Elements mapping in an industrial zone through the use of biomonitors

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Abstract: The industrial impact in a region of Asturias, Spain, was made by biomonitoring techniques. The biomonitors used in this work have been lichens. The lichens were collected in Montargil, an area considered to be clean, in relation to air quality, in April 2010. Its exposure occurred between April and September of same year. After lichens exposure, the study had three objectives, essentially: 1) explore spatial patterns of lichens conductivity in order to identify the impact of the industrial studied area; 2) study the spatial distribution of chemical elements concentrations (Al, Br, Cl, Cu, I, Mn, Na e V) determined by INAA technique; 3) establish a relationship between the distribution of conductivity and the concentrations measured in lichens and the characteristics of local sources. The obtained values confirmed that the highest conductivity coincided with the largest industrial zone in the study area. It was observed that the distributions of elements from the sea (chlorine, iodine and sodium) are identical. The highest elemental concentrations of pollutants (copper, manganese and vanadium) have focused on the industrial zone, more precisely, in metallurgy (emission source). Aluminum did not have a consistent distribution with any of the other elements, because it comes from the soil. Bromine is derived from a natural source (sea) and an anthropogenic source (metal production). One of the analyzed elements (calcium) was only identified in one of the points in the region; therefore, it was not made its mapping. However, this result was important to determine an emission source (sintering).

Keywords: Biomonitoring; Lichens; INAA; Pollutants; Sources; Mapping

1. Introduction

The biggest advantages of biomonitoring are its cheapness and ease of sampling. Lichens are the most valuable biomonitors, and these organisms are the result of a symbiosis between a fungus (mycobiont living) and one or more algae and / or cyanobacteria (photobiont living) [1,2].

Lichens are highly dependent on nutrients from the atmosphere, which makes also absorb pollutants. The morphology of lichens does not vary with the seasons, so the accumulation of contaminants is always happening. Lichens usually have a considerable longevity and are present in remote areas and in areas which are near from sources of pollution. These living beings are very sensitive indicators for different levels of pollution (even for low levels) [2].

For this work, the lichen species used was Parmelia sulcata, which exists in both hemispheres, from polar to temperate climates. This species is found in urban areas and is very resistant to a high rate of pollution [1].
The highest concentration of pollutants increases the stress of the cell membrane of lichens, which means higher values of conductivity in lichens. The increase of cell membrane permeability provides higher concentrations of chemical elements and compounds, including pollutants [1,2].

Biomonitors have a big disadvantage because it informs about pollutant concentration in lichen, and not in the air [1,2,3].

However, biomonitoring is an ideal technique to do a large area mapping, for long time periods. Biomonitors can assess the impact and the distribution of pollutants, as well as determine the contribution of different sources. Furthermore, this technique is more practical and cheaper [1,2,3].

2. Material and Methods

In this work, the geographical distribution of some elements (Al, Br, Cl, Cu, I, Mn, Na and V) were studied in an area that is located in the region of Asturias, Spain. This region is an attractive tourist area but, on the other hand, there is a considerable industrial impact (power plant, cement and metal production).

Lichens exposed in the study zone were transplanted from Montargil, in Portugal, which is an area considered “clean” for air quality [4].

The Figure 1 shows Montargil and exposed area.

2.1. Lichens Transplantation

Lichens were collected from olive trees, at 1.5 meters above the soil, in April of 2010.

Before its transplantation, 10 lichen samples were separated as reference base levels [5].

After one week, a total of 68 lichen samples (still attached to their substrate olive bark) with an average of 3.3 grams were exposed, fixed to a nylon rope at 1.5 meters above the soil [5]. From total samples, 61 were distributed in a rectangle with 18 per 21 kilometers (in a regular grid with 2.5 per 2.5 kilometers). The remaining 7 samples were closed to the emission sources: power plant, cement and metal production.

Lichens exposure has started in April 27th and has ended in September 14th of same year.

2.2. Lichens Preparation

After its exposure, lichen samples were firstly cleaned from dust, leaf debris and degraded material, in the laboratory [5].

2.2.1. Lichens Preparation for Conductivity Measurement

Lichen material was cleaned and rinsed rapidly with deionized water, two to three times for 5 seconds. After drying, about 1 gram was weighed and immersed in 100 milliliters of demineralized water during, exactly, 1 hour. After removal of the lichens, the electric conductivity of the solution was
2.2.2. Lichens Preparation for Chemical Analysis

Lichens were freeze dried and ground in a Teflon ball mill, cooled with liquid nitrogen. After homogenizing the lichen material, it was prepared for irradiation with 100 to 150 milligrams, in ultrapure polyethylene containers [8,9].

2.3. Chemical Analysis

The determination of elemental concentrations was made using INAA technique (Instrumental Neutron Analysis Activation) with the absolute method, Factor $k_0$. This work was done in Portuguese Research Reactor, in Sacavém.

Two reference materials (NIST-SRM-1572 Citrus Leaves [10] and lichen IAEA-RM-336 [11]) were irradiated just to do quality control. For this absolute method, it was used a comparator (gold alloy with aluminum, IRMM-530RA [12]), which was irradiated on each work day.

Samples, reference materials and comparator were irradiated for 30 seconds in Portuguese Research Reactor, whose neutron flux was $2 \times 10^{16} \text{ m}^{-2} \text{s}^{-1}$, approximately. After irradiation, materials were measured in an hyperpure germanium detector.

Samples and reference materials were both measured twice: 1) first measurement was 5 minutes after irradiation and its length was 5 minutes, with the aim to get elements like Al, Cu and V (half-life times between 2 and 9 minutes [13]); 2) second measurement was 30 to 60 minutes after irradiation and its length was 10 minutes, with the aim to get the other elements (half-life times between 17 minutes and 15 hours [13]). The comparator was measured once, for 5 minutes, a few hours after irradiation (half-life time is 2.7 days [13]).

After measurements, the concentrations of different elements were determined at software $k_0$.

2.4. Mapping

Mapping of different elements and electrical conductivity was made with software GeoMS.$^{24}$

3. Quality Control

It was calculated the ratio between values obtained by absolute method and certified value, for both reference materials.

Results were approved for a maximum deviation about 25%, which was confirmed, and as shown in Figures 2 and 3.

4. Results and Discussion

4.1. Conductivity

Figure 4 shows the highest values in industrial zone (10 times bigger than the other exposed lichens).
4.2. Elemental Concentrations

4.2.1. Aluminum

Like as shown in Figure 5, aluminum concentration is not related with the big industrial zone in study area. In fact, the source of this element is soil, which means its concentration is just associated to the geology of the region.

Biggest value of aluminum coincides with a landfill, where there is deposition of soil and then dispersion of particles. There is in that zone an industrial polygon (Silvota polygon) and, in west from study region, there is an aluminum factory. These are three reasons for highest value of aluminum.

4.2.2. Bromine

Figure 6 shows a highest value of bromine in metal production and large values are present in highways, which show this element comes from combustibles and metal processes. This element has a natural source too (sea).

4.2.3. Chlorine, Iodine and Sodium

These three elements have the same source, the sea, like as shown in Figures 7 to 9. There are large values in the seaside but, the biggest ones are close from the metal industry and in land. The region’s relief is an explanation for what happened. These elements come from solid combustibles and reutilized products in industry, too.

4.2.4. Copper, Manganese and Vanadium

These three elements are pollutants and have the same source, metallurgy. Copper has large values in Silvota polygon and vanadium has another emission source (power plant). The results are shown in Figures 10 to 12.

5. Conclusion

Lichens are very sensitive and resistant to particulate concentrations in the atmosphere and, therefore, can also be transplanted to other locations, with the aim of studying the air quality.

The altitude and the wind are two important factors in geographical distribution of particles.

The result obtained in the mappings was minimally expected, showing the studied pollutants were derived from an anthropogenic source in common, the metal industry.

Aluminum distribution does not match with any of the other elements, because it comes from the soil, which means it depends of soil geology. Higher values of aluminum can be explained by landfill and aluminum factory in west from study area.

Sodium, chlorine and iodine come from the sea and their geographical distribution is identical.

Iodine and bromine are both from natural sources (sea) and anthropogenic sources (metal industry).
In Figure 4, there are red spots in the metal production and power plant areas, which mean electrical conductivity is a good parameter to indicate pollution.

Figure 1 – Origin of the lichens (1) and study area (2) (Adapted [5])

** - Consensus values [14]
Figure 2 – Quality control for Citrus Leaves: average (center), bars (standard deviation)

* - Informative values [11]
Figure 3 – Quality control for IAEA-336: average (center), bars (standard deviation)
Figure 4 – Electrical conductivity mapping

Figure 5 – Aluminum concentration mapping
Figure 6 - Bromine concentration mapping

Figure 7 - Chlorine concentration mapping
Figure 8 - Iodine concentration mapping

Figure 9 - Sodium concentration mapping
Figure 10 - Copper concentration mapping

Figure 11 - Manganese concentration mapping
Figure 12 - Vanadium concentration mapping

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