2.2	162 ± 5.0	1.12 ± 0.05	81.2 ± 3.5	183 ± 3
16.	0.13 ± 0.01	23.2 ± 1.1	75.8 ± 3.7	0.18 ± 0.01	26.5 ± 0.7	84.1 ± 5.8	0.11 ± 0.01	28.1 ± 0.8	90.1 ± 1.1
17.	0.09 ± 0.01	2.1 ± 0.1	29.2 ± 1.7	0.06 ± 0.01	1.7 ± 0.1	32.0 ± 2.5	0.05 ± 0.01	2.0 ± 0.1	33.1 ± 1.4
18	1.47 ± 0.06	118 ± 2.4	169 ± 1	1.29 ± 0.12	104 ± 5	177 ± 4	1.37 ± 0.05	106 ± 1	163 ± 3
19	0.06 ± 0.01	3.1 ± 0.2	27.6 ± 3.0	0.09 ± 0.01	22.2 ± 0.6	26.5 ± 1.0	0.08 ± 0.01	3.2 ± 5.9	29.8 ± 1.3
20	0.68 ± 0.03	43.1 ± 1.5	72.1 ± 4.1	0.81 ± 0.05	40.1 ± 1.1	72.1 ± 3.0	0.55 ± 0.05	47.1 ± 1.4	71.2 ± 3.3

TABLE III The mean concentration (X ± SD) of cadmium, lead and zinc in oak leaves in the Middle of September 1998 from sampling sites 1–20 (mean values in μg/g dry weight, n=3). Sampling sites are described in Table I

Sample Site No.	*1996*			*1997*			*1998*		
	Cd	*Pb*	*Zn*	*Cd*	*Pb*	*Zn*	*Cd*	*Pb*	*Zn*
1.	0.07 ± 0.01	10.7 ± 0.2	43.0 ± 1.2	0.06 ± 0.01	16.8 ± 0.3	35.2 ± 1.1	0.07 ± 0.01	15.0 ± 0.5	38.9 ± 1.1
2.	0.05 ± 0.01	3.8 ± 0.1	35.1 ± 0.7	0.05 ± 0.01	4.8 ± 0.1	30.9 ± 0.9	0.06 ± 0.01	5.0 ± 0.1	32.9 ± 0.4
3.	0.06 ± 0.01	5.4 ± 0.2	32.2 ± 0.8	0.07 ± 0.01	8.5 ± 0.3	38.8 ± 1.6	0.05 ± 0.01	6.1 ± 0.3	36.1 ± 0.8
4.	n.d.[a]	0.1 ± 0.01	19.5 ± 0.6	0.01 ± 0.001	0.1 ± 0.01	15.3 ± 0.8	0.01 ± 0.01	0.1 ± 0.01	21.7 ± 0.5
5.	0.05 ± 0.01	4.8 ± 0.2	32.2 ± 0.9	0.04 ± 0.01	9.2 ± 0.2	39.9 ± 1.7	0.07 ± 0.01	7.1 ± 0.3	36.8 ± 1.1
6.	0.06 ± 0.01	4.1 ± 0.2	28.8 ± 0.7	0.06 ± 0.01	3.7 ± 0.1	31.7 ± 1.9	0.08 ± 0.01	7.0 ± 0.3	29.7 ± 1.5
7.	0.05 ± 0.01	4.0 ± 0.1	23.0 ± 1.1	0.04 ± 0.01	6.0 ± 0.2	19.9 ± 1.2	0.04 ± 0.01	5.6 ± 0.2	27.2 ± 1.3
8.	0.06 ± 0.01	5.1 ± 0.2	48.2 ± 1.5	0.04 ± 0.01	4.1 ± 0.2	34.1 ± 1.7	0.07 ± 0.01	7.9 ± 0.2	39.0 ± 1.1
9.	0.03 ± 0.01	2.1 ± 0.1	19.9 ± 0.5	0.04 ± 0.01	1.3 ± 0.1	15.3 ± 1.2	0.03 ± 0.01	3.5 ± 0.1	29.8 ± 1.0
10.	0.05 ± 0.01	0.1 ± 0.01	24.9 ± 1.3	0.06 ± 0.01	0.8 ± 0.1	21.7 ± 1.5	0.07 ± 0.01	0.6 ± 0.04	27.1 ± 0.6
11.	0.01 ± 0.01	4.1 ± 0.2	22.5 ± 0.7	0.01 ± 0.01	6.2 ± 0.1	24.0 ± 0.6	0.02 ± 0.01	3.9 ± 0.2	23.1 ± 1.1
12.	0.06 ± 0.01	0.4 ± 0.03	25.0 ± 0.8	0.05 ± 0.01	0.5 ± 0.1	30.0 ± 0.6	0.03 ± 0.01	0.5 ± 0.03	24.0 ± 1.0
13.	0.03 ± 0.01	2.1 ± 0.1	20.1 ± 0.5	0.04 ± 0.01	3.2 ± 0.2	18.2 ± 0.6	0.06 ± 0.01	3.2 ± 0.2	26.0 ± 0.9
14.	0.05 ± 0.01	9.0 ± 0.3	42.0 ± 0.9	0.08 ± 0.01	6.2 ± 0.2	36.1 ± 1.1	0.06 ± 0.01	4.0 ± 0.1	22.0 ± 1.1
15.	0.04 ± 0.01	6.2 ± 0.3	32.9 ± 1.1	0.08 ± 0.01	3.2 ± 0.1	42.1 ± 1.2	0.04 ± 0.01	5.2 ± 0.2	34.6 ± 1.4
16.	0.02 ± 0.01	3.1 ± 0.1	21.1 ± 0.4	0.05 ± 0.01	2.6 ± 0.2	22.2 ± 0.8	0.02 ± 0.01	5.2 ± 0.2	23.2 ± 1.3
17.	0.02 ± 0.01	1.0 ± 0.1	21.4 ± 0.3	0.01 ± 0.01	1.2 ± 0.1	27.3 ± 1.0	0.02 ± 0.01	1.1 ± 0.1	22.3 ± 1.1
18.	0.0610.01	6.0 ± 0.2	41.3 ± 1.7	0.03 ± 0.01	5.1 ± 0.4	40.8 ± 1.1	0.09 ± 0.01	7.5 ± 0.2	36.4 ± 1.3
19.	0.01 ± 0.01	0.4 ± 0.1	23.9 ± 0.7	0.02 ± 0.01	0.6 ± 0.07	26.3 ± 0.8	0.01 ± 0.01	0.7 ± 0.04	21.1 ± 0.9
20.	0.07 ± 0.01	12.2 ± 0.3	29.8 ± 0.9	0.05 ± 0.01	10.9 ± 0.5	32.9 ± 0.7	0.06 ± 0.01	15.0 ± 0.7	32.8 ± 1.1

a. *none detected*

Figure 2 shows the variation of Cd, Pb and Zn concentrations in the leaves at four sampling sites since September 15, 1996 to March 31, 1997. Sites 15 and 18 are located very closed to a metallurgical plant and they are exposed to metal fallouts. Site 7 is situated in urban region of Sofia – less exposed, whereas site 4 is farther away in the Balkan Mountain – no exposed.

The results of the analysis of Cd, Pb, and Zn carried out confirm the effectiveness of dry oak leaves as a bioindicator. The plant collected in a non-polluted area showed low quantities of the monitored metals. The relatively higher variation in the concentration in leaves from industrial region are undoubtedly the influence of the metallurgical plant (sites 15 and 18). It can therefore be inferred that with an increase in the amount of heavy metals fallout the uptake of heavy metals by oak leaves is also increased

The accumulation of the investigated metals (Cd, Pb and Zn) in dry oak leaves were significantly dependent on their concentration in the atmosphere (rainwater) and the duration of exposure to these pollutants. Figure 3 shows the relation between concentration of Cd, Pb respectively Zn in dry oak leaves, collected in vicinity of the metallurgical plant (site 15) and heavy metal deposition which are measured by rain gauges. The results for Cd, Pb and Zn concentrations in soils in the middle of September and March don't show considerable changes for all investigated sample sites, with confirm the conclusion that only atmosphere deposition effects on heavy metal contents in oak leaves.

For 9 different couples "dry oak leaves – rain gauge" a straight line relationship has been established between Pb, Cd and Zn concentration in dry oak leaves and the heavy metal fallout – figure 4. Taking in account the threshold limits for Cd, Pb and Zn in air the threshold limits in oak leaves have been established. Threshold limit is respected under the concentration of investigated heavy metals in dry oak leaves as follow: 0.9 $\mu g\ g^{-1}$ Cd, 30 $\mu g\ g^{-1}$ Pb and 180–300 $\mu g\ g^{-1}$ Zn (Figure 4). The results have been compared with corresponding results, obtained by Martin et all, for similar study for the incineration plant in vicinity of Geneva [20]. The correlation for Cd and Zn were in good agreement with the correlation, obtained by Martin using dry oak leaves as bioindicator. In the case of Pb not the same relationship is observed probably due to the other antropogenic impute.

The current investigation illustrates that the concentration of toxic elements in dry oak leaves is determined by the degree of pollution at the sampling sites. Consequently, it is considered that *Quercus secciliflora* can be taken as bioindicator for heavy metal air pollution in polluted industrial and urban areas.

The industrial pollution gives a most serious contribution to global contamination of the environment. The samples around the metallurgical plant have elevated concentration of Cd (15 times background), Pb (40 times background) and Zn (9–10 times background). If we compare the two industrial region (for exam-

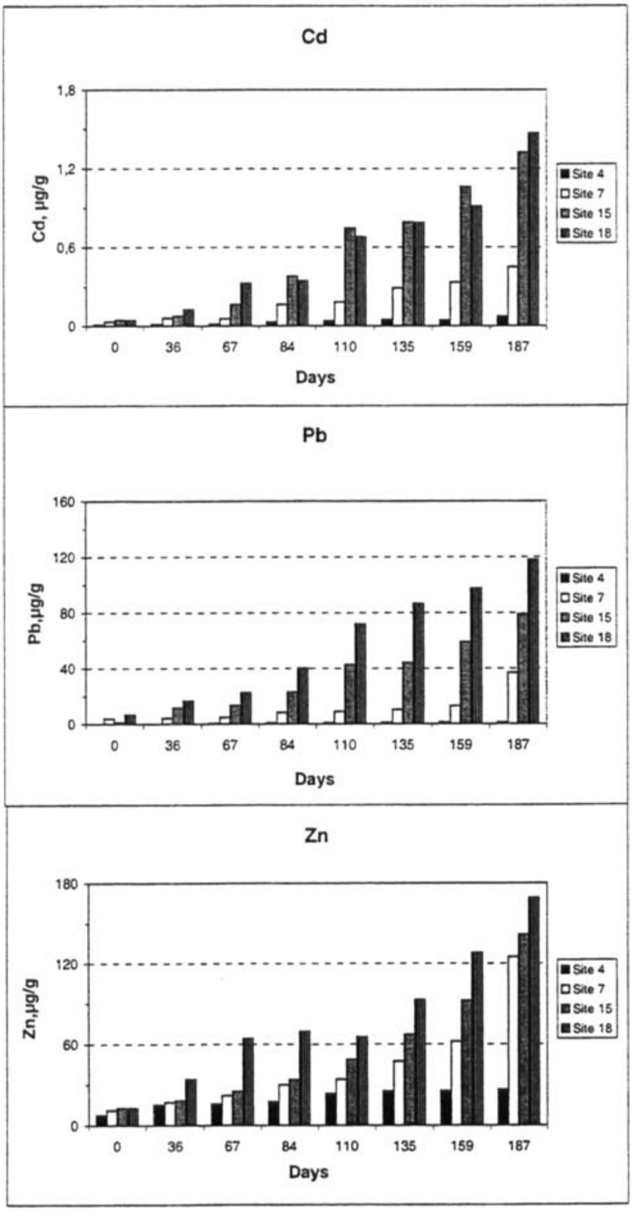


FIGURE 2 Variation of cadmium, lead and zinc concentrations in the leaves at four sampling sites from 15.10.1996 to 31.03.1997. Sites 15 and 18 are closed to the metallurgical plant, site 7 is situated in urban region of Sofia and site 4 is father away in the Balkan Mountains- blank value

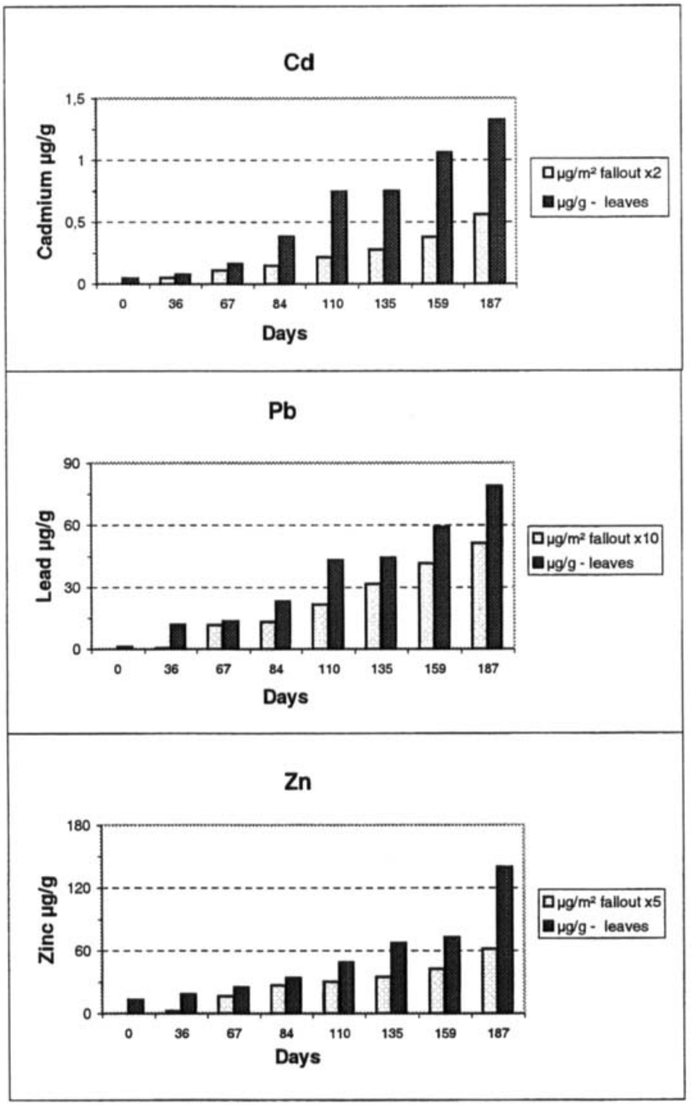


FIGURE 3 Comparison between the mean heavy metal rain fallout (µg/m^2.day) and the metal concentration in oak leaves µg/g from the tree situated close to the metallurgical plant (Site 15)

ple, sites 15 and 5 – site 5 is situated close to heating central) one can say that generally the pollution level around the metallurgical plant is much more higher. The relatively high value for Pb in this region is due also to the very intensive

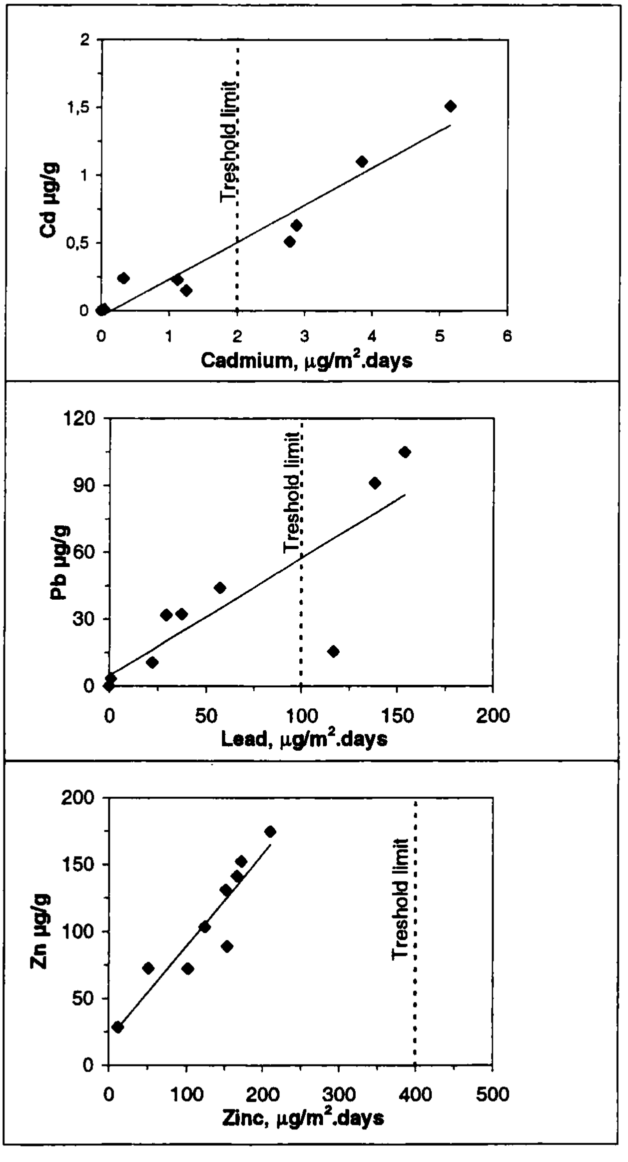


FIGURE 4 Correlation between the concentration of cadmium, lead and zinc in leaves and the heavy metal fallout measured by total rain deposit, during the period when the leaves are dry on the tree

lorry traffic extremely near to the metallurgical plant. Thus Pb pollution is connected indirectly to the operation of the emitter.

Investigations of the concentration in oak leaves collected at increasing distances from plant however prove, that the value decrease sharply and at a distance of 3 km are already to 2 times lower while at the 12 km from the plant the normal value for the region are obtained. This indicates that there is very strong, but local pollution.

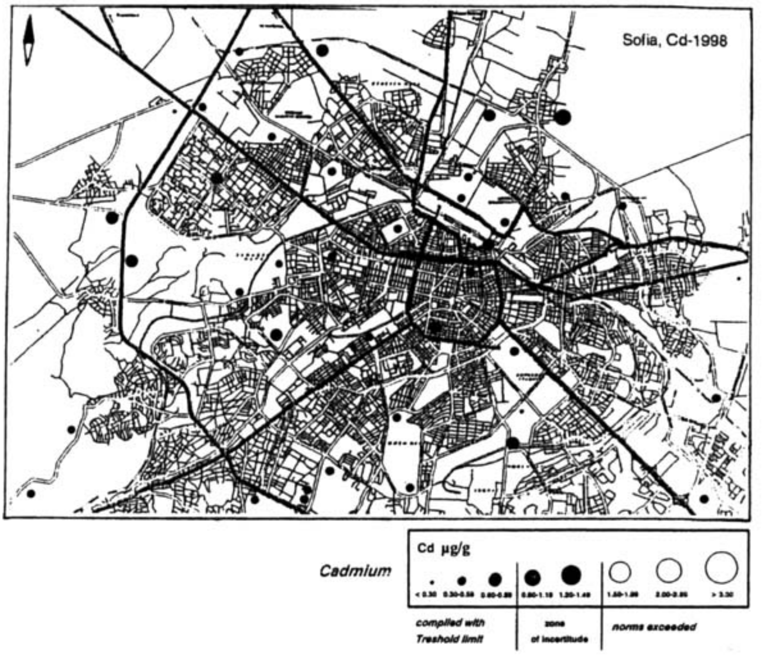
The direction of dominant local winds in Sofia Field is from south to north (Figure 1), hence a constant increased contamination of sites 15 and 18 was observed against site 8 for Cd, Pb an Zn.

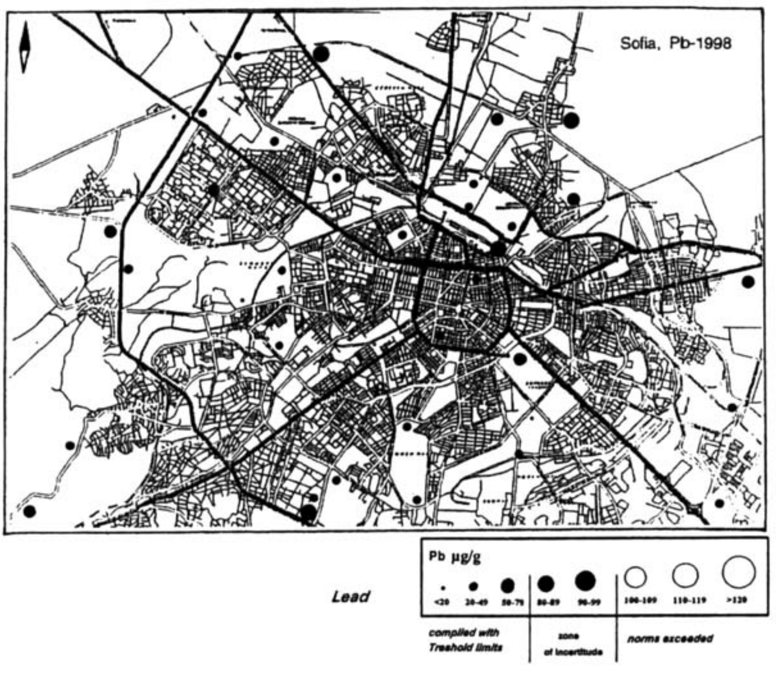
Results, obtained for urban regions of Sofia demonstrate that there is direct relationship between the concentrations of Pb, Cd, and Zn in leaves and the presence of pollution sources, especially as far as density of vehicular traffic is concerned. Lead contamination was not exactly proportional to the traffic load. Thus near the highway (site 2) lead concentration was higher than the concentration in other highway (site 9), although the traffic load was similar. Taking into account another factor, the number of road junctions where vehicles must wait longer times the described phenomena was then sufficiently explained.

For residential zones with essentially local traffic (site 11) the concentration of Cd, Pb and Zn in dry oak leaves were more elevated than the concentration of the same elements for the areas with high traffic, but surrounded at open spaces (site 13).

The high concentration of Pb is found in plants growing near the main roads (site 2). Many investigations have proved that besides Pb along roads higher levels of other elements may be detected such as Cd, Zn, etc. [9,10]. Our results are in good agreements with this opinion (see Tables II- sites 2,9).

The mean Cd concentration in urban sites (7) is slightly higher than the urban park sites (6, 10 and 12) and significantly higher than rural sites (4, 17 and 19) in the Balkan Mountain. The highest level of Zn were found in oak leaves from industrial zone (sites 1, 5 and 15) and highway (sites 2 and 9) and lowest in urban park and rural sites (4, 6, 17, 19). Elevated zinc levels near to highway show the effect of traffic volume. The oak leaves remain on the three during the winter (about 150 days). During this period the leaves are dry and accumulate heavy metals from atmospheric contamination. A linear correlation between the amount of metal deposited and its concentration in the leaves allows one to draw heavy metal fallout charts only by analyzing a few dry oak leaves collected just before they fall from the three (end of March). Figures 5a, 5b and 5c represent heavy metal fallout chart for the central part of Sofia for 1998. The oak leaves have been collected from 40 sampling sites in the central part of Sofia in the end of March and analyzed. The determination of Cd, Pb and Zn in oak leaves permits an evaluation of distribution of these elements. In comparison with other European sites the level of Cd, Pb and Zn is lower and sites with extreme values have


Sofia, Cd-1998
Cadmium
Cd µg/g
compiled with Treshold limit
zone of incertitude
norms exceeded


Sofia, Pb-1998
Lead
Pb µg/g
<20
20-49
50-79
80-89
90-99
100-109
110-119
>120
compiled with Treshold limits
zone of incertitude
norms exceeded

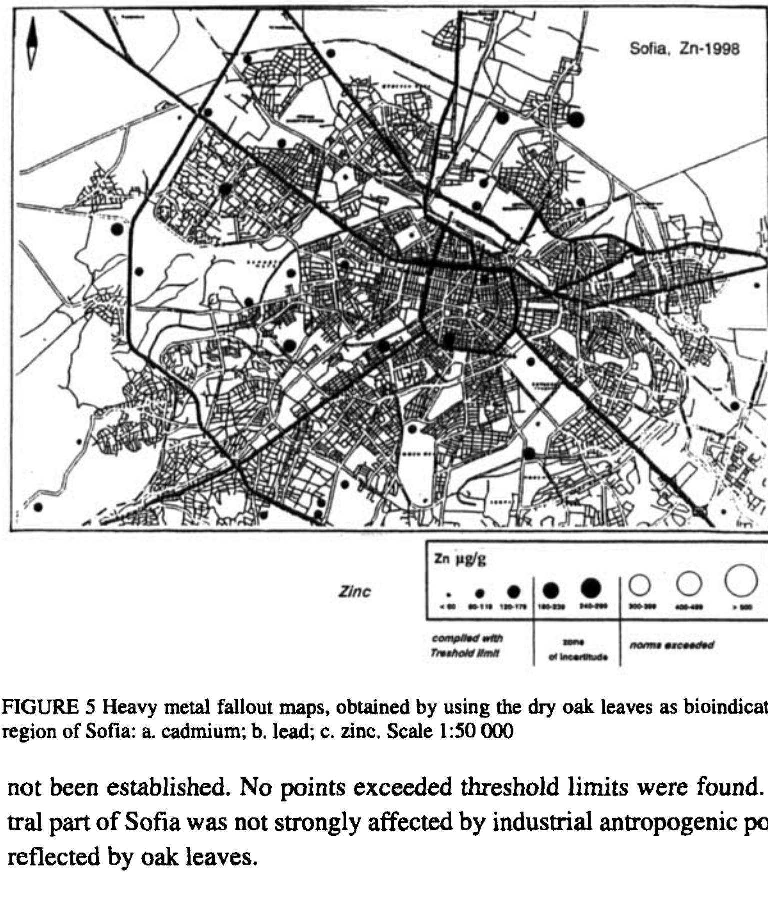


FIGURE 5 Heavy metal fallout maps, obtained by using the dry oak leaves as bioindicator for urban region of Sofia: a. cadmium; b. lead; c. zinc. Scale 1:50 000

not been established. No points exceeded threshold limits were found. The central part of Sofia was not strongly affected by industrial antropogenic pollution as reflected by oak leaves.

CONCLUSION

The current investigations illustrate that the concentrations of toxic elements in the dry oak leaves is determined by degree of pollution at the sampling sites. In non-polluted regions the concentration of heavy metals remain relatively constant over three years with a low degree of variation. The concentration of heavy metals in dry oak leaves for the polluted sites reflect the working activities, type and production volume of the near emitter source.

Acknowledgements

This work has been carried out within the scientific contract between the University of Sofia (Bulgaria) and the University of Geneva (Switzerland). We wish to thank to University of Geneva for the received financial support and for the opportunity to perform there all ICP-AES measurements. Mss F. Rosset – Bufle is thanked for coordination of the project.

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