CONTRIBUTION TO THE KNOWLEDGE OF AIR QUALITY IN A HIGHLY INDUSTRIALIZED SITE (TARANTO CITY, ITALY), BY BIOMONITORING TECHNIQUES

Extended abstract

Micaela Buonocore*, Cristina Annicchiarico, Nicola Cardellicchio, Antonella Di Leo, Santina Giandomenico, Lucia Spada

CNR- Institute for Marine Coastal Environment, via Roma 3, 74123 Taranto, Italy

Background

The city of Taranto (Southern Italy), close between large industrial plants is considered among the Italian cities most at risk of pollution, due of increased release of toxic substances in the environment. Monitoring of air quality, therefore, represents a problem of primary importance.

Traditional techniques are based on the use of monitoring stations and physical chemical methods.

The use of bioindicators is of considerable interest because it allows measurements on a large scale, relatively quickly at low cost. In particular, the use of mosses has gone increasingly spreading in monitoring high-risk areas for the environmental capacity to absorb atmospheric pollutants and provide integrated responses on the air quality, although there are critical issues regarding different storage capacity of the species used and the influence of environmental factors.

Mosses are used to study pollution in the surroundings of particular industrial plants (e.g., thermal power plants, steel works, metal smelters, cement works etc.) and their use in metal pollution monitoring was of significant importance, and subject of several, though limited, reviews (Fernandez et al., 2007).

These organisms are used as bioindicators and bioaccumulators. In the later case, the most commonly used biomonitoring techniques are of two types: active, taking advantage of carpets of mosses transplanted or using moss bags and passive ones that rely on indigenous/native peoples.

The first allow to obtain information concerning the effects of pollutants on the ground assessing the air quality as a whole, even in areas lacking or deficient in mosses. The majority of investigations have utilised epiphytic mosses as Hypnum cupressiforme, Hylocomium splendens and Pleurozium schreberi; these were widely used in Europe due their abundant (Gerold et al., 2000; Oniawa, 2001).

Among the pollutants, "heavy metals" are of particular interest (Schilling and Lehman, 2002) whose presence in particulate atmospheric is the result of complex interactions between natural and anthropogenic factors.

This paper illustrates the use of mosses in the monitoring of air quality in a highly contaminated industrial site. The obtained results, using mosses as biomonitors of trace metals, were compared with the data of atmospheric distribution of particulate matter (ISPESL, 2006).

Objectives

The purpose of this study was to evaluate the atmospheric deposition of heavy metals by native species, Hypnum cupressiforme and Pleurochaeta squarrosa, in four stations in Taranto area applying both active and passive biomonitoring techniques, to include the area of Taranto in a national network of biomonitoring.

The metals analyzed were chosen in relation to toxicity and specific situations of industrial pollution and vehicular traffic. It was set up a "network of biomonitoring" using mosses collected in contaminated areas.

The analyses were carried out in several seasons and in different environmental conditions.

* Author to whom all correspondence should be addressed: e-mail: buonomicaela@libero.it
Methods

The *Hypnum cupressiforme* for the preparation of moss bags and for active sampling, was collected in the woods Orimini (Martina Franca, Taranto), an area chosen because of funds not subject to obvious contamination. The carpets of moss were collected from the trunk of most trees and in different parts of the logs. In the laboratory, the mats of moss were subjected to a coarse cleaning and washing were performed seven successive period of ten minutes each, in order to enhance removal of metals, and especially metals associated with atmospheric particles. Finally, the washed material was dried in air. The development of moss bags was, made using pieces of nylon mesh particle 10x10 cm, with mesh 2.1 mm, previously conditioned with a solution of HNO$_3$ 10%, closed with a nylon thread to form spherical bags having diameter of 3-4 cm; in each bag was placed a quantity of moss equal to 400 mg. The moss bags were placed in four sampling stations of Taranto city (Fig. 1): Villa Peripato (city center), Piazza Garibaldi square (city center), Tamburi district, Paolo VI district at a height of 1,5-2 m from the ground. They were attached using nylon thread in support present in the monitoring stations placed in the sampling stations; before each exposure moss bags was carefully moistened with distilled water. The exposure period was six weeks and were carried out two rounds of exposure in two different seasonal periods: spring and summer. After exposure the moss bags were collected and placed in polyethylene containers. In the laboratory *H. cupressiforme* was removed from the bag and placed in a crystallizer and dried at 45 °C for 48 hours in an oven thermostat. In addition, a sample portion was dried at 105 °C to assess the loss of water.

The tissues were then ground in a centrifugal ball mill and stored in polyethylene containers, previously conditioned with 10% HN0$_3$, until mineralization in a microwave oven. For the determination of metals 0.25 g of each sample were then taken to the mineralization (2.5 ml of 30% H$_2$O$_2$ and 5 ml of concentrated HNO$_3$) with microwave model MARS X (CEM Corporation). The digestion of the soil was performed by placing 0.25 g of sample in Teflon containers (PTFE), in which were later added 9 ml 70% HNO3 and 3 ml HF 50%. The determination of mercury was performed using automated mercury analyzer (Advanced Mercury Analyzer AMA 254). For quantification of Cd, Cu, Zn, As, Pb, Ni, V, Pt, Pd, Cr, Mn, Al and Fe was used ICP-MS. For passive sampling *H. cupressiforme* and *P. Squarrosa* species were used. Only Villa Peripato has been selected as station of sampling because results to be the more one contaminated by heavy metals by previous studies (Buonocore et al., 2010). In the laboratory to obtain a sample of moss as homogeneous as possible we chose to take only the apical part (1-1.5 cm), green or yellow-green probably corresponding to the biomass produced during the last two years, until obtain at least 3 grams of sample. The analyses did not reveal any correlation between the analyzed metals and Al, so it was not necessary to apply the fix from contamination by soil.

Results and discussion

The moss bags analysis shows that in all stations there was an increased level of metals in *Hypnum cupressiforme* compared to blank. In particular levels of Ni are about ten times higher than the blank, those of Cd, As, V approximately six times; the levels of Zn, Hg, Al, Cr, Cu m, Fe and Mn are increased by three times while the Pb twice. High concentrations of metals were found in urban zone (Villa Peripato and Tamburi stations); the first levels of concentration for metals follow the order: Al>Fe>Mn>Zn>Cu>Pb>V>Cr>Ni>Cd>As>Pd>Hg. The highest concentrations of Cd, Ni, Al, Cr, As, Mn, V were found mainly in the sampling station of Villa Peripato while in the station of Tamburi district (near the industrial area) higher levels of Hg, Zn, Cr and Cu were found. In the summer, values of concentration of metals were reported even higher and levels follow more or less the same trend that you had in spring: Al>Fe>Mn>Zn>Pb>Cu>V>Cr>Ni>As>Cd>Pd>Hg.

Particularly in the station Tamburi were found higher concentrations of Zn>Cr>Fe>Mn>Pb and V. In the station of Villa Peripato and Tamburi district were found higher values of Al, Hg while V and Pb have the same concentrations in the stations of Villa Peripato, Piazza Garibaldi and Tamburi district. Regarding Cd, there was a decrease of concentrations at all stations, this could be justified by the fact that during the summer the source linked to the traffic impact is a lesser extent than the industry, as a result of repayment of the population in places tourism.
For Zn was found the same behavior except the Tamburi district station, located near the industrial zone, where it was observed an opposite situation.

Analytical results show that the most contaminated areas are to be urban areas where there is the influence of industrial pollution, vehicle traffic and harbor activities. In the station of Paolo VI, located to the northeast of the industrial area of Taranto, these contributions are approximately the same order of magnitude of other stations, although the concentration levels are lower because, due to the wind direction, remains on the edge of the polluted area for much of the year.

Rainfall in spring was higher than in the summer and this has negatively affected the uptake of metals sampling in the summer, promoting leaching. The obtained results with the active biomonitoring (moss-bags) using the moss *H. cupressiforme*, show that the most contaminated station is found to be Villa Peripato followed from the Tamburi district. In the second experiment, therefore, it was decided to carry out the passive biomonitoring only in the most contaminated area (Villa Peripato) using the same species of moss grown naturally (*Hypnum cupressiforme*).

The obtained data show that the epiphytic moss, in the passive sampling, has a higher bioaccumulation capability than that obtained in the active sampling with moss bags. For both types of biomonitoring, however, the order of the bioaccumulation levels of metals is the same: Al > Fe > Mn > Zn > Cu > Pb > V > Cr > Ni > Cd > As > Pd > Hg. A further comparison was carried out between the *H. cupressiforme* and another species of epiphytic moss present in the selected station (*P. squarrosa*).

The purpose was to compare the bioaccumulation capability between the two species of mosses. The sampling was carried out in two different seasons (spring and summer). For example, in Fig. 2, it are shown the results obtained: both species of mosses have a good bioaccumulation capability.

![Fig 2. Comparison in passive biomonitoring between *H. cupressiforme* and *P. squarrosa* for Cd, Hg, As, Pd](image)

As regards the following metals: Ni, Zn, Al, Cu, Pb, Cr and Hg result bioaccumulated in greater measure from the *H. cupressiforme* while Pd, As, Fe, Mn, Cd, V bioaccumulated mostly from the kind *P. squarrosa*.

This data are comparable with obtained data in active biomonitoring, in both cases Villa Peripato results to be the most contaminated area from heavy metals. Furthermore, data from ISPESL (National Institute for Prevention and Safety at Work) referring that concentrations of PM10 (mg/m3) detected by automatic monitoring systems of atmospheric pollution in Taranto area, show that Villa Peripato station is the most contaminated site in comparison to the Tamburi and Paolo VI stations.

Statistical analysis

The results of active biomonitoring were statistically processed, by testing the linearity of Pearson coefficient; analysis was performed (p <0.05) between the concentrations of metals in samples of *Hypnum cupressiforme* in both samples for the four monitoring stations.

Moreover, experimental data were processed by multivariate statistical analysis using the program STATISTICA (StatSoft Inc., Tulsa, OK, USA). The cluster analysis (HCA) was applied to a given set of four samples and 13 variables (Hg, Cd, Cu, Zn, As, Pb, Ni, V, Pd, Cr, Mn, Al and Fe). Tables 1 show the correlations between metals in the four stations sampled in spring and summer respectively.

The high correlation coefficient between the elements shows their common origin: V, Pb and Cd originating from petroleum refining processes, the same is true for As, Mn and Fe that may result from emissions from iron and steel center.

These metals are associated not only to particulate air pollution arising from industrial activities, but also arise in relation to vehicular traffic. Through dendrograms reveals that stations Garibaldi Square and Paolo VI district are correlated, in both samples, having similar levels of concentration and lower than the other two stations.

In fact in the spring sampling station of Villa Peripato is the most polluted sampling while in summer the same situation occurs for the station of Tamburi district. Marked correlations are significant at p < 0.05.
Table 1. Pearson product moment correlation coefficients between metal levels in sampling stations during spring and summer period in active biomonitoring

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Concluding remarks

The results obtained using *Hypnum cupressiforme* and *Pleurochaete squarrosa* as biomonitor for heavy metals are comparable with the data of atmospheric distribution of particulate supplied by ISPESL data. Heavy metals are good environmental indicators because they do not undergo degradation processes, are readily ascertainable from the analytical point of view and can be considered as typical tracers of contamination of the process of air pollution.

Moss-monitoring using *Hypnum cupressiforme* and *Pleurochaete squarrosa*, offers a more cost-efficient method with less available technology. It also allows to identify problem areas and local sources of emission. As a consequence it is recommended for ecological monitoring at a national and local scale. Both the active and passive biomonitoring, show good results for the determination of metal contamination in the atmosphere. The techniques are readily reproducible and low cost and can be used now commonly in other parts of the world. The active biomonitoring has as advantage, compared to the passive, the possibility of being able to be applied anywhere you want. For passive monitoring it is necessary that the moss is present in the chosen area. It is not always possible, however, find mosses growing in industrial areas. However, overall, the data obtained are in agreement with the literature for various Italian and European cities. This study provides a methodological approach that can monitor the environmental quality of areas at risk by entering the city of Taranto in a national network of biomonitoring.

**Keywords:** air pollution, biomonitoring, bryophyte, heavy metals, mosses.

**References**


