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Discussions

Assessment of atmospheric trace element concentrations by lichen-bag near an oil/gas pre-treatment plant in the Agri Valley (southern Italy)

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Abstract

The atmospheric concentrations of 17 trace elements (Al, Ca, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, S, Ti and Zn) were measured by means of the "lichen-bag" technique in the Agri Valley (southern Italy). The lichen samples were collected from an unpolluted site located in Rifreddo forest (southern Italy). The bags were exposed to ambient air for 6 and 12 months. The exposed-to-control (EC) ratio values highlighted that the used lichen species were suitable for biomonitoring investigations. The results showed that the concentrations of almost all the examined trace elements increased with respect to the control after 6–12 month exposures. Furthermore, Ca, Al, Fe, K, Mg and S were the most abundant trace elements both in the 6 and 12 month-exposed samples. Moreover, principal component analysis (PCA) results highlighted that the major sources of the measured atmospheric trace elements were related both to anthropogenic contributions due to traffic, combustion processes, agricultural practices, construction and quarrying activities, and to natural contributions mainly represented by the re-suspension of local soil and road dusts. In addition, the contribution both of secondary atmospheric reactions involving Centro Olio Val d'Agri (COVA) plant emissions and the African dust long-range transport were also identified.

1 Introduction

The growing interest aroused by atmospheric pollution is due to its impact on human health, air quality and global climate change (IPCC, 2013; Kulmatov and Hojamberdiev, 2010; Pope and Dockery, 2006). In this field, atmospheric particles play a key role also because they may contain high concentrations of several trace elements known to have toxic effects on human health and environment.

The trace element inputs into the environment have increased mostly over the last few years (Mbenguea et al., 2014; Achotegui-Castells et al., 2013; Ny and Lee, 2011; Gao et al., 2002). These inputs are due to both natural emissions – continental dust,

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volcanic dust and gas, sea spray, and biogenic particles – and human activities such as industrial sources, present and former mining activities, foundries, smelters and traffic (Aničic et al., 2009; Gong and Barrie, 2005). Frequently, the anthropogenic sources are more significant than the natural ones for most of the toxic trace elements (e.g. Pb and Cd) (Caggiano et al., 2010; Mazzei et al., 2008).

The monitoring of the trace element-related atmospheric pollution is a very complex problem due to a variety of reasons: the great number of potentially dangerous substances, the difficulty in estimating bioavailability, the large spatial and temporal variations of the pollution phenomena, the high costs of the recording instruments and hence the low sampling density of a purely instrumental approach (Achotegui-Castells et al., 2013; Wolterbeek, 2002).

For this reason, innovative techniques devoted to the atmospheric trace element monitoring have been developed and continuously improved. Among these, the biomonitoring has become a topical method for the assessment of the trace element presence in the atmosphere. The use of lichens as biomonitors for atmospheric deposition of trace elements has been reported in a large number of studies including local investigations, as well as regional, national and international surveys in different parts of the world (e.g. Cucu-Man and Steinnes, 2013; Abdullah et al., 2012; Guttová et al., 2011; Spagnuolo et al., 2011; Baptista et al., 2008). In particular, the lichen-bag technique has been widely applied and is a well-established methodology for the assessment of the atmospheric trace element deposition. The lichen-bag technique has a lot of advantages such as well-defined exposure time, the knowledge of the original concentration of chemical elements in the used biomonitors, flexibility both in site selection and number of stations that can be chosen. Moreover, it allows repeated assay of the same element, in the same place, with identical samplers, thus achieving comparable results over the time.

Since the assessment of the pollution levels is strictly connected to a detailed knowledge of the trace element concentrations and their major sources, multi-elemental surveys and advanced statistical techniques for the identification of their sources are

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necessary to gain insight into the characteristics of the atmospheric trace elements in order to assess the potential health risks and develop effective strategies for the control of the emission sources (Charlesworth et al., 2011; Viana et al., 2008).

In the light of this, the present study deals with the characterization of the atmospheric trace element concentrations using the "lichen-bag" technique and the identification of their main emission sources. The study was performed in the Agri Valley (Basilicata region – southern Italy), an area of international concern since it houses one of the largest European on-shore reservoirs and the biggest oil/gas pre-treatment plant (i.e. Centro Olio Val d'Agri – COVA) within an anthropized context (Trippetta et al., 2014). This plant produces the emissions of several pollutants that could exert a considerable impact on a widespread area. In particular, the concentrations of 17 trace elements (Al, Ca, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, S, Ti and Zn) were measured in lichen bags exposed in 59 selected monitoring points over period of 6 months (from October 2011 to April 2012) and 12 months (from October 2011 to October 2012). The principal component analysis was applied to identify the main sources of the trace elements determined.

The results of this study could give an important contribution both to the development of air quality control strategies and the evaluation of impact on human health, especially in an area where air pollution-related data are still lacking.

2 Materials and methods

2.1 Study area

The Agri Valley is located in the Basilicata region, southern Italy (Fig. 1). It is located at about 600 m a.s.l. and it is surrounded by mountains. Agriculture, pasture and woodland are the prevailing land uses. The Agri Valley gives hospitality to a wide variety of protected natural habitats and is partially situated within the Appennino Lucano – Val d'Agri – Lagronegrese National Park. At the same time, this area is characterized by

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the presence of one of the largest European on-shore reservoirs (crude oil and gas) and of an oil/gas pre-treatment plant (identified as Centro Olio Val d'Agri – COVA). The COVA plant is located in an anthropized area characterized by several small towns, from 1700 to 5400 inhabitants. The nominal treatment capacity of the COVA plant is of 16 500 $m^3\,d^{-1}$ of crude oil and 3 100 000 S $m^3\,d^{-1}$ of associated gas. The COVA plant represents the anthropogenic activity with the highest release of atmospheric pollutant emissions in the Agri Valley (Trippetta et al., 2013). Moreover, it represents the most important industrial activity in the area and its presence has also produced a significant increase in the anthropogenic activities linked with the extraction of the hydrocarbons.

2.2 Lichen-bag preparation and sample exposure

Samples of *Platismatia glauca* (L.) *W. L. Culb. & C. F. Culb.* (foliose species), *Evernia prunastri* (L.) Ach., *Ramalina fraxinea* (L.) Ach. and *Pseudevernia furfuracea* (L.) Zopf (fruticose species) lichen species were collected in October 2011 at an unpolluted site located in Rifreddo forest (hereafter named control site), southern Italy (40°33′53.37″ N, 15°50′22.34″ E, about 1146 m a.s.l.).

After the collection, the lichens were oven-dried at 30 °C to a constant weight and carefully cleaned under binocular microscope to remove soil, bark and extraneous material (Wolterbeek and Bode, 1995). Then, the samples were homogenized by manually stirring. About 5 g of oven-dried mixed material was used to prepare 2 bags. The bags were made of a polyethylene mesh (2 mm × 2 mm) cut into pieces of approximately 12 cm × 12 cm and packed loosely with a nylon rope.

The biomonitoring network consisted of 59 sites distributed around the COVA plant and covering an area of about 100 km^2 also including the major towns located in the area (Fig. 1). Each sampling point was selected using Agri Valley maps and taking the landscape characteristics into account. A portable Global Positioning System (GPS) was used for providing geo-references of the on-site points. In each site, 2 bags were hung on tree branches at a height of about 3 m above the ground. In order to explore the temporal variation of the trace elements, in each site one bag was collected after

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6 months (from October 2011 to April 2012) and the other one after 12 months (from October 2011 to October 2012) of continuous exposures. All samples were stored in polyethylene bags until chemical analysis.

2.3 Trace element analysis

In order to determine the total concentration of 17 trace elements (i.e. Al, Ca, Cd, Cr, Cu, Fe, Li, K, Mg, Mn, Na, Ni, P, Pb, S, Ti and Zn), 500 mg dry weight (dw) of lichen samples were acidic digested in a solution of 6 mL HNO_3 + 1 mL H_2O_2 (Loppi and Frati, 2006).

Then, the samples were measured by means of Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) or Graphite Furnace Atomic Absorption Spectrometry (GF-AAS). In particular, the total concentrations of Al, Ca, Cr, Fe, Li, K, Mg, Mn, Na, P, S, Ti and Zn were measured by means of ICP-OES while Cd, Cu, Ni and Pb total concentrations were determined by means of GF-AAS. The blank (reagent + beaker) contribution was evaluated and the resulting values were subtracted from the ICP-OES or GF-AAS measurements of real samples. For all the elements blanks were found to be < 10 % of the measured values.

The method detection limit (MDL) was used to determine the lowest concentration level that could be detected, statistically different from a blank. To this aim, ten blanks were prepared and analyzed and MDLs were determined by adding 3 standard deviations of the blank readings to the average blank values (Yatkin and Bayram, 2007). The results obtained are reported in Table 1. Moreover, the validity of the whole analytical procedure was checked by using the International Atomic Energy Agency (IAEA) standard reference material, IAEA 336. The obtained values were in good agreement with the certified values (Table 1).

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2.4 Data analysis

In order to identify the main trace element sources, the principal component analysis (PCA) was used. PCA is a multivariate statistical technique widely applied both to the study of the correlation structure between the different atmospheric pollutants and the identification of the source types which can give rise to their presence in the atmosphere (Yatkin and Bayram, 2007; Quiterio et al., 2004; Vallius et al., 2003; Dìaz et al., 2002). In this study, each variable was normalized to unit variance, and all the principal factors with eigenvalues > 0.8 were retained. To clarify the meaning of the principal components (PC_s), the retained factors were subsequently subject to the varimax normalized rotation.

SPSS© for Windows version 12.0 was used for the multivariate statistical analysis.

3 Results and discussion

3.1 Exposed to control ratio

The ratio of the concentrations of each trace element in exposed samples with respect to control samples (i.e. "exposed to control ratio" – EC ratio) was used for calculating the accumulation rates in the lichen bags (Fig. 2). According to Frati et al. (2005), a five-class interpretative scale based on the deviation of the EC ratio from the control condition, assumed to be ±25 % from the ratio of 1, was used (Table 2).

By analyzing the mean values of the EC ratios calculated for each trace element after 6 and 12 month exposures, it can be observed that there were no cases of "severe loss" ($0 < EC < 0.25$) and only one case of "loss" ($0.25 < EC < 0.75$) occurred. Moreover, the "normal" condition ($0.75 < EC < 1.25$) was observed for 9 times. The "accumulation" ($1.25 < EC < 1.75$) and "severe accumulation" ($EC > 1.75$) were the most occurring conditions with 13 and 11 cases, respectively.

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Focusing on the single trace element, severe accumulation was observed for Al, Fe, Li, Na after both 6 and 12 month exposures and for Cd, P and S after a 12 month exposure. A significant increase was observed for Mg, Ni and Ti whose EC values fell within the "accumulation" class after both 6 and 12 month exposures. An increase in the EC values was also recorded for Ca and P after a 6 month exposure and for Cr, Pb, Mn and Zn after a 12 month exposure. In fact, all these elements fell within the "accumulation" class.

Regarding Cr, Cu, Pb, S and Zn, they showed a moderate change with EC values falling within the "normal" class after a 6 month exposure, while K and Mn fell in the "normal" class for both the exposure periods. Finally, a decrease was observed for Ca and Cu only after a 12 month exposure. A loss of Ca and Cu after a long period of exposure has also been observed in literature (Culicov et al., 2006; Yurukova and Ganeva, 1997).

Therefore, the results highlight that the accumulation capacity of the lichens in relation to the analyzed trace elements is different but that the used lichen species are suitable for the biomonitoring investigation.

3.2 Trace elements after 6–12 month exposures

The mean concentration values of the 17 trace elements analyzed in the lichen bags after 6 and 12 month exposures in 59 selected monitoring sites located in the Agri Valley and the concentration values measured at the control site are presented in Table 3.

As Table 3 shows, Al, Ca, Fe, K, Mg and S were the most abundant elements both in the 6 and 12 month exposed samples.

By comparing the mean values of the trace element concentrations measured in the lichen samples after a 6 month exposure with those measured in the control ones, it can be seen that the major increase was observed for Na (229 %), Li (116 %), Fe (91 %) and Al (80 %). An increase was also observed for 9 trace elements: P (40 %), Ca (39 %), Ni (36 %), Mg (35 %), Cd (32 %), Ti (29 %), K (23 %), Cr (22 %) and S (21 %). Finally, no significant increase (less than 10 %) was recorded for the remaining elements.

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By focusing on the comparison between the trace element concentrations measured in 12 month-exposed samples and in the control samples, it can be seen an increase of 282, 231, 203, 189, 119 and 118 % for Na, S, Li, Al, Fe and P, and Cd, respectively. An increase was also observed for Mg (69 %), Pb (68 %), Ni (65 %), Ti (61 %), Zn (59 %), Cr (58 %), Mn (28 %) and K (20 %). Finally, Ca and Cu were the only two elements showing a decrease in their concentrations after a 12 month exposure.

Regarding the difference in concentrations as a function of the time of exposure, the results pointed out an increase of almost all the trace element concentrations during longer exposure periods. Particularly, the S concentration measured in samples exposed for 12 months was higher than the S concentration measured in the samples exposed for 6 months with an increase by 174 % (from 1265 to 3466 mg kg^{-1}). The results also highlight an increase in Cd (64 %), Pb (63 %), Al (60 %), Zn (58 %) and P (57 %) concentrations after a 12 month exposure. As for Fe, Mg, Mn, Na, Ni, and Ti, the mean concentration values measured in the samples exposed for 12 months showed percentage increases ranging between 14 and 25 % with respect to the 6 month-exposed samples. No difference was found in K concentrations between samples measured after 6 and 12 months of exposure. Finally, a decrease in the Ca and Cu concentrations (36 and 33 %, respectively) was observed with the increase in the exposure time.

In order to gain a better understanding of the correlation structure between the trace elements in lichen samples, the Pearson's correlation coefficients (ρ) were calculate between the trace element concentrations measured in the lichen samples after a 6 month exposure and between the trace element concentrations measured in the lichen samples after a 12 month exposure.

Significant positive correlations ($\rho > 0.70$) were found between elements generally considered of natural origin i.e. Al-Fe, Ti-Al and Ti-Fe after a 6 month exposure and between Ti-Al after a 12 month exposure. Significant correlations were also found between elements of anthropic origin i.e. Cr-Cu, Ni-Cu, Pb-Cr and Zn-Pb in the samples exposed for 6 months and between Cd-Cr, Ni-Cd, Pb-Cd, Zn-Cd after a 12 month

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exposure. Moreover, the results also showed a correlation between elements of different origin such as Al-Cr and Fe-Cr.

3.3 Principal component analysis (PCA)

By applying the PCA to the concentrations of the trace elements measured in the lichen samples after a 6 month exposure, five significant components ($PC_{s-6\,months}$) were obtained (Table 4a).

As reported in Table 4a, $PC_{1-6\,months}$ is characterized by high loadings of Al, Ti, Fe, Li and Cr. Al, Ti and Fe are chemical elements typically used as tracers for soil dust and/or crustal re-suspension (Pant and Harrison, 2012). Regarding Li and Cr, they are found in vehicle exhausts, diesel vehicle engines and coal fly ash (Chandra Mouli et al., 2006; Wang et al., 2003). Therefore, $PC_{1-6\,months}$ can be related to contributions of natural origin associated with those coming from traffic and coal combustion processes.

$PC_{2-6\,months}$ is characterized by Zn, Cd, Pb, Cu and Ni. These elements are generally related to anthropogenic sources represented by motor vehicle emissions, wear and tear of brake linings and other vehicle metallic parts. Therefore, this component could be associated to the contribution of anthropogenic sources identified as traffic.

$PC_{3-6\,months}$ is related to P, Mn and K. As for P, its presence in the local atmosphere could be due to the re-suspension of soil particles containing naturally-occurring and fertilizer-derived P, primary biogenic aerosols and combustion sources (fossil fuel, biomass burning, biofuels) (Lettino and Fiore, 2013; Mahowald et al., 2008). As far as Mn is concerned, it is an element widely distributed in the Earth's crust and it is considered to be the twelfth most abundant element and the fifth most abundant metal (WHO, 2001). Mn enters the atmosphere through several processes which include soil erosion by winds and the re-suspension both of road dusts by vehicles and soils as a consequence of farming, construction and quarrying activities. Finally, K usually occurs in coarse particles coming from soil but fine particles of potassium also result from wood combustion (Calvo et al., 2011; Khare et al., 2008; Zunckel et al., 2003). Therefore, this component should be related both to natural contributions mainly represented

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by the re-suspension of local soil as well as road dusts and anthropogenic emissions deriving from combustion processes (wood and fossil fuels), agricultural practices and construction and quarrying activities.

Regarding $PC_{4–6\,months}$, it is related to Na and S. Sodium sulphates may form through reactions between Na^+ and H_2SO_4. In particular, S-rich compounds mainly emitted from the COVA plant very likely condense onto or react with pre-existing Na-rich particles that act as condensation nuclei. Moreover, Aden and Buseck (1979) observed significant Na_2SO_4 quantities in emissions from combustion processes. Therefore, this component may be related to secondary atmospheric reactions involving COVA plant emissions.

Finally, $PC_{5–6\,months}$ is related to Ca and Mg. Since the local soil is mainly composed of marls and dolomite limestone (Lettino and Fiore, 2013) including Mg and Ca in their composition, this component should be related to the contribution of local soil re-suspension.

By applying PCA to the concentrations of the trace elements measured in the lichen samples taken after 12 months of continuous exposure, five significant components were pointed out (Table 4b).

The results highlight that $PC_{1–12\,months}$ is characterized by the same elements found in $PC_{1–6\,months}$ such as Al, Li, Fe, Cr and Ti, but it is also characterized by the occurrence of Ni. The origin of this last element, especially in the same component with Cr, may be related to industrial emissions (Bari et al., 2009; Mazzei et al., 2008; Negral et al., 2008). Therefore, $PC_{1–12\,months}$ identifies contributions of natural sources associated with those coming from traffic and coal combustion processes.

As to $PC_{2–12\,months}$, $PC_{3–12\,months}$ and $PC_{4–12\,months}$, the results point out that S is present in all the three components.

In particular, $PC_{2–12\,months}$ is related both to Cd, Ca, Pb and Zn – trace elements typically related to traffic emissions and already found in $PC_{2–6\,months}$ – and Ca and S. As regards Ca, when it is associated with traffic tracers, it is one of the potential markers of re-suspended road dust, but its association with S could also be indicative

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both of secondary atmospheric reactions of sulfur gaseous compounds such as those emitted from the COVA plant and particles coming from the local soil (Lettino and Fiore, 2013). Finally, calcium sulphates (mainly formed as gypsum) may also be related to the long-range transport of African dust (Dall'Osto et al., 2010), whose occurrence is very frequent in the Mediterranean countries during the summer season (e.g. Pey et al., 2013; Boselli et al., 2012; Mona et al., 2006). Therefore, $PC_{2–12\,months}$ identifies traffic-related contributions and secondary atmospheric reactions involving COVA plant emissions and local soil particles with a possible minor contribution of natural emissions from long-range transport of African dust.

Regarding $PC_{3–12\,months}$, it is characterized by P, K, Cu, Zn and S. The presence of Cu, K, P, and S in the same component could suggest the influence of emissions deriving from agricultural practices. In fact, all these elements are found in fertilizers. Moreover, the copper sulphate is commonly used in grapes farming whose presence in the local atmosphere could be related to several vineyards characterizing the area under study. Finally, K, P and Zn could also be associated to the contribution of combustion processes such as biomass burning, wood burning and forest fires whose occurrence is very frequent during the warm season. Therefore, this component identifies the contribution of anthropogenic sources such as agricultural practice-related emissions and biomass and wood burning.

The fourth component (i.e. $PC_{4–12\,months}$) is related to Na and S. By comparing this component with $PC_{4–6\,months}$, it can be observed that they are characterized by the same elements. Therefore this component keeps being essentially related to secondary atmospheric reactions involving the COVA plant emissions.

Finally, the fifth component (i.e. $PC_{5–12\,months}$) is characterized by Mn and Mg. The origin of these elements is mainly related to local soil, therefore this component identifies natural contributions deriving from the re-suspension of particles originating from the local soil.

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4 Conclusions

The study presented highlights that the accumulation capacity of the lichens in relation to the analyzed trace elements is different and that the used lichen species are suitable for biomonitoring investigations. The application of PCA to the trace element concentrations measured in the lichen samples after 6 and 12 month exposures points out that anthropogenic emissions deriving from traffic, combustion processes (wood and fossil fuels), agricultural practices, construction and quarrying activities, and natural emissions mainly related to the re-suspension of local soil and road dusts, represent the main sources contributing to the presence of the trace elements in the local atmosphere. Furthermore, the contribution of secondary atmospheric reactions involving COVA plant emissions was also highlighted. Finally, a possible contribution of natural emissions related to African dust long-range transport was observed when the trace elements measured in the samples exposed for 12 months were considered. All this is consistent with the natural and anthropic features of the study area and also highlights a contribution due to the COVA plant and a seasonal contribution mainly related to the warm season such as long-range transport of African dust, biomass burning, wood burning and forest fires.

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Table 1. Experimental values (mean value ± SD) and certified values are referred to the International Atomic Energy Agency (IAEA) standard reference material, IAEA 336. Recovery percentage and method detection limit (MDL) results are also reported.

Element	Experimental value ($mg\,kg^{-1}$)	Certified value ($mg\,kg^{-1}$)	Recovery (%)	MDL (ppm)
Al[a]	482 ± 71	680	71	0.04665
Ca[a]	–	not reported	–	0.20283
Cd[b]	0.155 ± 0.12	0.117	133	0.00152
Cr[a]	1.265 ± 0.20	1.060	119	0.00324
Cu[b]	4.952 ± 1.16	3.600	138	0.00865
Fe[a]	361 ± 6	430	84	0.13140
K[a]	1734 ± 41	1840	94	0.00867
Li[a]	–	not reported	–	0.00006
Mg[a]	–	not reported	–	0.00423
Mn[a]	48 ± 2	63	76	0.06187
Na[a]	310 ± 24	320	97	0.03230
Ni[a]	–	not reported	–	0.00354
P[a]	522 ± 27	610	86	0.00415
S[a]	–	not reported	–	8.16875
Pb[b]	4.919 ± 0.98	4.900	105	0.08070
Ti[a]	–	not reported	–	0.01488
Zn[a]	31 ± 3	30.4	103	0.00282

[a] ICP-OES
[b] GF-AAS

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Table 2. Scale for the interpretation of the exposed to control (EC) ratios (Frati et al., 2005).

EC ratio	Accumulation/loss
0–0.25	Severe loss
0.25–0.75	Loss
0.75–1.25	Normal
1.25–1.75	Accumulation
> 1.75	Severe accumulation

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Table 3. Mean value ± SD (m ± sd) of the trace element concentrations measured in the control sample and in lichen bags after 6 and 12 month exposures. The mean values of the trace element concentrations are highlighted in bold.

Trace element	Control sample	6 month exposure	12 month exposure
Al	**770** ± 110	**1385** ± 370	**2223** ± 639
Ca	**10 665** ± 928	**14 867** ± 2274	**9589** ± 1021
Cd	**0.5** ± 0.1	**0.7** ± 0.4	**1.1** ± 0.5
Cr	**1.7** ± 0.3	**2.1** ± 0.6	**2.7** ± 0.7
Cu	**9** ± 3	**10** ± 2	**7** ± 1
Fe	**609** ± 87	**1165** ± 325	**1333** ± 390
K	**2785** ± 393	**3426** ± 697	**3336** ± 1023
Li	**0.6** ± 0.1	**1.3** ± 0.4	**1.9** ± 0.5
Mg	**1046** ± 102	**1417** ± 174	**1768** ± 335
Mn	**100** ± 21	**108** ± 36	**128** ± 39
Na	**190** ± 42	**626** ± 376	**727** ± 191
Ni	**0.7** ± 0.2	**1.0** ± 0.3	**1.2** ± 0.3
P	**67** ± 4	**93** ± 16	**147** ± 33
Pb	**7** ± 2	**7** ± 4	**12** ± 9
S	**1046** ± 331	**1265** ± 361	**3466** ± 606
Ti	**24** ± 7	**31** ± 8	**38** ± 10
Zn	**47** ± 11	**47** ± 22	**75** ± 31

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Table 4. PCA results after the normalized varimax rotation for trace element concentrations measured in lichen samples after (a) 6 month and (b) 12 month exposures. Loadings and percentage of explained variance (P%) are reported.

(a) $PC_{1–6\ months}$ $P\% = 30$		$PC_{2–6\ months}$ $P\% = 22$		$PC_{3–6\ months}$ $P\% = 12$		$PC_{4–6\ months}$ $P\% = 9$		$PC_{5–6\ months}$ $P\% = 9$	
Al	0.97	Zn	0.92	P	0.80	Na	0.85	Ca	0.88
Ti	0.97	Cd	0.91	Mn	0.72	S	0.65	Mg	0.58
Fe	0.96	Pb	0.91	K	0.67				
Li	0.88	Cu	0.68						
Cr	0.84	Ni	0.53						
(b) $PC_{1–12\ months}$ $P\% = 31$		$PC_{2–12\ months}$ $P\% = 19$		$PC_{3–12\ months}$ $P\% = 17$		$PC_{4–12\ months}$ $P\% = 8$		$PC_{5–12\ months}$ $P\% = 7$	
Al	0.97	Cd	0.90	P	0.82	Na	0.91	Mg	0.83
Li	0.95	Ca	0.81	K	0.73	S	0.41	Mn	0.53
Fe	0.94	Pb	0.75	Cu	0.69				
Cr	0.92	Zn	0.66	Zn	0.65				
Ti	0.77	S	0.49	S	0.43				
Ni	0.71								

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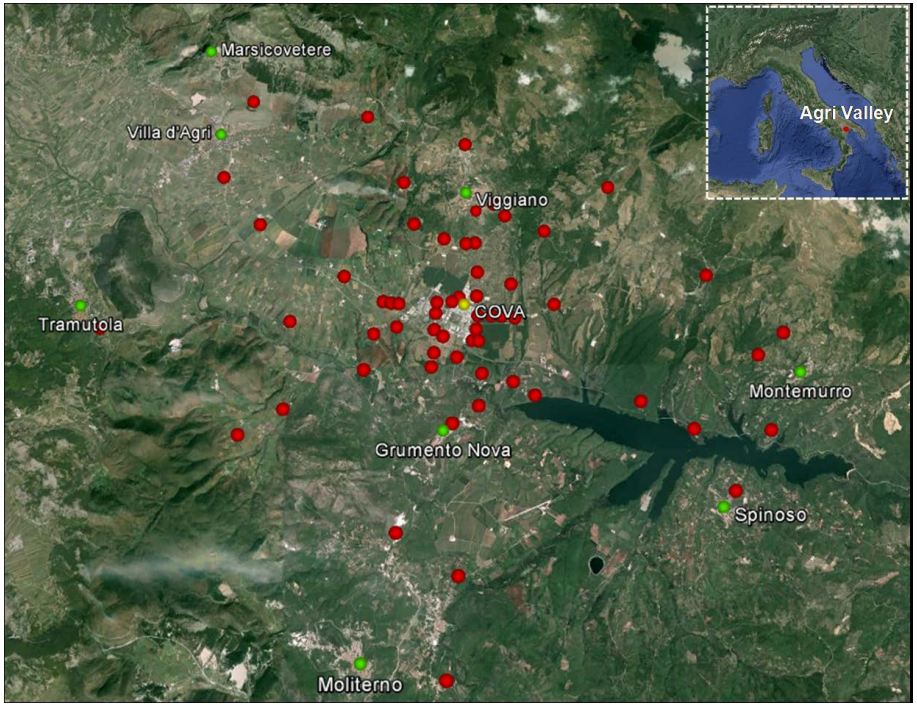

Figure 1. Location of the sampling site. The image also reports the location of the Centro Olio Val d'Agri (COVA) plant and of some towns. Aerial photography to courtesy of Google Earth (http://earth.google.com/).

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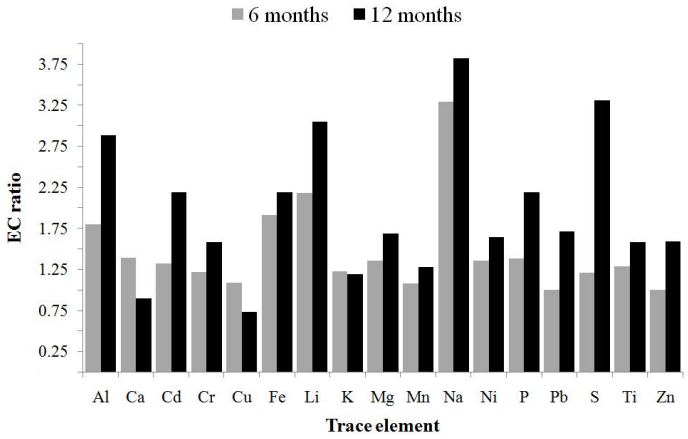

Figure 2. Exposed to control (EC) ratios calculated for the trace element concentrations measured in lichen samples after 6 and 12 month exposures.

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