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Comparative Studies of Metal Air Pollution by Atomic Spectrometry Techniques and Biomonitoring with Moss and Lichens

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Abstract Our study was dedicated to the analysis of air pollution level with metals in Dambovita County, Romania; maps of the concentration distributions for air pollutants were drawn; statistical analysis includes calculation of the background concentrations and the contamination factors. The highest values of the contamination factor *CF* is **63.1 ± 6.63** for mosses samples and **33.12 ± 3.96** for lichens and it indicates extreme contaminations in the surroundings of steel works and an electric plant. The comparison of the distribution maps for **Cr**, **Cu**, **Fe**, **Ni**, **Pb** and **Zn** concentrations enables the identification of the pollution sources, the limits of areas with very high levels of pollution, the comparison of the concentration gradients in some areas and the influence of woodlands on the spread of pollutants through the air.

Keywords Moss · Lichen · Biomonitor · Air · Pollution · Metal · EDXRF · AAS

Dambovita County is located in the south of Romania and its main sources of metal pollution are the steel and cement works, agricultural activities, roads and railways traffic and pit ballasts. The aim of this work was the assessment of air pollution with metals using the biomonitoring method with mosses and lichens; many studies which were dedicated to the biomonitoring method showed its possibilities to provide significant results regarding the quality of the environment. Studies about moss properties (Frontasyeva et al. 1994; Fernández and Carballeira 2001; Aničić et al. 2009; González-Miqueo et al. 2010) and lichens as biomonitors (Brunialti and Frati 2007; Dymytrova 2009) but

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also about the comparison of their characteristics as biomonitors (Bargagli et al. 2002; Adamo et al. 2007; Coskun et al. 2009) reveal its certain advantages such as: the capacity to accumulate dust particles from air, the stability of accumulation in time, the low cost of monitoring, etc. Our studies was focused on the comparisons between the distributions of the **Cr**, **Cu**, **Fe**, **Ni**, **Pb** and **Zn** concentrations in a given area as they are reflected by mosses and lichens samples while taking into consideration the following aspects: the number of samples is limited by the number of trees in the given area, especially in the areas with high values of element concentrations, which require an significant covering with biomonitors; the economical activities or road traffic, as random pollution factors, may influence the experimental results in a way that cannot be anticipated.

Materials and Methods

The analytical methods used in our research were *Atomic Absorption Spectroscopy* (AAS) and *Energy Dispersive X-ray Fluorescence* (EDXRF); instruments used were *GBC Avanta AAS* spectrometer and *Elvatech Elvax EDXRF* spectrometer; both instruments are part of specialized laboratories from the *Multidisciplinary Institute for Scientific and Technological Researches* of *Valahia University* from *Targoviste*. The lichen species sampled were *Xanthoria Parietina* (in most of the cases), *Parmelia Furfuracea* and *Peltigera Canina* and the moss ones were *Hylocomium Splendens.* All the samples were collected between April and June 2009. For each sample the information regarding the characteristics of location, weather and time of sampling was noted. Through EDXRF method was analyzed 31 mosses samples and 27 lichen samples; also, through AAS method, 18 moss and 18 lichen samples were analyzed. For EDXRF analyses, the samples were prepared by drying followed by shredding and placing them into plastic cylinders covered with Mylar foils. For AAS analyses the samples were prepared by digestion with nitric acid followed by a specific heat treatment program in a microwave oven. All processes like sampling, storage and the treatments of the samples were made in accordance with standard operating procedures. The detection limits for each element and for both methods are shown in Table 1.

Table 1 Detection limits for AAS and EDXRF methods

Element/method	Cr	Cu	Fe	Ni	Pb	Zn
AAS detection limit (mg/kg)	5	1.6	8.3	15	16.6	0.83
EDXRF detection limit (mg/kg)	3.78	0.81	89.5	0.61	3.78	10.2

Results and Discussion

Figures 1, 2, 3 ("Appendix") represents the distribution curves of equal concentrations (isoconcentrations) for metals corresponding to the data obtained by the EDXRF method for the samples of mosses and lichens. The graphs were drawn with Surfer 9 software. Colours were associated to the numeric values and their significance is shown in the legend from the right of each map; they allow an easy identification of the pollution sources. The maps are different for the two biomonitors and they reveal that lichens are useful to monitoring the open areas because they grow particularly in areas with low humidity, on roadsides or in open lands; mosses grow especially inside forests, in places with high humidity or on the bark of old trees and these features recommend them for background pollution monitoring. It can distinguish two main sources of pollution: factories producing and processing steel in the centre of the map and a power plant which is located in the north. Also, it highlights the low level of pollution in forests from West and South–West of each map *(Ungureni, Frasin Vale, Cobia, Picior de Munte)*. In Tables 2, 3 there are shown the AAS element concentrations for mosses, respectively lichens which is necessary to determine the *contamination factor* CF (Fernández 2001) by formula

$$\mathrm{CF} = \frac{c_m}{c_b}, \qquad (1)$$

where c_m is the maximum value of element concentration measured in that area and c_b is the background concentration.

The CF values are interpreted as follows (Fernández 2001): for $1 \leq \mathrm{CF} < 2$—no contamination, for $2 \leq \mathrm{CF} < 3.5$—low contamination, for $3.5 \leq \mathrm{CF} < 8$—moderate contamination, for $8 \leq \mathrm{CF} < 27$—severe contamination; for $\mathrm{CF} > 27$—extreme contamination. Our values show that on the industrial area of *Târgoviște* and near the power plant of *Doicești* there are severe or extreme levels of pollution, with maximum CF of 63.1 ± 6.63 for mosses and 33.12 ± 3.96 for lichens. The values of CF in one place from *Târgoviște* (Table 4) and the comparisons between the CF values from another place in from *Târgoviște* and village Văcărești (Table 5) allows the evaluation of the altitude of airborne particles. While *National College "Ienăchiță Văcărescu"* from *Târgoviște* is located at about 3 km from the industrial area within the town, village *Văcărești* is located at about 10 km in the open land. It can see that for **Cu**, **Fe**, **Ni** and **Pb** contamination factor values are close, which indicates that the altitude of the dust particles is low, because the first location and the mains sources of pollution are separated by many buildings, some with 10 floors. This conclusion is

Table 2 Statistical analysis on the concentrations obtained by AAS method for mosses

Element	Concentration (mg/kg)
Cr	
c_m	1,021.00 ± 22.07
c_b	19.13 ± 2.05
CF	53.37 ± 6.63
Cu	
c_m	49.24 ± 0.575
c_b	5.46 ± 0.087
CF	9.018 ± 0.24
Fe	
c_m	7,012.00 ± 101
c_b	728.15 ± 66
CF	9.63 ± 1.01
Ni	
c_m	38.74 ± 1.684
c_b	2.11 ± 0.002
CF	18.36 ± 0.81
Pb	
c_m	157.76 ± 5.788
c_b	2.5 ± 0.17
CF	63.104 ± 1.024
Zn	
c_m	158.00 ± 4.304
c_b	6.25 ± 0.377
CF	25.28 ± 2.21

Table 3 Statistical analysis on the concentrations obtained by AAS method for lichens

Element	Concentration (mg/kg)
Cr	
c_m	64.5 ± 3.73
c_b	5.8 ± 0.6
CF	11.11 ± 1.79
Cu	
c_m	34.08 ± 2.3
c_b	2.76 ± 0.14
CF	12.34 ± 1.45
Fe	
c_m	6,071.29 ± 473
c_b	412.01 ± 28
CF	14.73 ± 2.14
Ni	
c_m	10.48 ± 0.102
c_b	0.76 ± 0.062
CF	13.78 ± 1.25
Pb	
c_m	75.12 ± 6.85
c_b	5.56 ± 0.45
CF	13.51 ± 2.32
Zn	
c_m	155.7 ± 7.02
c_b	4.7 ± 0.351
CF	33.12 ± 3.96

Table 4 The values of CF from an inhabited area (AAS concentrations for mosses samples are presented in mg/kg)

Inhabited area	Cr	Cu	Fe	Ni	Pb	Zn
Central park from Târgoviște	8.66 ± 1.04	2.51 ± 0.06	1.475 ± 0.29	2.46 ± 0.42	1.7 ± 0.29	3.18 ± 0.66

Table 5 The values of metal contamination factor from 2 inhabited areas (AAS concentrations for lichen samples are presented in mg/kg)

Inhabited area	Cr	Cu	Fe	Ni	Pb	Zn
National College "*Ienăchiță Văcărescu* " Târgoviște	4.05 ± 0.81	5.59 ± 0.66	3.01 ± 0.38	3.26 ± 0.54	4.78 ± 0.48	14.12 ± 1.76
Văcărești	1.93 ± 0.29	4.46 ± 0.32	2.26 ± 0.3	8.32 ± 1.21	4.29 ± 0.74	4.93 ± 0.59

supported also by the significant attenuation effect of the forests situated in West and South-West of each map on the spread of airborne particles containing metals (the trees have heights up to 10 m).

This comparative study showed that the simultaneous use of mosses and lichens as bioindicators can provide important information on air pollution with metals on a given area, even if they are spread unevenly. Element concentrations were compared with the values obtained from other studies for the same type of biomonitor and the same species (Dzubaj et al. 2008; Aničić et al. 2009; Coskun et al. 2009). We have found that the concentrations obtained in this study are within the range of values from mentioned studies.

Appendix

See Figs. 1, 2, and 3.

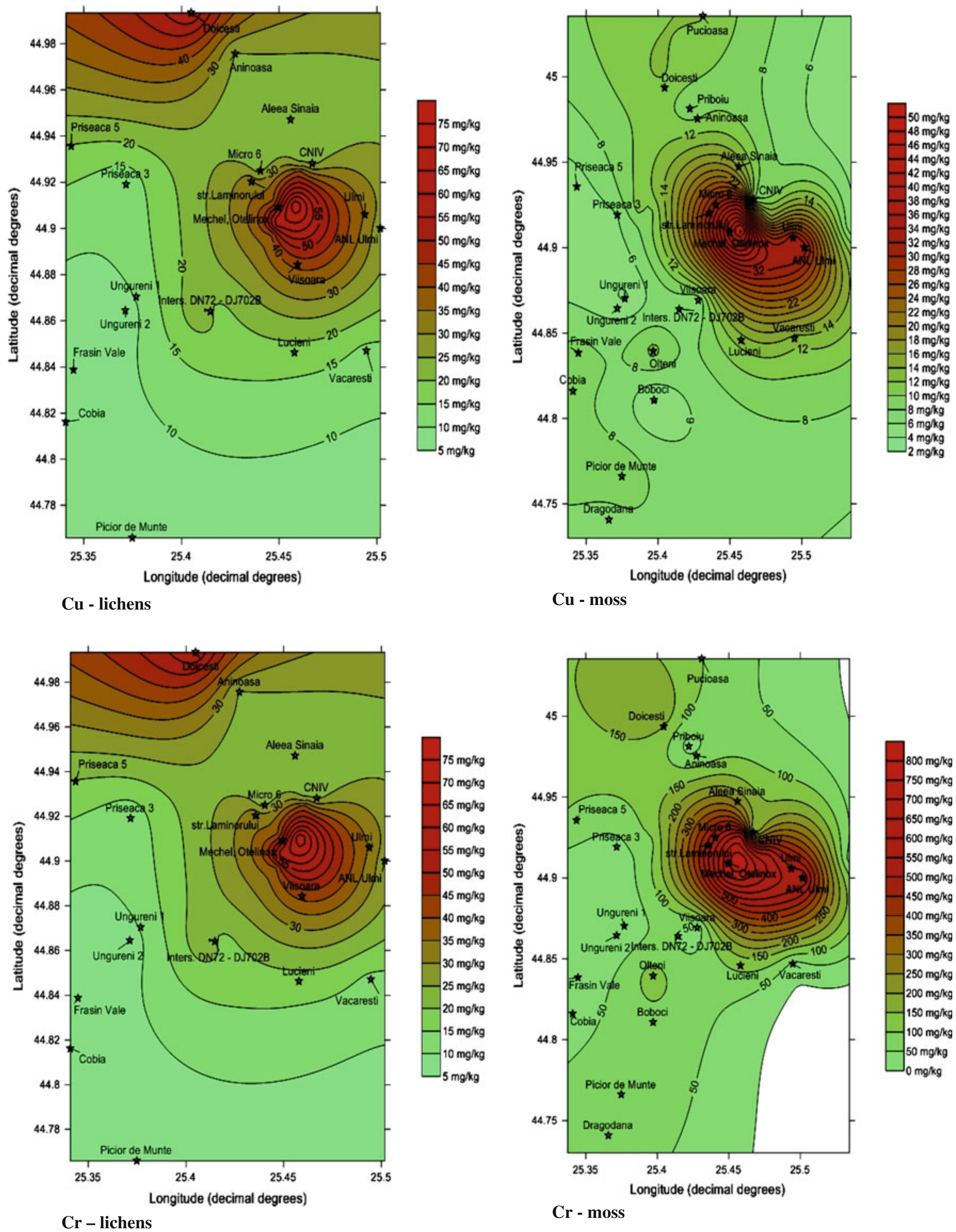

Fig. 1 Isoconcentrations maps of Cr and Cu in lichens and moss samples

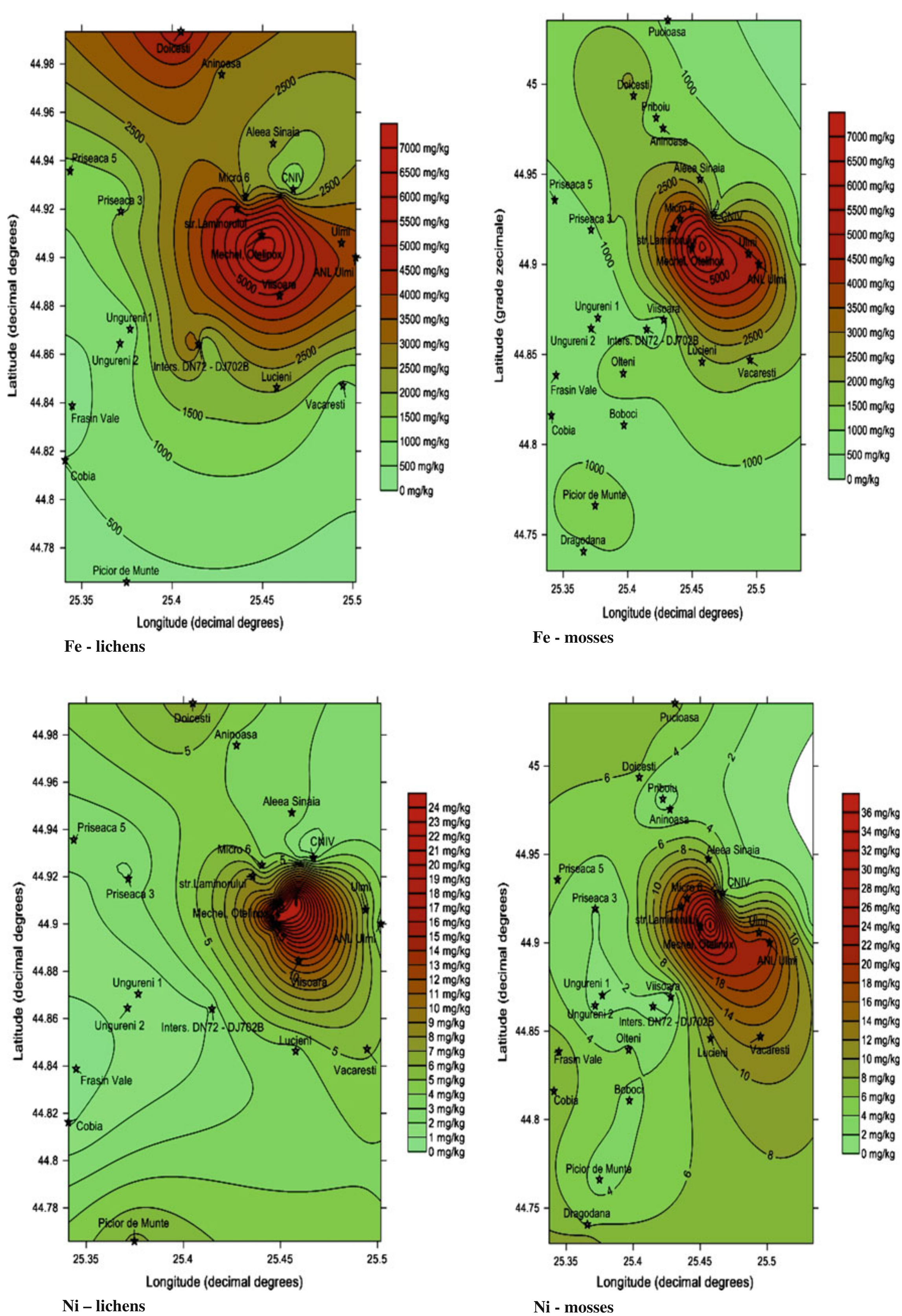

Fig. 2 Isoconcentrations maps of Fe and Ni in lichens and moss samples

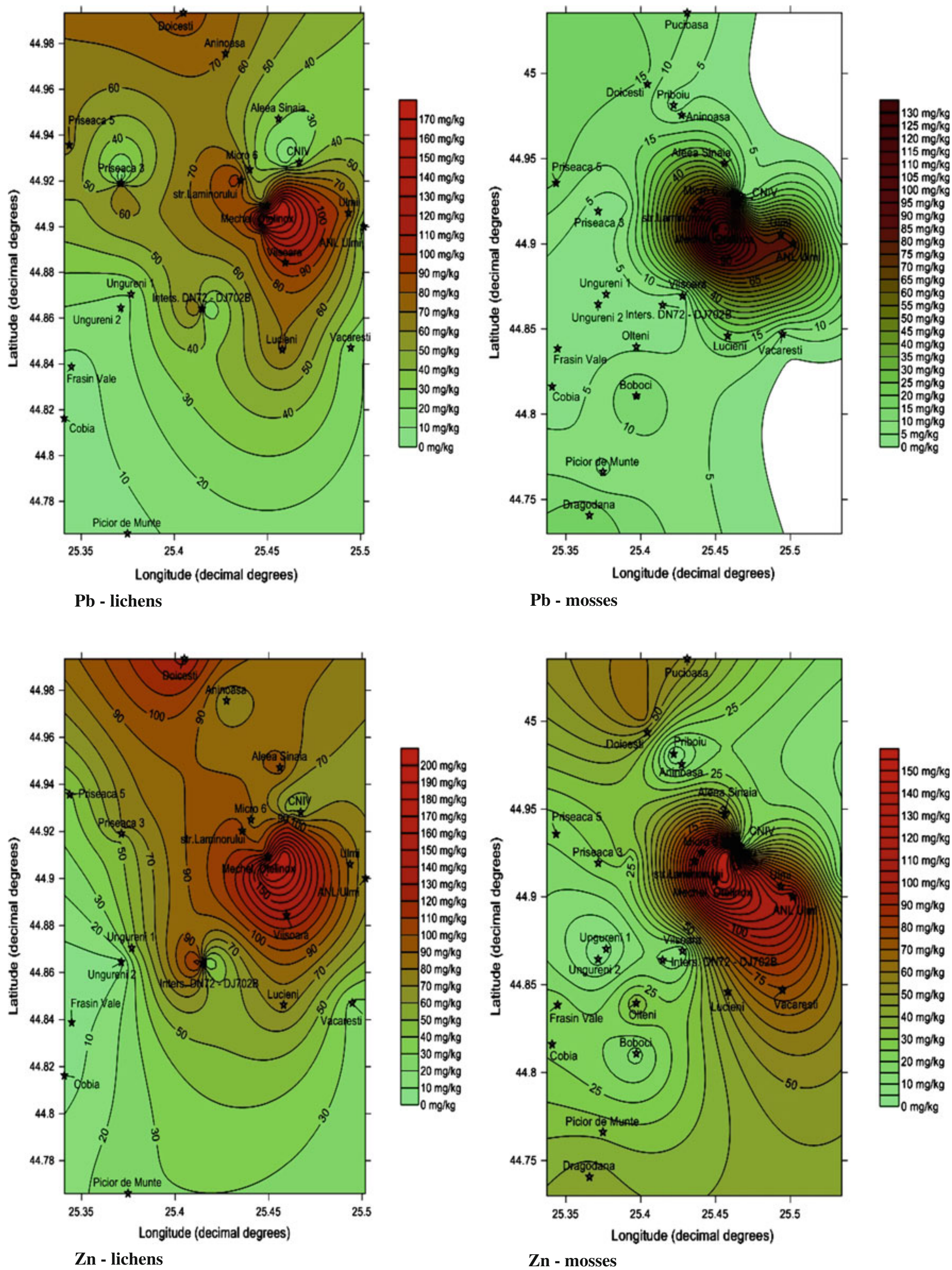

Fig. 3 Isoconcentrations maps of Pb and Zn in lichens and moss samples

References

Adamo P, Crisafulli P, Giordano S, Minganti V, Modenesi P, Monaci F, Pittao E, Tretiach M, Bargagli R (2007) Lichen and moss bags as monitoring devices in urban areas. Environ Pollut 146:392–399

Aničić M, Tasić M, Frontasyeva M, Tomasević M, Rajsić S, Mijić Z, Popović A (2009) Active moss biomonitoring of trace elements with Sphagnum girgensohnii. Environ Pollut 157:673–679

Bargagli R, Monaci F, Borghini F, Bravi F, Agnorelli C (2002) Mosses and lichens as biomonitors of trace metals A comparison study on Hypnum cupressiforme and Parmelia caperata in a former mining district in Italy. Environ Pollut 116:279–287

Brunialti G, Frati L (2007) Biomonitoring of nine elements by the lichen Xanthoria parietina in Adriatic Italy: a retrospective study over a 7-year time span. Sci Total Environ 387:289–300

Coskun M, Steinnes E, Cayir A (2009) Comparison of Epigeic Moss (*Hypnum cupressiforme*) and Lichen (*Cladonia rangiformis*) as Biomonitor Species of atmospheric metal deposition. Bull Environ Contam Toxico 82:1–5

Dymytrova L (2009) Epiphytic lichens and bryophytes as indicators of air pollution in Kyiv city (Ukraine). Folia Cryptogam Est 46:33–44

Dzubaj A, Bačkor M, Tomko J, Peli E, Tuba Z (2008) Tolerance of the lichen *Xanthoria parietina* (L.) Th. Fr. to metal stress. Ecotoxicol Environ Saf 70:319–326

Fernández J, Carballeira A (2001) Evaluation of contamination, by different elements, in terrestrial mosses. Arch Environ Contam Toxicol 40:461–468

Frontasyeva M, Nazarov V, Steinnes E (1994) Moss as a monitor of heavy-metal deposition—comparison of different multi-element analytical techniques. J Radioanal Nucl Ch 181:363–371

González-Miqueo L, Elustondo D, Lasheras E, Santamaría J (2010) Use of native mosses as biomonitors of heavy metals and nitrogen deposition in the surroundings of two steel works. Chemosphere 78:965–971