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Spatiotemporal distribution of airborne elements monitored with the moss bags technique in the Greater Thriasion Plain, Attica, Greece

C. J. Saitanis · M. V. Frontasyeva · E. Steinnes · M. W. Palmer · T. M. Ostrovnaya · S. F. Gundorina

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Abstract The well-known moss bags technique was applied in the heavily polluted Thriasion Plain region, Attica, Greece, in order to study the spatiotemporal distribution, in the atmosphere, of the following 32 elements: Na, Al, Cl, Ca, Sc, Ti, V, Cr, Mn, Fe, Ni, Co, Zn, As, Se, Br, Sr, Mo, Sb, I, Ba, La, Ce, Sm, Tb, Dy, Yb, Hf, Ta, Hg, Th, and U. The moss bags were constituted of *Sphagnum girgensohnii* materials. The bags were exposed to ambient air in a network of 12 monitoring stations scattered throughout the monitoring area. In order to explore the temporal variation of the pollutants, four sets of moss bags were exposed for 3, 6, 9, and 12 months. Instrumental neutral activation analysis was used for the determinations of the elements. The data were analyzed using the Pearson correlations, the partial redundancy analysis, and the biplot statistical methods. Some pairs of elements were highly correlated indicating a probable common source of origin. The levels of the measured pollutants were unevenly distributed throughout the area and different pollutants exhibited different spatial patterns. In general, higher loads were observed in the stations close to and within the industrial zone. Most of the measured elements (e.g., Al, Ca, Ni, I, Zn, Cr, and As) exhibited a monotonic accumulation trend over time. Some elements exhibited different dynamics. The elements Mn, Mo, and Hg showed a decreasing trend, probably due to leaching and/or volatilization processes over time. Na and Br initially showed an increasing trend during the winter and early spring periods but decreased drastically during the late warm period. The results further suggest that the moss bags technique would be considered valuable for the majority of elements but should be used with caution in the cases of elements vulnerable to leaching and/or volatilization. It also suggests that the timing and the duration of the exposure of moss materials should be considered in the interpretation of the results.

Keywords Pollution · Heavy metals · Sodium · Aluminum · Chlorine · Calcium · Scandium · Titanium · Vanadium · Chromium · Manganese · Iron · Nickel · Cobalt · Zinc · Arsenic · Selenium · Bromine ·

C. J. Saitanis (✉)
Agricultural University of Athens,
Iera Odos 75 Votanikos,
11855 Athens, Greece
e-mail: saitanis@aua.gr

M. V. Frontasyeva · T. M. Ostrovnaya · S. F. Gundorina
Joint Institute for Nuclear Research,
141980 Dubna, Russian Federation
e-mail: marina@nf.jinr.ru

E. Steinnes
Department of Chemistry,
Norwegian University of Science and Technology,
7491 Trondheim, Norway
e-mail: eiliv.steinnes@chem.ntnu.no

M. W. Palmer
Department of Botany, Oklahoma State University,
Stillwater, OK, USA

Strontium · Molybdenum · Antimony · Iodine · Barium · Lanthanum · Mercury · Uranium

Introduction

Increased levels of heavy metals have been monitored in many urban and industrial areas but also in rural towns of Greece (Riga-Karandinos and Saitanis 2004; Riga-Karandinos et al. 2006; Massas et al. 2009, 2010). Air quality assessment based on instrumental monitoring is highly accurate but it has many disadvantages (i.e., high cost, need of technical support, etc.). An alternative and widely accepted way to assess metal pollution is by conducting "biomonitoring", that is, by measuring the accumulation of several elements, including radionuclides, in biological materials, such as leaves of higher plants or tissues of lichens or mosses (Goodman and Roberts 1971; Pilegaard 1979; Mäkinen 1987, 1994a, b; Riga-Karandinos and Karandinos 1998; Ellis et al. 2007; Cristofolini et al. 2008; Sawidis et al. 2009). Due to their unique morphological features, moss tissues materials are utilized, either "in situ" or "transplanted", in biomonitoring studies of airborne persistent pollutants (Cuny et al. 2004; Harmens et al. 2008; Tretiach et al. 2011; Harmens et al. 2011). In situ monitoring refers to the observation or chemical analysis of indigenous (naturally grown) mosses in the area under investigation (Steinnes et al. 1992) while "transplanted" refers to the use of moss material collected elsewhere, in a clean area, and intentionally exposed to monitor air quality in the polluted area under investigation (Godinho et al. 2004, 2009; Cao et al. 2009). The later technique is often the only possible approach to trace airborne pollutants in urban and remote areas (Sardanas and Penũelas 2005; Giordano et al. 2009) since it overcomes the problem of lack of indigenous moss species, especially at relatively highly polluted urban areas with unsuitable climatic and environmental conditions (the so-called moss deserts) (Giordano et al. 2009; Cao et al. 2009). The moss bag technique was originally introduced by Goodman and Roberts (1971) and later modified by Little and Martin (1974). This technique allows a relatively inexpensive simultaneous monitoring of a large number of elements, in a great number of sites; such wide range monitoring could not be practically conducted by sophisticated high-tech methods. It also allows repeated assay of the same elements, in the same places, with identical samplers (moss bags), thus achieving results comparable over time.

In the framework of this investigation we utilized the above mentioned advantages of the "moss bags" technique to explore the spatial and temporal distribution of a wide variety of airborne trace elements in a heavily polluted area in Greece where they have never been studied before. The primary questions to be answered were: (1) which of the monitored pollutants occur at measurable (by the moss bags technique) levels in air in the study area? (2) Are all the pollutants observed evenly distributed throughout the area? (3) If not, do all the pollutant elements exhibit the same uneven spatial pattern, or are some pollutants associated with specific monitored sites (suggesting some nearby pollution source)? (4) Is there any variation of pollutant levels over time, and if yes, is it a monotonic one? (5) Do all the pollutant elements follow the same temporal variation?

Materials and methods

Study area

The investigation was conducted in the highly populated Thriasion-Elefsis basin located west of Athens Metropolitan City. The area covers ca. 345 km^2 including industrial, urban, suburban, and rural districts (Lykoudis et al. 2008); 20.6% of this area is cultivated land, 35.4% is pastures, 29% is forests, and 4.4% is urban area (Karavitis et al. 2001). The total population in the area is around 78,000. Geographically, the area is separated into four municipalities, namely Elefsis (26,000), Aspropyrgos (28,000), Mandra (13,000), and Nea Peramos (7,000), and the community of Magoula (4,000) (2001 census in parentheses). All these people are obviously potentially impacted by the pollutants occurring in the greater region. Moreover, taking into account that the pollution of the region is transferred to the nearby metropolitan areas of Athens, (~4,000,000) (Asimakopoulos et al. 1992), the total population exposed to the pollution originating in this area is quite large.

Concerning the topography, the area is separated from Athens by the Egaleo Hills to the east; it is limited by a mountain chain (Parnitha Mt.) to the north and northwest, while to the south it opens to the Bay

of Elefsis. The basin is almost flat, with a slope <3% towards the sea (Lykoudis et al. 2008) (Fig. 1).

Unlike Athens, where air pollution is mainly due to traffic, in the Thriasion Plain air pollution is clearly due to industrial activities (Mavrakis et al. 2005). Thriasion Plain probably exhibits the highest (a) industrial activity concentration, (b) fuel consumption, and (c) pollution related to the production processes, in all Greece (Lykoudis et al. 2008). The region has some of the largest industries of the country, among which two oil refinery plants, two steel plants, two cement plants, an ammunition factory, and two big shipyards. In addition, a number of chemical, mechanical, transportation, tire, and plastic industries have been established. The majority of these activities are concentrated near the coastal part of the plain, within an area of approximately 100 km^2. This coastal part includes 25 km^2 of industrial areas, 15 km^2 of urban development, and 12 km^2 of a military airport (Karavitis et al. 2001). The 15 km coastline is mainly occupied by 13 harbor and docking facilities, serving about 5,500 ships per year. The operation of industrial activities over several decades in the Thriasion-Elefsis Basin and the local traffic, along with the two national roads passing through the region, have resulted in a high pollution pressure on the area.

The local Bureau of Pollution Control and Environmental Quality of the Development Association of the Municipalities and Communities of the Thriasion Plain (GERPPE) has established a network of four monitoring stations equipped with automatic monitors to assess the air pollution levels in the region and to follow up trends in air quality over time. Based on the monitored air pollutants, GERPPE has shown that the main contributor of pollution is the local industry. However, this instrumental monitoring is restricted to a limited number of gaseous pollutants (O_3, NO, NO_2, SO_2, CO, and HCs) and the total concentration of dispersed particles (Mavrakis et al. 2008; Lykoudis et al. 2008). Several studies have shown high levels of metal pollution in the water and sediments of the Bay of Elefsis (Abatzoglou 1987; Mavrakis et al. 2004). It is reasonable to assume that these metals may have reached the Bay water and sediment not only through effluent water but also directly through atmospheric deposition.

Preparation of moss bag samplers

Moss bags are low technology samplers consisting of mesh or grid bags, generally made of nylon, and filled with properly pre-treated material of a suitable moss species, collected from areas negligibly (or not at all) influenced by airborne trace elements. Moss bags have high collection efficiency for most elements and eliminate the possibility of contamination via root uptake (Culicov & Yurukova 2006). Moreover, in comparison with dust fall jars or bulk samplers, they offer lower cost and higher efficiency (Adamo et al. 2003). Material from *Sphagnum* moss species is particularly suitable for the moss bag method due to its very high element retention properties (Clymo 1963).

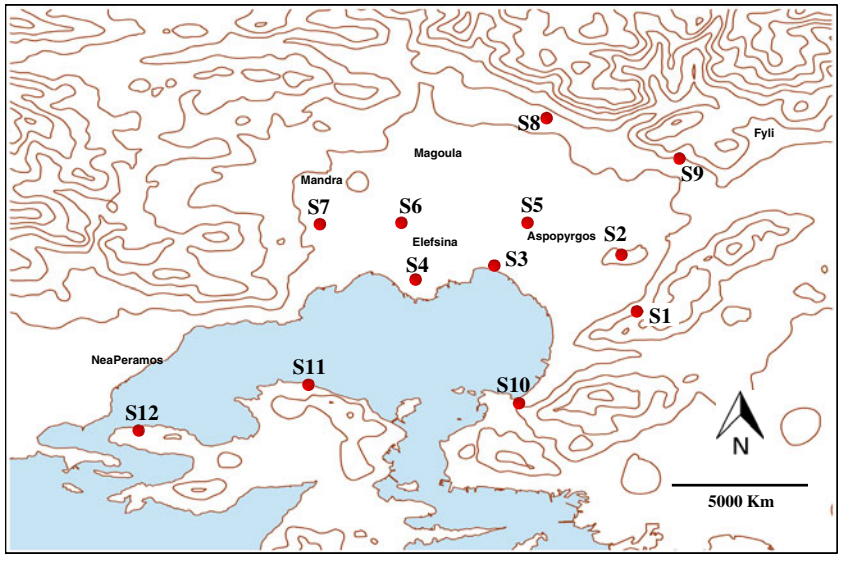

Fig. 1 Map of the investigated area; the *numbers* indicate the monitoring sites as they appear in the other partial RDAs and cluster analyses

For this study, we used the moss *Sphagnum girgensohnii*, Russow, which is easy to identify and to handle in the laboratory and has been repeatedly used in other biomonitoring studies with moss bags (e.g., Culicov et al. 2005; Aničić et al. (2009a, b). Materials of this species were collected from a pristine wetland area located near Dubna, Russian Federation (Lat.=56°44′ N, Lon.=37°09′ E, Alt.=120 m). This area is considered uncontaminated of airborne elements; materials from this area have been previously successfully used by Culicov et al. (2005) and Aničić et al. (2009a, b). Apical sections (3–4 cm) were separated from the shoots of the moss, cleaned carefully from adhering soil particles. Exclusive use of apical sections eliminates the variability of moss samples since it is known that the concentrations of element is higher in the older parts of the mosses than in the younger tissues (Grodzinska et al. 1990; Bargagli et al. 1995). The moss materials were washed with bi-distilled water for 30 min with shaking to eliminate any remaining foreign matter, and then air-dried at 50°C for 24 h. About 3 g of air-dried moss material was packed in 10×10-cm bags made of nylon mesh (6.5 mesh/cm) and stored in sealed plastic envelopes at room temperature until exposure.

Sample exposure scheme

Using maps and taking into account the landscape characteristics, and the spatial distribution of industries and restricted military areas, 12 monitoring sites scattered throughout the Thriasion-Elefsis basin where selected to form a balanced and effective monitoring network (Fig. 1). The coordinates of the sampling sites were recorded with a GPS (model Garmin Etrex Legend H) to allow re-location of the sites on the future visits (Table 1). The network was established in October 2004, when 96 moss bags where simultaneously exposed at all monitoring sites (eight moss bags at each site).

The bags were hanged on tree branches at a height of ~2 m above the ground. The branches where carefully selected so to jut out of the canopy; any other branches above and close beside were removed to leave the moss bags freely exposed to ambient air. In order to explore the temporal variation of the trace elements, the bags were collected at four different times (I, II, III, and IV), after 3, 6, 9, and 12 months of exposure, respectively (two bags per station per time). The collected moss bags were stored at room temperature in sealed plastic envelopes until chemical analysis.

Chemical analyses

The determination of minor and trace elements in the moss samples was carried out by instrumental activation analysis using epithermal neutrons (ENAA) (Brunfelt and Steinnes 1969), according to a procedure described by Frontasyeva and Pavlov (2000). The following 32 elements were determined: Na, Al, Cl, Ca, Sc, Ti, V, Cr, Mn, Fe, Ni, Co, Zn, As, Se, Br, Sr, Mo, Sb, I, Ba, La, Ce, Sm, Tb, Dy, Yb, Hf, Ta, Hg, Th, and U. The detection limits varied among the elements and ranged from 0.01 to 10 $\mu g\ g^{-1}$. Short-term irradiation (2 min) was used to determine elements associated with short-lived radionuclides (e.g., Al, V, and Mn) while long irradiation (100 h) was used to determine elements associated with long-lived radionuclides (e.g., Na, Cr, Fe, Ni, Zn, and As) (Aničić et al. 2009a, b). Each sample concentration measurement was repeated three times. All concentrations were reported as mean values on a dry weight basis ($\mu g\ g^{-1}$ dw).

Quality control

Quality control of the analytical procedures was performed by analyzing, with the same procedure used for the samples, three international reference samples of moss (Steinnes et al. 1997) and a sample of tea leaves GBW-07605 (Institute of Geophysical and Geochemical Exploration, Langfang, China). The reference materials were also analyzed in triplicate; the results ranged between 90 and 115 % of the certified values for the elements concerned.

Statistical analysis

Based on the initial data, we prepared maps for each element separately for each monitoring period to depict spatiotemporal patterns. All pair-wise Pearson correlations between elements were calculated on the initial data. Prior to multivariate analysis, the concentration values were log-transformed, as they varied by orders of magnitude (cf. Palmer 1993). We employed partial redundancy analysis (pRDA) (Borcard et al. 1992; Lepš and Šmilauer 2003) to evaluate the spatial and temporal distributions of pollutants. pRDA allows one to 'factor out' covariables in order to focus on

Table 1 The geographical coordinates and the altitude of the stations of Thriasion-Elefsis basin monitoring network

AA	Lat.	Lon.	Alt. (m)	Description
1	38.02942	23.62820	151	DEH (relative close to the industrial zone)
2	38.05075	23.62711	159	Hill (relatively close to the industrial zone)
3	38.04650	23.56998	2	Aspropyrgos beach (close to metallurgic factory in the industrial zone)
4	38.04165	23.53688	24	Museum (within the Elefsis city and relative close to a cement factory)
5	38.06448	23.58374	32	Ministry (urban station—relatively close to the industrial area)
6	38.06391	23.53236	25	Hospital (out of the city—close to highway)
7	38.06880	23.50610	69	Mandra (relatively clean rural village)
8	38.09903	23.55805	94	Slope (meadow field—relatively clean rural area)
9	38.08952	23.63981	178	Liosia (meadow field—relatively clean rural area)
10	37.99771	23.59857	86	Navy base (close to the Hellenic shipyard)
11	38.00103	23.49551	17	Batsi (beach in Salamina island—relatively clean rural area)
12	37.98346	23.42250	16	Port (beach in Salamina island—the expected most clean rural area)

particular sets of explanatory variables. To evaluate the spatial distribution of pollutants, we employed dummy-encoded sampling dates as four covariables in pRDA, with dummy-encoded monitoring sites as 12 explanatory variables. To evaluate temporal effects, we switched the roles of explanatory variables and covariables. We displayed the relationships between elements and the explanatory variables using ordination biplots. We evaluated significance (α=0.05) using a Monte Carlo permutation procedure, conditioned upon the covariables, with 999 permutations (ter Braak and Šmilauer 2002; Lepš and Šmilauer 2003)

For storing, initial manipulation and mapping of the data and for calculation of the correlations matrix of the elements, MS Office EXCEL v10 was used. Partial RDAs were conducted using CANOCO (ver. 4.5). All statistical significance tests were performed at level α=0.05.

Results and discussion

Correlations between elements

Figure 2 shows the correlations map between the elements, based on the entire initial data set. The correlation analysis demonstrates high positive correlations between the majority of the measured elements. For the following pairs of elements: Fe-Yb, Na-Cl, Al-Sc, La-Ce, La-Sm, and Ce-Sm the correlation coefficients were higher than 0.95 (Fig. 2) and for the following pairs: Al-Ti, Al-Fe, Al-Yb, Sc-Ti, Sc-Fe, Sc-Yb, Sc-Th, V-Ni, Cr-Zn, Sr-La, Sr-Ce, Sr-Th, Sr-U, La-Th, Ce-Yb, Ce-Th, Ce-U, Sm-Th, and Yb-Hf they were between 0.90 and 0.95. The strong correlations between some the elements may imply a common origin. In some pairs, a common source is known; e.g., for Na–Cl (r=0.97) the common origin is obviously sea salt. The Br–Na (r=0.85) and Br–Cl (r=0.97) may also be attributed to marine input since it is known that seawater contains about 85 ppm Br (Hammond 2000). The correlations between Zn, Cr, and Ni are considered indicative of vehicle emissions (Galun et al. 1985; Ward 1989, Adamo et al. 2003); and Cr, Cu, and Zn may come from tires, brakes, engines, and vehicle component wear (Basile et al. 2008).

Other elements indicative of urban environment are: As (from various anthropogenic sources including coal burning); V (from oil combustion, Aničić et al. 2009b); and Mn, Al, and Fe (from suspended geogenic particles, Basile et al. 2008). The concentrations of Fe and Cr in the air seem to be influenced from particle residues from iron and steel industries (Markert et al. 1996; Adamo et al. 2003). High correlation between V and Ni has been attributed to oil combustion (Bargagli 1998) since it is known that these elements co-occur in crude oil (Herpin et al. 1996). Elements obviously originating from different sources were uncorrelated; e.g., Hg was uncorrelated with Cr and Zn (Fig. 2). It has been found Cr and Zn to occur at higher levels in areas close to cement factories while Hg occurs at higher

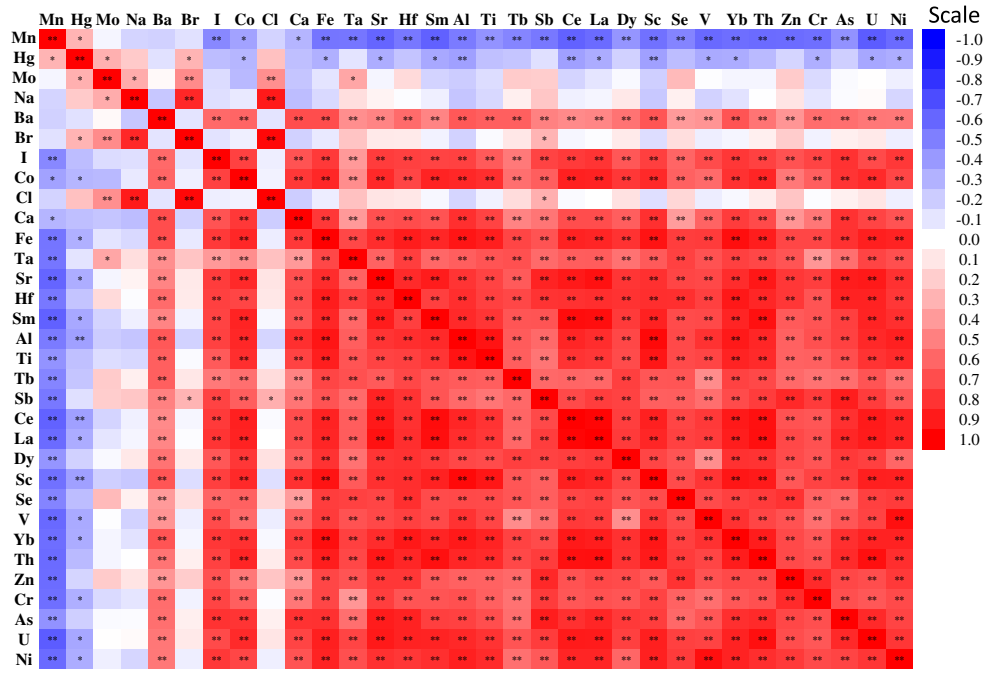

Fig. 2 Blue-red correlation map of the measured elements: low correlations are displayed with *cold colors* (correlations that are close to −1 are displayed in *deep blue color*) while the high correlations are indicated with *hot colors* (correlations close to 1 are displayed in *deep red color*). The * and ** stand for $p<0.05$ and $p<0.01$, respectively. The *lack of asterisk* indicates none statistically significant correlations coefficients between the corresponding pair of elements. The elements are ordered according to their loadings on the first PCA axis

levels in areas close to chlor-alkali plants from which is emitted as Hg^0 (Fernández et al. 2004).

Diesel fuel is the common source of many elements. Wang et al. (2003), who studied the emissions of fuel metals from diesel vehicle engines, found that the contents of Al, Ca, Fe, Mg, and Si (that were considered "crust elements") accounted for ~82% of the total metal content in the diesel fuel. The emitted concentrations of the crust elements were much higher than those of Ag, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Sr, Ti, V, and Zn, that were considered "anthropogenic elements". In the study of Wang et al. (2003), the top four abundant anthropogenic elements in the diesel fuel were Zn, Cr, Mo, and Ti. Similarly, in the study of Weckwerth (2001), the top two abundance metals in diesel-soot were Zn and Cr.

A specific outcome of this study is the negative correlation of Mn with all the other elements. Mn is originally present in the moss because it is an essential element, but is easily replaced by other elements during exposure (Steinnes 1995) and is thus normally not useful for identifying sources of air pollution.

Spatial distribution

In order to reveal the spatiotemporal pattern of each element, for each monitoring period, we initially prepared a total of 124 (32 elements×4 monitoring periods) spatial distribution maps. Some examples of these maps are shown in Fig. 3. Those maps demonstrate that the majority of the elements were not evenly distributed throughout the region in any monitoring period.

In the first pRDA the concentrations of the elements were analyzed against the monitoring stations, after removing the effects of exposure period as covariables, in order to reveal the spatial association between elements and monitoring stations. The resulting biplot (Fig. 4) clearly shows that the first two axes account for 78.5% of the total variance explained, with the first axis explaining 54.8%. The majority of the elements have high loadings on the first axis with the highest shown by Sb (0.939), Mo (0.913), and Sr (0.910). Considering the second axis, high positive loadings are evident for Fe (0.624), Al (0.570), Yb (0.545), and Hf (0.496) and high negative loadings for Na (−0.809), Cl (−0.748), and Br

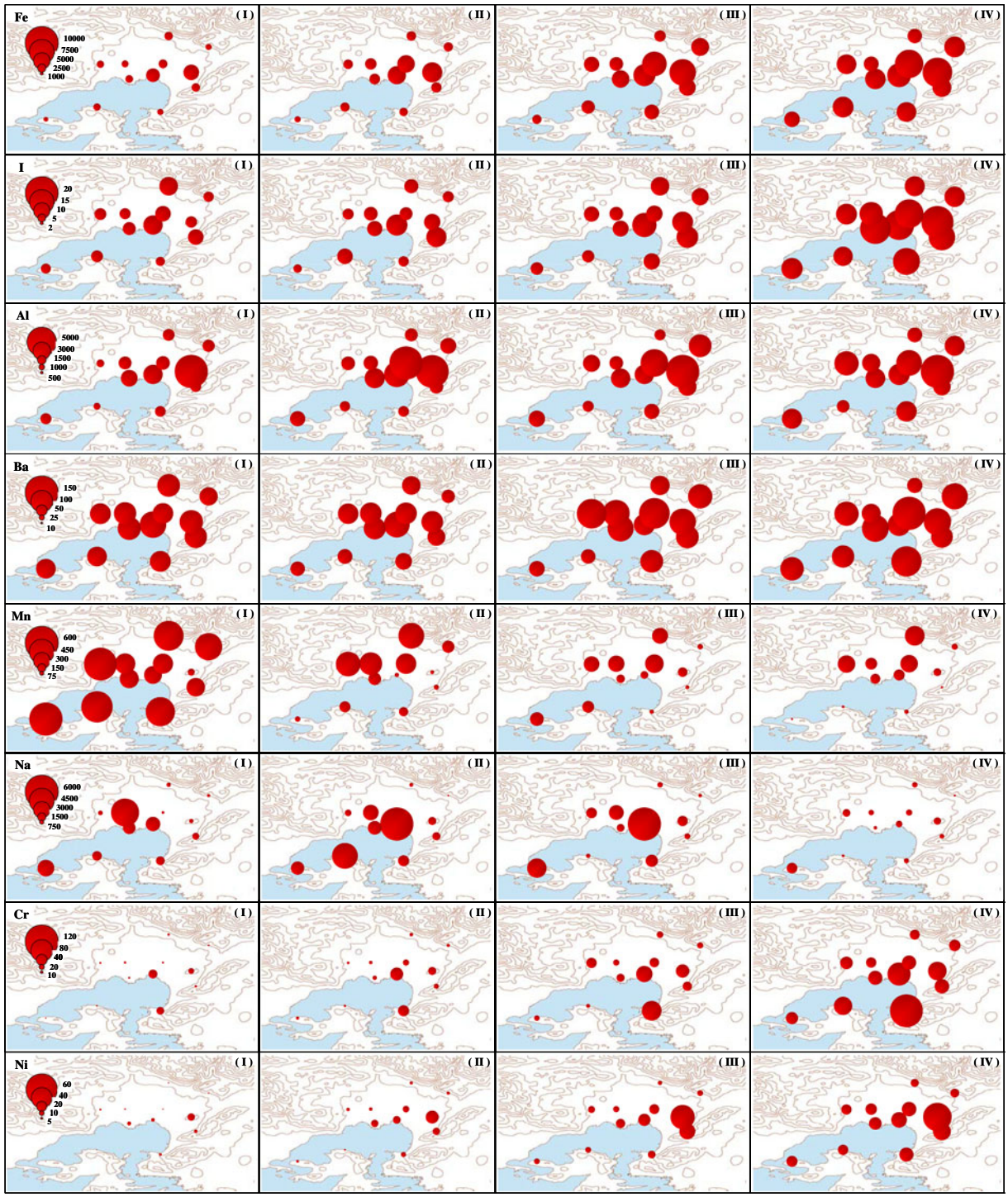

Fig. 3 Typical examples of spatiotemporal patterns of pollutant elements accumulated on moss materials after, (*I*) three, (*II*) six, (*III*) nine, and (*IV*) 12 months of exposure. At the upper left corner the name of each element along with the scale (on the base of the bubbles diameter) is given

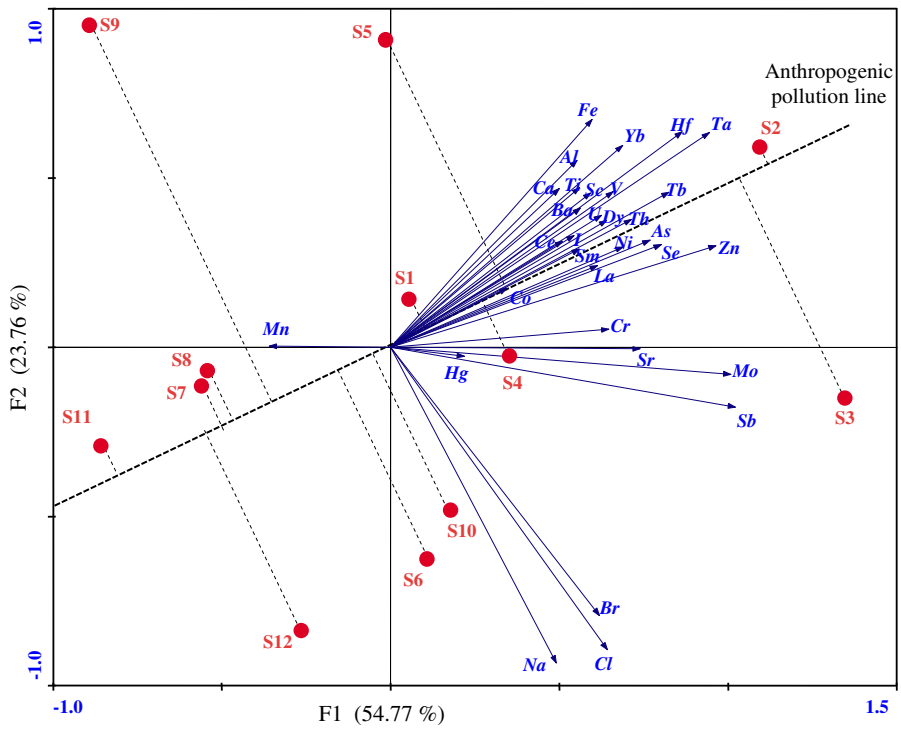

Fig. 4 Biplot resulting from partial RDA in which the exposure periods constituted the co-variable. The first two major axes accounts for 78.53% of the total inertia explained. The vectors correspond to the elements while the points correspond to the monitoring sites (*S1* to *S12*)

(−0.715). The highest loadings for Mn (0.837) and Hg (0.850) were on axis F3 while the highest loading for Co (0.580) was on axis F4 (not shown in Fig. 4).

Although the concentrations were generally higher at the monitoring sites close to the industrial zone (stations S2 and S3) than at the remote ones, it appears that different elements showed maximum levels at different monitoring sites (Table 2). For example, the maximum concentration for Ta (0.23 μg/g) was observed at station S2 while Hg showed its maximum value (7 μg/g) at station S6. Hg is known to occur at higher levels in the surrounding of chlor-alkali plants, using mercury cell technology (Garty 1992). It is not known if some chlor-alkali plant is operating in the area. Cr showed its maximum value (119 μg/g) at station S10, which is close to the largest shipyard in the eastern Mediterranean with activities mainly related to building and repairing naval ships and trains. Cr is known to be emitted by diesel vehicle engines (Wang et al. 2003). Besides, it is used in alloys and is expected to occur at higher levels close to places where anthropogenic activities, related to hardening steel, manufacturing stainless, and tanning leathers, are taking place (Hammond 2000). The maximum values for Sb and Mo were 6.52 and 4.67 (μg/g), respectively, both observed at station S5. According to Zechmeister et al. (2005), Sb and Mo, in urban air, can be attributed to wear of automobile brake linings. For Ca and Ba the maximum values were observed at station S3. Ca and Ba are also known to constitute important brake compounds (Zechmeister et al. 2005). The main source, however, of Ca was obviously the soil since it is known that the soils in the greater area of Attica are chiefly calcareous (Riga-Karandinos et al. 2006).

Table 2 The station and the period where the maximum cumulative concentration of each element was recorded

Station	Period	Elements (maximum cumulative concentration in μg/g dw)
S6	I	Hg (6.99)
S12	I	Mn (600)
S3	I	Mo (4.67), Tb (0.18)
S3	II	Na (15,633), Cl (16,700), Br (920)
S2	III	Ta (0.23)
S2	IV	Al (12,320), Sc (1.98), Ti (880), V (74.13), Fe (8,860), Ni (54.45), Se (0.90), Yb (0.36), I (19.64)
S5	IV	Ca (85,860), Co (4.26), Ba (161.69)
S10	IV	Cr (119)
S3	IV	Zn (440), As (5.47), Sr (100.4), Sb (6.52), La (6.47), Ce (11.9), Sm (0.92), Dy (1.14), Hf (1.24), Th (1.5), U (0.56)

Some elements such as I, Co, and especially Ba, were more evenly distributed spatially than the other elements, indicating a nonpoint source of origin or easy dispersion to areas relatively far away from their source. Iodine, for example, is likely to originate from seawater as it is known that the major iodine source in the atmosphere is the emission of organic iodine compounds from the oceans (Vogt 1999). Co and Ba are also known to be emitted by diesel vehicle engines (Wang et al. 2003) which would be considered nonpoint sources.

Opposite to the majority of the other elements, Mn exhibited increased values at the stations far away from the industrial zone (Fig. 3); this is a confirmation that the main source of Mn in the greater region is not of anthropogenic origin. Unlike the majority of elements, Mn exhibited a decreasing trend over time suggesting that the leaching of Mn from the moss materials was the driving factor of Mn content in the moss over time; the Mn deposited on the moss surface was insufficient to counterbalance the loss of Mn through leaching. It also seems (Fig. 3) that the leaching was more intense in the industrial zone in comparison to the areas far away; this may be explained by a higher supply of competing major cations (Na, Mg, K, Ca, and possibly H^+), under these conditions. It is well known that the replacing power of H^+ in cation exchange processes is much lower than that of the other cations inserted above. Especially the doubly charged cations Mg^{++} and Ca^{++} are likely to be important in the replacement of Mn^{++} on the moss surface. Loss of Mn due to washing out and leaching has also been previously reported in other investigations (Steinnes 1995; Čeburnis and Valiulis 1999; Couto et al. 2004; Aničić et al. 2009b).

Projection of the stations on the vectors of each element indicates the order of the stations at which the elements appear to be most abundant. For example, Mo and Sb were more abundant at the stations S3 and S2 and less abundant at the stations S11, S7, and S8 than the average; Na, Cl, and Br were more abundant at stations S12, S3, and S10 and less abundant at station S9 and S5. In general the majority of elements were most abundant at stations S2 and S3. For the majority of the elements, it is difficult to relate their increased levels with some particular source, because (a) the composition of the emissions from specific sources are unknown and (b) some pollutants may be transported far away from their source. It is known, for example, that the elements Ag, As, Cd, Bi, Hg, Mo, Pb, Sn, V, and Zn are likely to be transported over long distance in the atmosphere (Kabata-Pendias and Pendias 2001).

It was interesting to order the stations according to the bulk anthropogenic pollution (i.e., the levels of all the studied pollutants except Na, Cl, Br, Ca, and Mn, which seem to be of nonanthropogenic origin) load. Thus, in Fig. 4, we draw a line passing through the origin and the point indentified by the average of the scores of the "anthropogenic" pollutants' on the axis F1 and F2; this line would be considered the "line of anthropogenic pollution". Projection of the stations on this line orders them according to their bulk anthropogenic pollution load as follow: S2>S3>S5>S4>S1>S10>S6>S9>S8~S7~S12>S11. The order of the monitoring stations seems to summarize perfectly the pollution status of the region revealing the power of pRDA in the description of the spatial and temporal pattern of the elements.

Temporal distribution

The spatiotemporal maps showed clearly that most of the elements exhibited a gradually increasing trend due to cumulative sampling procedure. However, some of them exhibited differed time trends (Fig. 3).

In the second pRDA, the time trends of the cumulative concentrations was analyzed after covarying out spatial variation. Figure 5 shows the biplot resulting from the second pRDA, and seems to describe perfectly the time course of the cumulative load of elements on the moss material samplers. The first two major axes account for the 98.64 % of the explained variance, with the first axis accounting for 80.61 %. The majority of the elements have very high loadings (>0.90) on this first axis; they also have small or relatively small angle between each other. This confirms the results of the correlation analysis that these elements are highly correlated with each other; the smaller the angle the higher the correlation.

The elements Al, Ca, Sc, Ti, V, Cr, Fe, Ni, Co, Zn, As, Se, Sr, Sb, I, La, Ce, Sm, Dy, Yb, Hf, Th, and U exhibited a gradual accumulation in moss materials, over time. This suggests that all these elements were well fixed on the moss surface and less influenced from leaching and/or evaporation due to meteorological conditions.

In the case of Tb and Ta, this trend was not so clear while Ba exhibited relatively even spatial distribution with a small fluctuation over time; its average levels

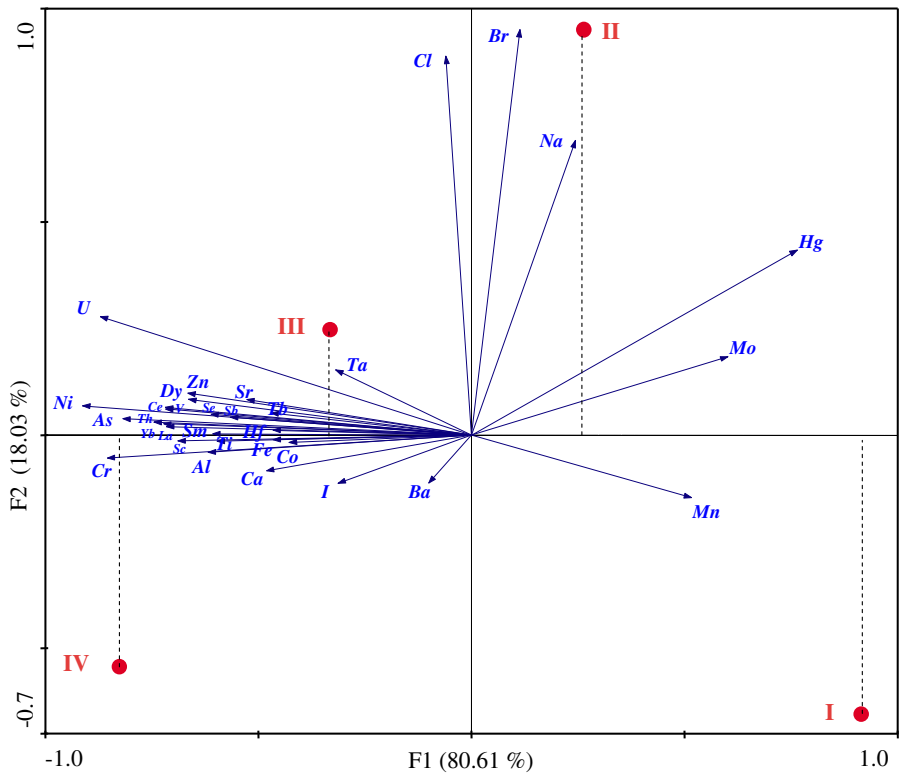

Fig. 5 Biplot resulting from partial RDA in which the monitored sites constituted the co-variable. The first two major axes accounts for 98.64% of the total inertia explained. The vectors correspond to the elements while the points correspond to the exposure periods (*I*, *II*, *III*, and *IV*)

(±SE) for the periods I, II, III, and IV were 98.46±3.82, 86.32±4.92, 105.64±6.57, and 118.90±6.87, respectively, which are about four to six times higher in comparison to the initial (before exposure) moss materials (19.54 μg/g). Barium is fairly abundant on the Earth, (0.0425% in the Earth's crust and 13 μg/L in seawater) (Kresse et al. 2007). It is emitted by diesel vehicle machines (Wang et al. 2003) and also enters the air through refining process and coal and oil production.

The elements Mo and Hg exhibited an inverse trend, in comparison to other metals; they show higher concentrations in the first quarter of the monitoring period (cold or relatively cold months) and then gradually decreased during the warmer months. For Mo, the average levels (±SE) for the periods I, II, III, and IV were 2.39±0.4, 1.86±0.29, 1.49±0.28, and 0.66±0.11, respectively, which are about 19, 15, 15, and six times higher in comparison to the initial moss materials (0.126 μg/g). For Hg, the average levels (±SE) for the periods I, II, III, and IV were 2.32±0.73, 1.34±0.18, 1.04±0.27, and 0.24±0.04, respectively, which are about 86, 50, 39, and nine times higher in comparison to the initial moss materials (0.027 μg/g). This decreasing pattern would be attributed to the tradeoff between leaching and evaporation processes on the one side and deposition process on the other. Mo is presumably present as an anion on the moss surface, likely to be less firmly bound as most cations and replaced by the major anions chloride and sulfate. The decrease of Hg points to its presence at least partly as Hg^0 in the moss.

The elements Br, Cl, and Na exhibited an increasing trend over the first half of the monitoring period and then decreased to very low levels. The decrease of the concentrations of these elements during the second half of the monitoring period (the warmer months of the year) would be attributed to volatilization. It is known that Br is volatilizing readily at room temperature (Hammond 2000).

Projection of the time period points on this first axis reveals the gradual increase in the cumulative loads of the elements from the first monitoring period (I, on the right) to the last monitoring period (IV, on the left). The elements Mn, Mo, and Hg lying on the right of the first axis exhibit a negative correlation through time with the majority of the elements lying on the left of the first axis. The vectors of the elements Na, Cl, and Br are associated with the second axis and they have

small angles between each other suggesting highly correlated elements; these elements are uncorrelated with the majority of the other elements lying along the first axis. All these correlations are in agreements with the species correlations depicted in the correlation map (Fig. 2). Projection of the points of the monitoring period on the vectors of the elements reveals the period in which the elements exhibited its maximum concentrations. The majority of the elements lying on the left of the first axis exhibited a gradual increase in the cumulative load from period I to period IV. The elements Mn, Mo, and Hg exhibited maximum concentrations at the first exposure period and then their concentrations in the samples declined probably due to leaching and/or evaporations. The elements Cl, Br, and Na exhibited higher load during the second monitoring period (see also Fig. 3).

The temporal variability in the accumulation of the elements clearly suggests that moss bags technique cannot be considered a reliable method for elements strongly susceptible to leaching. Although the leaching mechanism is not exactly known, it has been suggested that, in lichens, under high precipitation rates, rainwater, through leaching and washout processes, can remove elements from the lichen surface, and to some extent, from exchangeable sites, at least for elements with lower ionic affinities with such sites in the cell wall (Figueira et al. 2003). In moss, Mn (Čeburnis and Valiulis 1999; Castello 2007) and Cr (Castello 2007) have been reported being much more susceptible to leaching than other elements.

Besides, elements likely to be present in volatile forms, such as Hg, may be underestimated when the monitoring is conducted during warm periods.

Conclusions

The Thriasion-Elefsis Basin is considered to be a highly polluted area. The moss bag technique was utilized to reveal the spatiotemporal distribution of airborne elements. This study revealed the presence in air of at least 32 elements. No data on the atmospheric deposition of these elements in this area existed before this investigation was conducted. The levels of the measured pollutants were unevenly distributed throughout the area and different pollutants exhibited different spatial patterns. However, in general, higher loads were observed in the stations close to the industrial zone, but with no clear indication of which local anthropogenic activity is responsible for what elements. A few elements, such as Cr, exhibited higher loads in the vicinity of particular anthropogenic activities. The majority of the elements exhibited a monotonic cumulative course in the moss over time. However, some elements showed different temporal patterns; Mn, Mo, and Hg showed a decreasing trend, probably due to leaching and/or volatilization processes over time; Na and Br initially showed an increasing trend but decreased drastically during the late warm period; this suggest that the season of monitoring affects the accumulation of some elements. Thus, air pollution monitoring with the moss bags technique would be considered valuable for the majority of elements but should be used with caution in the cases of elements vulnerable to leaching and/or volatilization processes. It also suggests that the timing and the duration of the exposure of moss materials should be considered in the interpretation of the results.

Finally, this study provides a good baseline dataset that will allow comparisons with studies in the same area in the future, in order to evaluate the progress in air quality in the region, as well as with studies in other urban and industrial regions where data is lacking.

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