LICHENS AS BIOMONITORS OF HEAVY METAL AIR POLLUTION IN THE TARGOVISTE AREA

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Abstract: *In this work we have been used the advantages of EDXRF method to identify the presence of heavy metals (Cu, Fe, Pb and Zn) in the air of Targoviste town and its surroundings. The measurements were performed in the laboratories of the Faculty of Sciences and Arts from Valahia University of Targoviste. The samples have been taken from places with different levels of pollution.*

Keywords: *Lichen, EDXRF, air pollution, biomonitors, bioaccumulation.*

1. INTRODUCTION

Many air quality studies [1-4] are based on the using of biomonitors; the lichens take part from this category and they have been used in our study because of their presence in places with different levels of pollution from Targoviste and its surrounding areas (our study is referring to an area of about 300 km^2), at distances below 20 km (Fig.1).

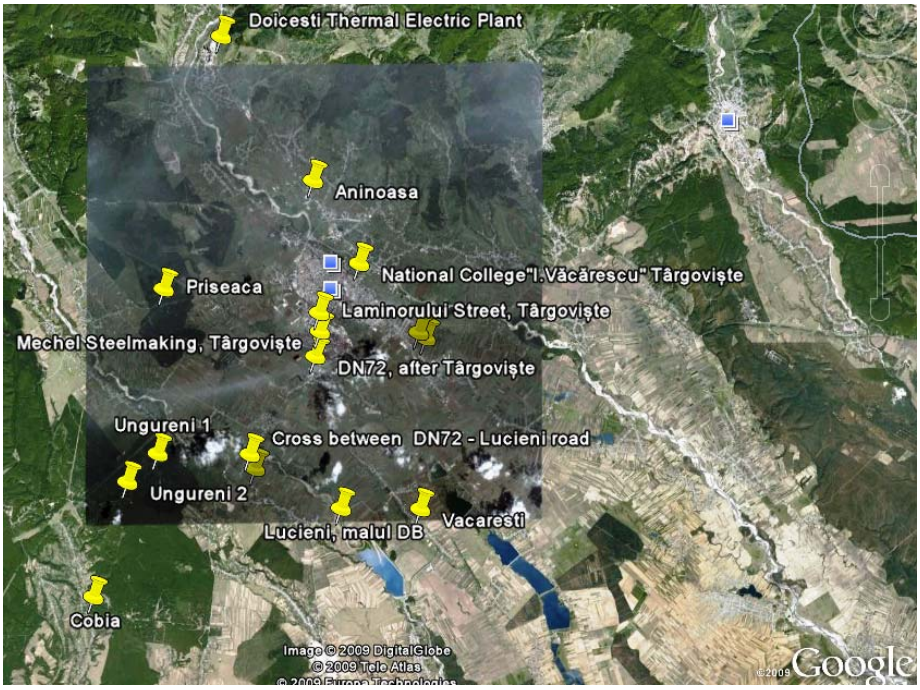


Fig.1. The places of lichens sampling from Târgoviste and localities around it (the map was exported from Google Earth)

Some of the advantages of their using are: higher area contact with atmosphere, slowly growing, insignificant change of their morphology, long life during the year, etc. Samples were collected in the interval 16th – 28th April 2009. Moreover, in order to achieve the elemental analysis with a high sensitivity and precision for the environmental samples, there can be used the Neutron Activation Analysis (NAA) [8], Chlorophyll Fluorescence(CF) [9] Electron Spectroscopy (ES) [10,11], Particle Induced X Ray Emission (PIXE) [12-14], Total Dissolved Solids (TDS) [15] and Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) [7,13].

2. SAMPLING AND INSTRUMENTS

The trees for the lichen sampling were chosen from the areas with different pollution levels: some were collected near the economical units which produce gaseous pollutants, others were taken near the roads which had different traffic values and the others were also collected from the forest, far away from any sources of pollution. Thus, we have the possibility to make a comparative analysis between heavy metal air pollution in those places. For each sample we recorded the following characteristics: the moment of sampling, the day, the name of the place and the GPS coordinates.

The lichen specie collected in our work was *Xanthoria Parietina*. As quality and quantity analysis we have been used the Energy Dispersive X-ray Fluorescence (EDXRF), which, although is not a very high sensitivity method, it have some advantages such as reduced time for samples preparation and obtaining experimental data, the simultaneous completion of qualitative and quantitative analysis, the possibility of interpretation and comparison of experimental data using specialized software, etc.

The samples were first washed with water then dried for 2 hours at 60^0 C. After that, a quantity of about 5g of every sample was powdered and put in clean testing chambers covered with 2.5 μm *Fluxana* TF-125-345 Mylar thin film to be studied by the EDXRF method. The data acquisition time was set to 5 min.

The *Elva X EDXRF* spectrometer have been used as analysis instrument, which has the energy resolution of 200 eV at 5.9 keV (^{55}Fe isotope). The instrument software provides the qualitative and quantitative analysis of the samples by quadratic stepwise multiple regressions.

3. ASSUMPTIONS AND THEIR CHECKS

We have verified the dependencies between element concentrations in lichens and their concentrations in soil and substrate (shell) samples collected from the same places.

The results from soil samples indicate that the element concentrations are about the same in all the cases and they can not influence the lichen concentrations ones, which are very different. In the case of elements concentrations from substrate, they are very different, having some of the higher values for samples that were collected from places with low pollution level.

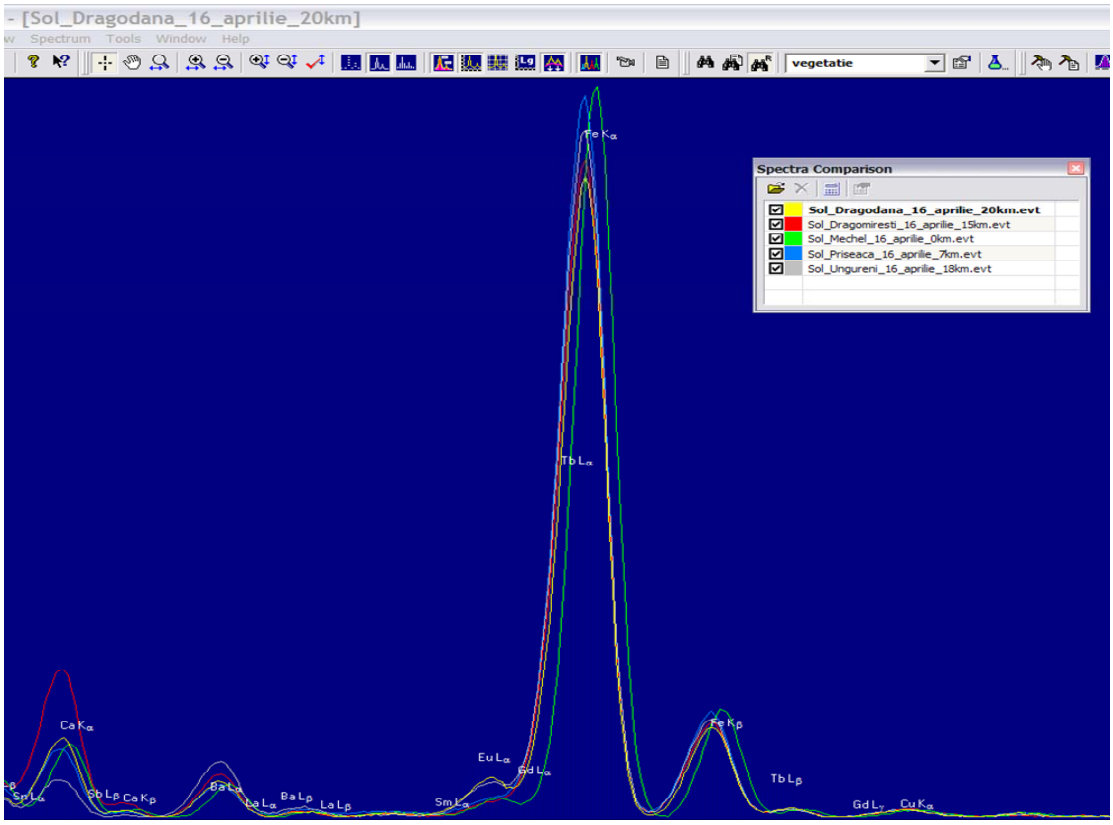


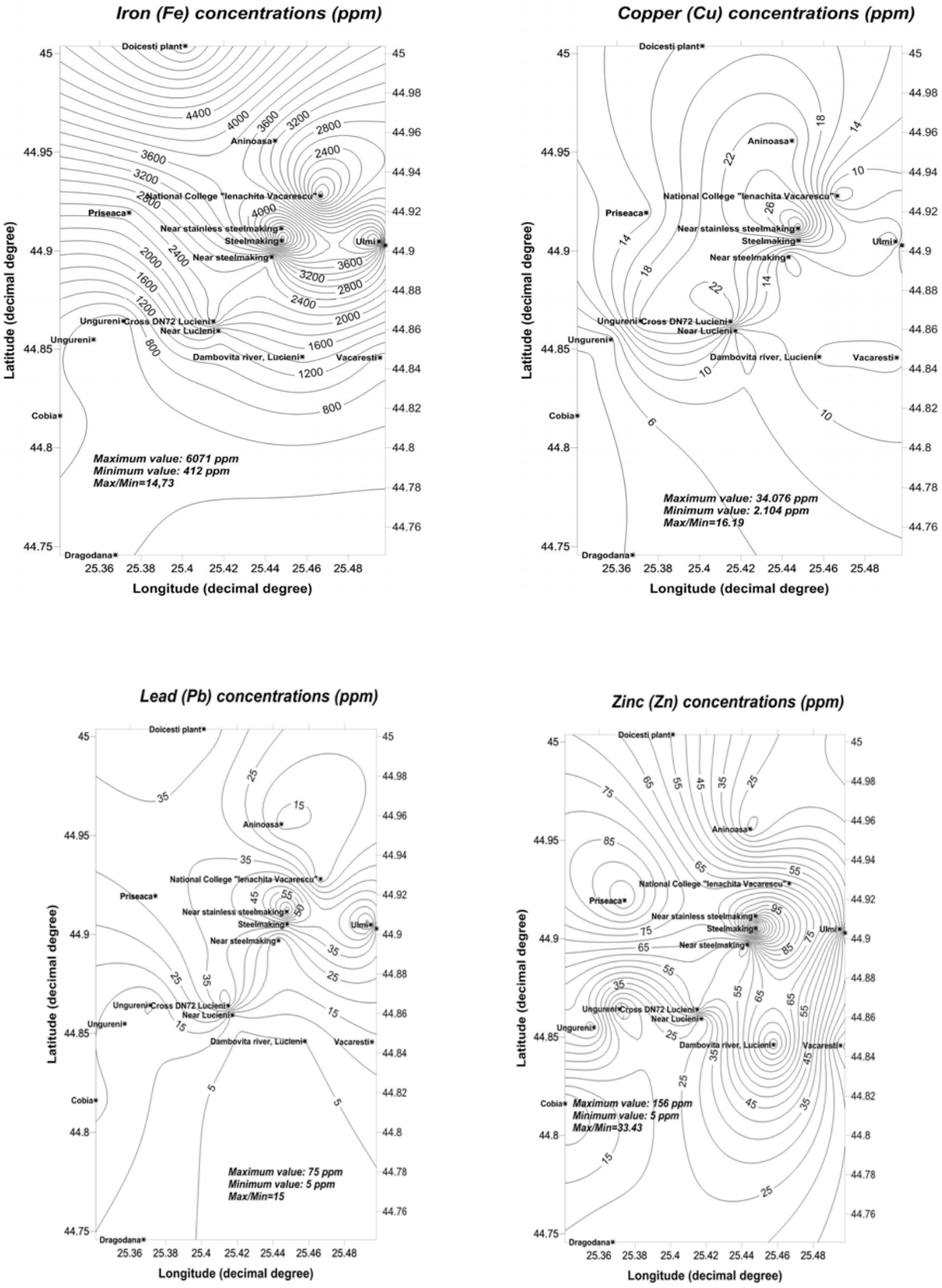
Fig.2.The element peaks in XRF spectrum of soil samples

Then we decide that this assumption may need future studies, but most probably these values can not influence the element accumulation in lichens (most of the elements comes from the air).

In the case of lichen samples, the concentrations decrease with distance from the sources of pollution.

4. RESULTS AND DISCUSSIONS

Figs. 3-6 shows the concentrations obtained by EDXRF methods for Cu, Fe, Pb and Zn from places referred by its GPS coordinates. In each graph the maximal and the minimal concentration (with errors below 8%) as well as the ratio between them is included.



Figs.3-6. The isoconcentrations curves of studied elements

Table 1. The extreme values of the element concentrations and their sampling places

Element		*Minimal value (ppm)*	*Error (ppm)*	*Maximal value (ppm)*	*Error (ppm)*	*Max/Min*
Cu	***c(ppm)***	2.66	0.14	34.08	2.3	12.81
	Place	Between Cobia and Dragodana, inside the forest		Steel factories Targoviste		
Fe	***c(ppm)***	412	28	6071	473	14.73
	Place	Ungureni, inside the forest		Steel factories Targoviste		
Pb	***c(ppm)***	5.00	0.45	75	7	15.01
	Place	Cobia, inside the forest		Steel factories Targoviste		
Zn	***c(ppm)***	5	0.22	156	7.02	31.20
	Place	Between Cobia and Dragodana, inside the forest		Steel factories Targoviste		

The samples concentrations of heavy metals such as Cu, Fe, Pb and Zn (Table 1) and the ratios between the maximum and the minimum value for every element clearly indicate the air pollution with these elements near steel and steelmaking factories, where the values are maximal, and the propagation of this effect at distances of about 10 km in open areas (without forests); it is also shown the positive effect of forestation revealed by the significantly lower values than those from open areas, at the same distance from the source of pollution.

5. CONCLUSIONS

The EDXRF as analysis method allows the qualitative analysis of elements with z>13 in lichen samples; if element concentrations are greater than 10 ppm, the EDXRF method also provides also a good quantitative analysis. The measurements are faster than the other methods, due to fact that is a multielemental analysis and require a reduced time for sample preparation. Then, even if EDXRF is not a high sensitivity method, it can be used in preliminary studies or to verify some assumptions.

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