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RESEARCH ARTICLE

Validation of particulate dispersion models by native lichens as point receptors: a case study from NE Italy

Lorenzo Fortuna[1] · Guido Incerti[2] · Daniele Da Re[3] · Denis Mazzilis[4] · Mauro Tretiach[1]

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Abstract

Atmospheric dispersion model (ADM) simulations are increasingly used as management tools in air pollution monitoring programs, even in the absence of proper validation. Biomonitors can provide important information for ADM validation, but an open question is their temporal frame of application, particularly when native organisms are used. In this study, we tested two alternative ADM simulating the total suspended particulate (TSP) released by a coal power station, against the element content of two native lichens collected at 40 sites, integrated by soil samples. The ADM simulations differed by the time references: the 6-month period preceding lichen sampling, approximately corresponding to the estimated age of the samples (Mod. A), and the whole year 2005, representative of the local average conditions and used in the plant authorization processes (Mod. B). A generalized regression model analysis clearly showed that the Cr, Pb and V content of lichen samples was spatially associated to the outcomes of Mod. A, but not with Mod. B. Interestingly, the Cr content of lichen samples consistently correlated to TSP concentration predicted by Mod. A along two transects placed downwind from the coal power station. This result was corroborated by an air particulate matter sampling which pointed out that air Cr concentrations increased during the operative period of the source. Overall, our results suggest that lichen bioaccumulation data can proficiently be used to validate ADM simulations if the exposure time of the biological samples is consistent with the temporal domain of the ADM simulations.

Keywords Air pollution · Dispersion models · Bioaccumulation · Enrichment factor · Exposure time · Lichen growth

Introduction

The European Union adopted restrictive air pollution regulation policies, which define maximum atmospheric concentration levels for the most harmful pollutants (Directive 2008/50/EC). The compliance to air pollutant limit values is ensured by complementary regulatory instruments, which, on one side, force the industrial companies to implement the best available technologies (BATs) to reduce pollutant emissions and, on the other side, provide a coordinate program for air pollution monitoring and assessment, managed by local environmental protection agencies (Wolterbeek et al. 2010). In 2008, the so-called atmospheric dispersion models (ADMs) were introduced as a new regulatory instrument for air pollution control (Directive 2008/50/EC). These models simulate pollutant dispersion scenarios in a given area depending on the meteorological and geomorphological input datasets, chemical-physical properties of air pollutants and pollutant emission rates from a point or non-point pollution source (Holmes and Morawska 2006). However, the reliability of ADM simulations needs to be tested with proper validation studies, based on the comparison between simulated and observed data of air pollutant concentrations. Especially at a small spatial scale, the validation procedure suffers from the limited number and inadequate

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✉ Mauro Tretiach
tretiach@units.it

[1] Department of Life Sciences, University of Trieste, Via Licio Giorgieri, 10, I-34127 Trieste, Italy

[2] Department of Agri-Food, Animal and Environmental Sciences, University of Udine, Via delle Scienze, 206, I-33100 Udine, Italy

[3] Earth and Life Institute, Université catholique de Louvain, Louvain-la-Neuve, Belgium

[4] Laboratorio Analisi Matrici ambientali e Matrici Sanitarie, Agenzia Regionale per la Prevenzione dell'Ambiente, Via Colugna, 42, I-33100 Udine, Italy

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distribution of ground-measuring points, which generally correspond to the extant network of air pollution monitoring stations. An effective alternative is provided by the use of organisms as biomonitors of airborne pollutants, provided that the term "validation" is not used with the accepted meaning of (statistically) testing a model performance, but rather as the comparison between dispersion models of air pollution, and its effect on target biomonitors (Kansanen and Venetvaara 1991; Balestra et al. 1992; Nimis et al. 2000; Moreno et al. 2003; Giordano et al. 2009; Demiray et al. 2012). Under such assumption, the biomonitoring approach generally ensures optimal sampling density, and readily available biological materials (Rai 2016).

Lichens are excellent biomonitors of air pollution, particularly of airborne trace elements (Kodnik et al. 2017; Fortuna et al. 2019a), polycyclic aromatic hydrocarbons (Augusto et al. 2013; Kodnik et al. 2015) and dioxins (Augusto et al. 2007), because they lack roots, stomata and waxy cuticle and acquire inorganic nutrients predominantly from dry and wet depositions (Knops et al. 1991). Their elemental content is correlated with that of site-specific bulk deposition (Sloof 1995; Van Dobben et al. 2001), and the contribution of soil particulate matter eventually present can profitably be excluded by using the enrichment factor (EF) (Bargagli 1998; Bergamaschi et al. 2002; Kłos et al. 2011). Foliose epiphytic lichens grow radially by extending their margins few millimetres per year (Armstrong and Bradwell 2011; Fortuna and Tretiach 2018). Consequently, the inner parts of foliose thalli have a higher elemental content, being older than the outermost ones, hence exposed for a longer time to the environment (Loppi et al. 1997), evidences of horizontal transport within the lichen thallus being limited to the physiologically important elements (Coccaro et al. 2000). For these reasons, the standard protocols commonly used in lichen biomonitoring surveys state that only the last millimetres from the tip of juvenile, peripheral lobes should be sampled and analysed (Bargagli and Nimis 2002). In this manner, the occurrence of biased data related to lichen material with different ages is minimised (Nimis et al. 2001). Moreover, by knowing the annual radial growth rate of foliose lichen biomonitors, it is possible to estimate the age of sampled lobes and thus their exposure time. The straight relationship between the elemental content and exposure time of the lichen material encourages the implementation of lichens as alternative point receptors for the validation of ADM simulations. To date, however, only few authors tried to validate the outcomes of ADM simulations of air pollutants (e.g. PAH, PM_{10} and trace elements) by using lichens and mosses, at a large (Sloof and Wolterbeek 1991) or a small (De Nicola et al. 2013) geographical scale, and nobody considered as important the exposure time of native lichens as well as the contribution of soil particulate to the thalline elemental composition.

In this study, we explore the hypothesis that a proper methodological approach taking into account both the exposure time of the sampled lichen material and the contribution of soil dust resuspension phenomena can provide a useful dataset for the validation of ADM simulations. As such, testing a multispecies and multisite dataset including lichen and soil information and the two ADM simulations of total suspended particles with different time references, we expect that the lichen element concentrations, once purified from possible exposure and soil-dependent confounding contributions, are significantly and positively associated to the outcomes of ADM simulations of a particulate matter containing different elements.

Material and methods

Study area

The study area is located in NE, Italy, at the boundary between the Friulian floodplain and the Classical Karst plateau and is faced to the Adriatic Sea (Fig. 1a). It has a surface of 176 km^2 and hosts a resident population of over 50,000 inhabitants (2017). The climate is fully humid temperate with a mean year temperature of 13.4 °C and annual average precipitations of 1135 mm y^{-1} (Osmer FVGa, 2018). The yearly anemometric regime shows a strong seasonality: in winter cold, dry and intense ENE winds are predominant, whereas in summer SW sea breezes are frequent (Osmer FVGb 2018). The study area, whose altitude varies between 0 and 251 m a.s.l., is highly heterogeneous in terms of pedology (Fig. 1b; Michelutti et al. 2006) and land cover classes (Fig. 1a; see Bossard et al. 2000). The main land cover classes are semi-natural forests (39.9%) on *Rendzic leptosols* (E soil) in the north-eastern part of the study area (Fig. 1b). Urban-industrial (15.6%) and agricultural (42.8%) areas are concentrated in the central and in the south-western parts of the study area, on *Calcari-fluvic-Cambisols* (C soil) and *Gleyi-fluvic Cambisols* (D soil), respectively (Fig. 1a-b). The remaining 1.7% of the study area is occupied by terrestrial water bodies such as a river and wet lands or by the Adriatic Sea. The main potential pollution sources are: **a** a coal power plant with a total gross power of 992 MW (Ministero dell'Ambiente 2013); **b** a large industrial park, with naval shipbuilding facilities of international relevance, mechanical and chemical industries; **c** vehicular and ship traffic; **d** the Trieste regional airport; **e** agricultural activities, mostly related to ploughing (in late summer and winter), and threshing (in summer); **f** domestic heating (mostly in winter).

Lichen biomonitoring survey (LBS)

The study area was divided in 44 primary sampling units (PSUs) of 4 km^2 each, according to the systematic design proposed at national level for lichen biomonitoring sampling

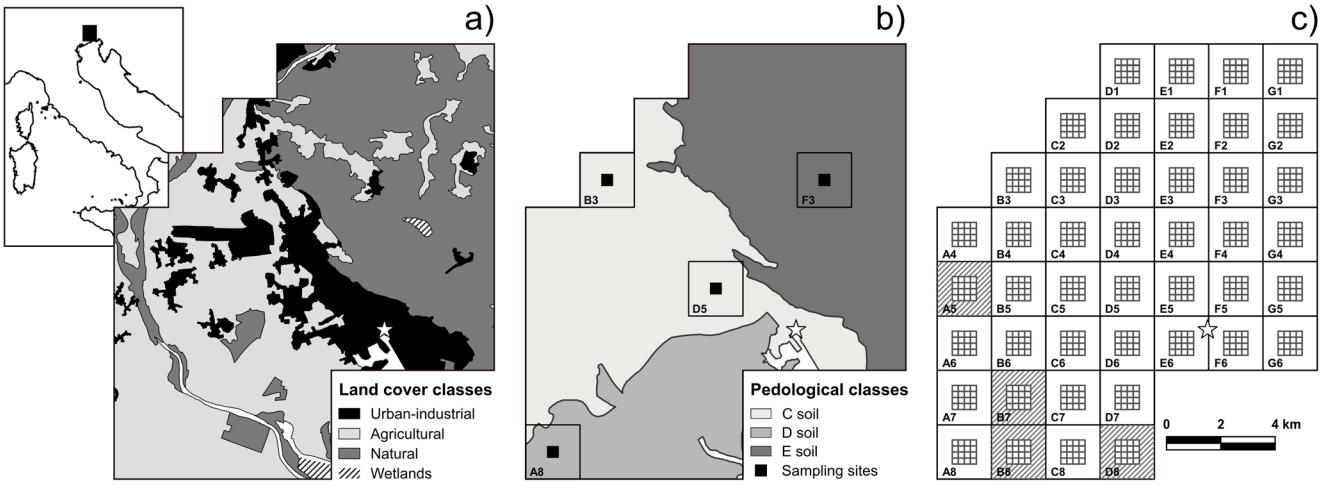


Fig. 1 Distribution of land cover (a) and soil pedological classes (b) within the study area, and subdivision of the study area (c) into 44 primary sampling units (PSUs), of 4 km^2 each, containing 16 Secondary Sampling Units (SSUs) of 0.05 km^2 each. In (b), black squares indicate the location of soil sampling sites. Dashed PSUs (A5, B7, B8 and D8) in (c) were not sampled for absence of material. The white star indicates the location of the coal power plant. The upper left insert shows the geographical location of the study area

(ANPA 2001). Then, in each PSU 16 secondary sampling units (SSUs) of 0.05 km^2 each were defined (Fig. 1c). A preliminary field survey revealed that no macrolichen is uniformly present in the study area. The two most common species are *Flavoparmelia caperata* (L.) Hale and *Xanthoria parietina* (L.) Th. Fr., which have an allopatric distribution (see Barkman 1958; Supplementary Material; Fig. 1), with *F. caperata* occurring more frequently in the north-eastern part of the study area, corresponding to a portion of the Classical Karst plateau and *X. parietina* mostly occurring in the south-western part of the study area, where it is favoured by agricultural activities (Nimis et al. 2001).

Lichen sampling was carried out between 12 and 14 February, 2014 according to the guidelines of Nimis and Bargagli (1998). In each PSU, one to three samples of *F. caperata* and/or *X. parietina* were collected by sampling the outermost parts of the five to ten thalli growing on 1–13 straight, healthy trees placed in one or more SSUs. The material was sampled using a ceramic knife and immediately stored in a sterile petri dish. The geographic location of the lichen-hosting trees was assessed using a mobile device (Samsung Galaxy Nexus GT-I9250). Overall, 4 out of 44 PSUs (namely, A5, B7, B8 and D8) could not be sampled due to lack of sufficient lichen material.

Sample preparation and estimation of lobe age

In the laboratory lichen samples were air-dried for 24 h and then cleaned from bark debris and senescent or damaged portions under a stereomicroscope. A painstaking sample preparation was performed by selecting only the outermost marginal lobe portions. Since the two species had different annual growth rates (Supplementary Material; Table 1), the last 4–5 mm from the lobe tips in *F. caperata* and 2–2.5 mm in *X. parietina* were selected, also avoiding portions with attachment structures (i.e. rhizinae and hapters, respectively). In order to estimate more precisely the average age of lichen samples, the length of 50 lobes of 3 samples of each species was measured under a stereomicroscope, and the exposure time was derived as a function of the local species-specific growth rates of the two species (Supplementary Material; Table 1). Finally, lichen samples of 100–250 mg each were grinded in an agate mortar with liquid nitrogen (20 ml), dried at 40 °C overnight and stored in closed Eppendorf tubes until chemical analyses.

Collection of reference soil samples

The average elemental composition of each soil class was measured in two soil samples collected in sites hosting semi-natural vegetation. In particular, C soil samples were collected in PSUs B3 and D5, D soil samples in A8, and E soil samples in F3. At each sampling site, four subsamples of the first 15–30 cm of soil were collected within a 10 m^2 plot, mixed among them and stored in a glass flask of 10 L until chemical analysis. Before chemical analysis, soil samples were oven-dried, disaggregated and sieved at 2 mm.

Chemical analysis

Lichen and reference soil samples were individually mineralised in Teflon bombs with an acid solution of 7 ml of HNO_3, 3 ml of H_2O_2 and 0.2 of HF following a four-step heating program in a microwave oven (Ethos 1 – MILESTONE). The element concentration of 16 (Al, As, Ba, Be, Ca, Co, Cd, Cr, Cu, Fe, Hg, Mn, Pb, Tl, V and Zn) and 15 elements (the previous ones except Ca) were respectively measured in a mineralised lichen and soil samples by a

mass spectrophotometer (Perkin-Elmer DRCII) following UNI EN ISO 17294-1/2007 and UNI EN ISO 17294-2/2005. The repeatability of the measurements as a relative standard deviation (RSD%) was always lower than 5%. The reliability of the analytical results was checked by analysing nine samples of certified reference material CRM 482 (Quevauviller et al. 1996). Analytical results of CRM indicate that the element recovery percentage was included between 80% and 125%, with the exception of Ca and Cd whose values were 71.9% and 74.6%, respectively.

ADM simulations

The outcomes of two ADM simulations (herein Mod. A and Mod. B) were provided by the environmental modelling centre of ARPA FVG as GIS shapefile georeferenced in EPSG:3004 reference system with the following attributes: latitude, longitude and TSP concentration values expressed as μg m^{-3}. The two ADM simulations represent two different source emission scenarios because they were run with different meteorological input dataset and assumed different source emission conditions. Mod. A was run by selecting a meteorological reference period, which approximately corresponds to the estimated exposure time of lichen samples, i.e. the 6-month period preceding lichen sample collection (September 2013 – February 2014) (see *supra*). Mod. A modelled the TSP emission according to a variable rate depending on the duration of both operational and non-operational state of the source (Supplementary Material; Table 2). On the other side, Mod. B simulated the average distribution of TSP concentration values over a 1-year period by assuming a source emitting an inert pollutant at a constant rate of 4.8 g s^{-1} corresponding to the average rate measured at the plant chimney (Supplementary Material; Table 2). The meteorological input dataset in the Mod. B simulation was the yearly climatic series of the year 2005, commonly used by ARPA FVG as a meteorological reference period for ADM simulations. Mod. B has been used in the most recent authorization processes of the coal power plant, and also in an investigative procedure aimed at verifying the environmental impact of the emissions, which has been carried out by officers of the enquiring justice court of Gorizia.

Data analyses

Descriptive statistics of element concentrations were expressed as mg kg^{-1} and calculated separately for the two species. Then, in order to contextualize the entity of element emission load in the study area, element concentration values of lichen samples were interpreted according to (i) the bioaccumulation scales recently proposed by Fortuna et al. (2019b) for native lichens and (ii) the total charge index of Nimis et al. (1999). By using bioaccumulation scales, the accumulation of 8 elements (Al, As, Cd, Cr, Cu, Hg, Pb, and Zn) in both species and that of V in *F. caperata* was qualitatively assessed as the ratio between the element concentrations measured in the lichen samples and the species-specific background elemental composition. Results expressed in this way are called *B ratio* values and were then classified according to five bioaccumulation classes whose upper thresholds values correspond to the 25th, 75th, 90th and 95th percentiles of the distribution function of thousands of measurement carried out over the Italian territory in the last 11 years (Fortuna et al. 2019b). Consequently, by assigning a progressive number to each bioaccumulation class (i.e. from 1 to 5), the total charge index was calculated as the sum of the bioaccumulation classes ascribed to the *B ratio* values observed in each PSU, and then by normalizing the totals within a ten-classes ordinal scale (Nimis et al. 1999).

Soil contribution to elemental composition of lichen samples was taken into account by computing the element enrichment factors (EFs) as proposed by Bargagli (1998). In particular, the element concentrations of each lichen sample were standardized as a function of the elemental composition of the soil class occurring in the respective PSU (Fig. 1b-c). In order to evaluate whether the elemental composition of lichen samples reflected the ADM simulation outcomes, the geographic coordinates of lichen-hosting trees, TSP concentration values predicted by both ADM simulations and the spatial distribution of the three soil pedological classes were georeferenced in EPSG:3004 reference system using QGIS (version 2.6). Then, both element concentrations (EC dataset) and element EFs (EF dataset) of lichen samples were geographically paired to the ADM simulation values at tree scale and averaged for each lichen species and PSU. Then, both EC and EF datasets were submitted to a Principal component analysis (PCA) including binary dummy variables, indicating the presence/absence in each PSU of each soil pedological class and lichen species, as supplementary variable, i.e. variables not used to calculate the principal components (PCs) but plotted on the ordination space based on their correlations with the PCs (Legendre and Legendre 1998), whereas the values of the two ADM simulations and, limited to the PCA of the EF dataset, the Al concentration in lichen samples, were used as continuous supplementary variables. Consequently, the relationships among simulated TSP concentration values and both EC and EF datasets were further investigated through Generalized Regression Models (GRMs). The GRM is a flexible generalization of ordinary linear regression, and, in particular, it can profitably be used to assess the association between a non-normally distributed response variable and one or more explanatory ones via different link functions. In our case, we run GRMs in order to test whether the outcomes of either Mod. A or Mod. B, i.e. the explanatory variables, can be statistically related to the content of an element in the lichen samples (expressed as EC or EF values), which are the response

variable. This approach was repeated three times for each response variable using linear, logarithmic or polynomial (degree 2) link function. Finally, the trends of the element EFs significantly correlated with ADM simulation outcomes were analysed along two transects following TSP concentration gradients. The two transects were respectively extended along those PSUs downwind from the source accordingly to: (i) main wind direction (transect T1: PSUs A6, B6, C6, D6, E6, F6 and G6) and (ii) main wind direction and presence of a single biomonitor species (transect T2: PSUs C8, C7, C6, D6, E6 and G6). Unfortunately, the second condition could be satisfied only for *F. caperata*.

Results

Exposure time and element concentrations of lichen samples

Flavoparmelia caperata was collected in 73% of the 40 sampled PSUs ($n = 29$), whereas *X. parietina* was collected in 45% ($n = 18$). The two species co-occurred in seven PSUs (A4, B3, C3, C6, D4, D5 and G1). According to the measurements of the length of the sampled lobes and the local species-specific radial growth rates, the material of *F. caperata* was estimated to be at most 7-month -old, whereas that of *X. parietina* was approximately 12–15 month-old (Supplementary Material; Table 1).

The descriptive statistics of elemental composition of the two species (Table 1) showed that the mean element concentrations expressed as *B ratios* can mostly be ascribed to the class of low bioaccumulation. Maxima *B ratios* calculated for *F. caperata* samples were ascribed to the "high" and "severe" bioaccumulation classes, whereas those of *X. parietina* to "moderate" and "severe" ones (Table 1). In particular, the maxima concentrations of Al, Cr, Cu, Pb and V in *F. caperata* samples were observed in the same PSU, i.e. G6, which is located 3 km W from the coal power plant, near a paper factory. In proximity of the coal fired power plant, in PSU E6 and F5 where urban and industrial activities are concentrated, *F. caperata* samples had the highest concentrations of As and Cd, respectively. On the other hand, the maximum concentrations of Al, As, Cd, Cr and V in *X. parietina* samples were found in PSU D7, which is located 3 km SW from the coal fired power plant in an open crop area. Interestingly, the maximum Hg concentration values in both *F. caperata* and *X. parietina* samples were observed in PSUs crossed by the Isonzo river, which is known to transport cinnabar from a closed mining site from Idrija (Slovenia) and is the most important natural source of Hg in the study area.

Table 1: Descriptive statistics of element concentrations (mg kg^{-1}) measured in samples of the epiphytic lichens *Flavoparmelia caperata* and *Xanthoria parietina* collected in the SSUs of Fig. 1. The bioaccumulation classes for maximum and mean element concentrations are reported in brackets below the values. Min and Max: minimum and maximum values, respectively; Bc: bioaccumulation classes (see footnote); SD: standard deviation; CV: coefficient of variation expressed as percentage.

	Al	As	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe	Hg	Mn	Pb	Tl	V	Zn
F. caperata																
Min	110	0.14	1.5	0.002	7200	0.11	0.16	0.36	4.9	94	0	8.3	0.98	0.030	0.34	22
Max	1600	0.67	13.0	0.027	37,000	0.67	0.75	5.80	9.9	1100	0.200	26	11.0	0.180	3.70	80
($Bc^{\dagger}$)	(S)	(H)				(H)		(S)	(L)		(H)		(H)		(S)	(M)
Mean	303	0.27	4.9	0.008	20,707	0.24	0.31	1.27	6.7	232	0.073	16	2.7	0.016	1.25	44
($Bc^{\dagger}$)	(L)	(L)				(L)		(L)	(L)		(L)		(L)		(L)	(L)
Median	255	0.24	4.4	0.007	21,000	0.21	0.30	0.89	6.4	195	0.068	15	2.3	0.007	1.10	41
SD	218	0.11	2.5	0.005	6584	0.12	0.10	1.05	1.2	155	0.033	5	1.9	0.027	0.63	13
CV	71.9	40.5	50.1	55.4	31.8	49.3	32.7	82.8	17.8	66.9	45.7	28.3	71.2	169.0	50.8	30.9
X. parietina																
Min	150	0.12	1.6	0.003	520	0.04	0.04	0.69	3.2	140	0	9.2	0.36	0.004	0.51	13
Max	1300	1.00	6.8	0.029	1400	0.75	0.37	5.10	15.0	1600	0.290	37	2.6	0.019	4.10	56
($Bc^{\dagger}$)	(H)	(S)				(S)		(M)	(M)		(S)		(M)			(M)
Mean	453	0.28	3.3	0.009	866	0.14	0.11	1.64	5.6	360	0.047	16	0.9	0.008	1.05	23
($Bc^{\dagger}$)	(L)	(L)				(L)		(L)	(L)		(L)		(A)			(L)
Median	380	0.25	2.9	0.008	850	0.09	0.10	1.45	4.6	285	0.038	15	0.7	0.006	0.90	21
SD	234	0.20	1.4	0.005	218	0.17	0.07	0.92	2.7	287	0.053	6	0.5	0.004	0.70	10
CV	51.7	70.6	41.1	55.8	25.2	120.3	62.8	55.9	47.6	79.9	114.6	38.3	59.1	48.6	66.2	42.2

† Bioaccumulation classes: (A): Absence of bioaccumulation; (L) Low bioaccumulation; (M): Moderate bioaccumulation; (H): High bioaccumulation; (S): Severe bioaccumulation.

The total charge index (Fig. 2a) indicates relatively high trace element contents in the PSUs placed within or in close proximity of urban and industrial areas, namely in D7, G6, E6, C6 and C7.

ADM simulations

The maximum yearly average of TSP concentration values predicted by the two ADM simulations (Fig. 2b-c) differed both in magnitude and spatial distribution within the study area. That of Mod. A was 0.095 μg m^{-3} and was concentrated in the south-western part of the study area (Fig. 2b). On the other hand, that of Mod. B was 2.5 less than that of Mod. A (i.e. 0.038 μg m^{-3}) and was localized in the south-western part of the study area as well as in its north-eastern part (Fig. 2c). This distribution difference depends on the anemometric data of the meteorological input datasets used in the two simulations (see Supplementary Material; Fig. 2): although both anemograms show high frequency of NE and ENE winds, that of Mod. A has significant lower frequencies of SWS winds.

PCA of element concentration values (EC dataset)

The PCA of EC dataset (Fig. 3a) revealed two distinct clusters of elements, segregated on the basis of the element composition of the species. *F. caperata* had on average significantly higher concentrations of Ba, Ca, Co, Pb and Zn with respect to *X. parietina*, and lower concentrations of Al, As, Be, Cr and Fe (Table 1). These two groups of elements were, respectively, negatively and positively correlated with the second principal component of the PCA, in good accordance with the arrangement of the two vectors representing the supplementary variables of the two species (Fig. 3a). Mn, Cd, Cu, Hg and Tl were little related to both two first principal components indicating that they were weakly correlated with the remaining elements. V was unrelated to species, soils and ADM simulations, but it was highly and negatively correlated with the first principal component. The arrangement of E and C soil supplementary variables reflected the relative abundance of *F. caperata* and *X. parietina* samples in the Classical Karst and in the floodplain, respectively, with D soil apparently unrelated to both species because an equal number of *F. caperata* and *X. parietina* samples ($n = 4$; Fig. 3a) were collected in sites with that soil type. The predicted TSP concentration values of both models were unrelated to the first two principal components of this PCA and to the majority of selected elements. Accordingly, the results of GRM analysis clearly indicate that the goodness of fit of GRMs based on TSP concentrations predicted by the outputs of both ADMs (Table 2) and the element content of lichen samples are very low ($R^2 < 0.20$), independently by the selected link function in the GRM setting. However, when the GRMs were run using the EC values of a single species, the GRM fitting performance increased, especially when the polynomial link function was used. In particular, the concentration of Cr in the *F. caperata* samples was significantly related to the outcomes of both ADMs, with R^2 values comprised between 0.120 and 0.365. For *X. parietina* samples a significant polynomial relationship ($R^2 = 0.435$) was observed between Zn concentration and Mod. B values only. However this last result should not be considered as fully reliable for the restricted spatial distribution of *X. parietina* samples in the study area, when the spatial distribution of *F. caperata* is on the contrary quite homogeneous.

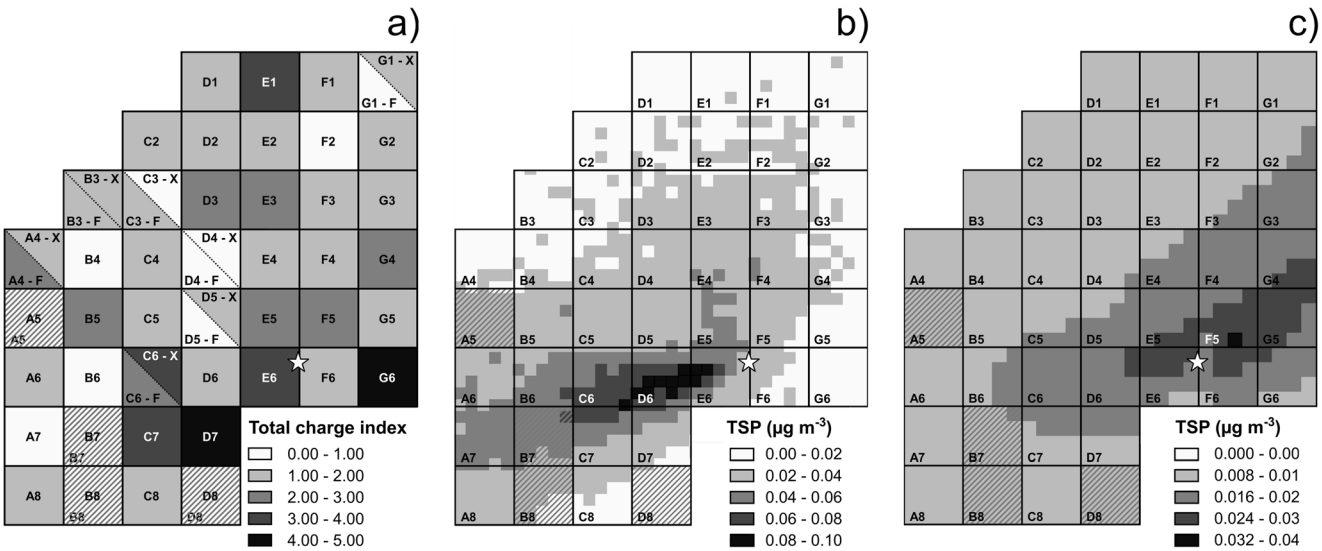


Fig. 2 Classification of the 40 sampled primary sampling units (PSUs) according to the total charge index calculated as proposed by Nimis et al. (1999) (a); the seven PSUs subdivided into triangles refer to the sampling sites where both epiphytic lichens *Flavoparmelia caperata* (F) and *Xanthoria parietina* (X) were sampled. Distribution of TSP concentration values as predicted by Mod. A (lichen sampling pre-collection period) (b) and Mod. B (yearly reference period) (c)

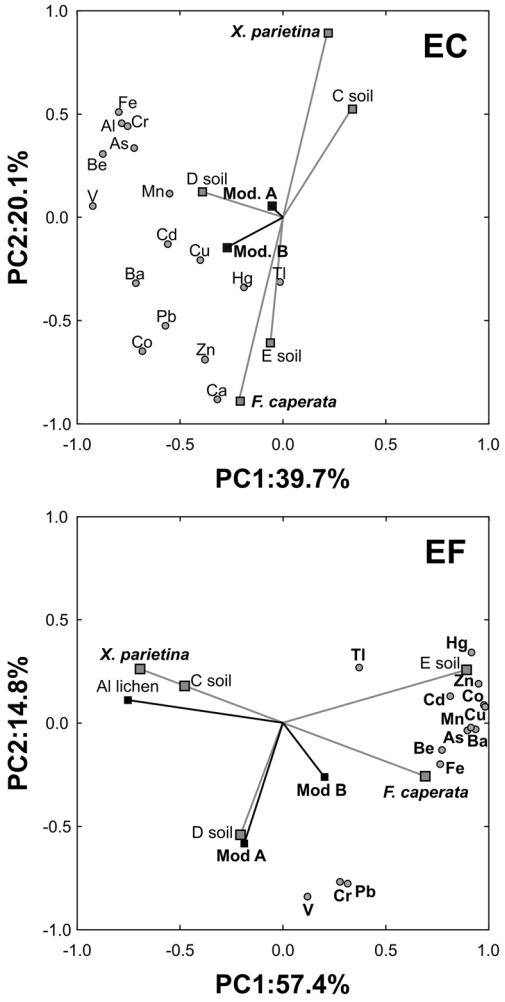


Fig. 3 PCA results for the element concentration (EC) and enrichment factor (EF) datasets are reported in the upper and lower panel, respectively. Grey continuous vectors represent the binary supplementary variables: lichen species (*F. caperata, X. parietina*) and pedological classes (C, D and E soil). Black vectors represent the continuous supplementary variables: ADM simulation values (Mod. A, Mod. B) in both EC and EF, and lichen Aluminium concentration (Al lichen) in EF only. Mod. A and Mod. B are TSP concentration values predicted for yearly reference conditions and for the lichen sampling pre-collection period, respectively

PCA of element EF values (EF dataset)

The PCA based on EF values (Fig. 3b) revealed two distinct, well-defined clusters of elements. The first one included As, Ba, Be, Cd, Co, Cu, Fe, Hg, Mn, Tl and Zn, with high EF values observed in *F. caperata* samples from the Karst sites. These elements were uncorrelated with the TSP concentration values of both ADM simulations. On the other hand, the second one included only Cr, Pb and V, which were positively associated to the TSP concentration values of Mod. A and to a lesser extent with those of Mod. B (Table 2). Besides, the goodness of GRMs fit increased when the EF values were related to the simulated values of Mod. A rather than to those of Mod. B. Moreover, it is worth noting that also in this case the GRM fitting performance increased when the analysis was restricted to the EF values of a single species. In particular the results of GRMs clearly show that Cr, Pb and V EFs calculated for *F. caperata* samples were significantly related to the outcomes of Mod. A using linear or polynomial link function in GRM settings. The R^2 values associated to the GRMs based on the EF values of these three elements were among the highest observed ($0.415 \leq R^2 \leq 0.644$). Also the Cd EF values of *X. parietina* samples were highly and significantly related to the simulated values of Mod. A, but the low recovery value of this element suggests caution in the interpretation of this result. The following analysis of the two transects was thus restricted to EFs of three elements only: Cr, Pb and V.

Trends of Cr, Pb and V EFs along wind-based transects

Along the two transects built according to the main wind direction and position of the putative emitting source (Fig. 4), the maximum values of Pb and V EFs did not coincide with the highest TSP concentration values predicted by both ADM simulations, although the EFs values of both elements were more closely related to Mod. A than to Mod. B (Fig. 4; Table 2). On the contrary, the EF values of Cr showed several good, interesting matches. Along transect T1, disposed in W-E direction, and where samples of both species were collected, the TSP concentration values predicted by Mod. A (but not by Mod. B) fitted consistently the observed values (Fig. 4). Along transect T2, whose samples belonged exclusively to *F. caperata*, the results were even more satisfactory, since maxima and variation trends of predicted and observed values were perfectly congruent (Fig. 4).

Discussion

The present work was aimed at investigating the potential of a lichen biomonitoring survey (LBS) in providing useful data to validate the outcomes of ADM simulations, which model the distribution of TSP emissions from a coal power plant localized in an environmentally complex area. In the literature, the validation of ADM simulations based on bioaccumulation data collected in the surroundings of urban and industrial environments is documented, to the best of our knowledge, by three studies only. De Nicola et al. (2013) tested the use of the transplanted moss *Hypnum cupressiforme* Hedw. to validate the outcomes of the so-called street canyon models, which specifically simulate the pollutant dispersion related to urban traffic in a town street. In their pioneering works, Sloof and Wolterbeek (1991) and Sloof (1995) compared the model-simulated values of a diffusive trace element pollution scenario with the results of an extensive, large-scale LBS. This was performed at low spatial resolution (1 sampling site × 100 km^{-2}), without taking into account the factor "age of

Table 2 R^2 values of significant GRMs (p value <0.05) testing the linear (L), logarithmic (Log) or polynomial (P; degree 2) relationship between TSP concentration values predicted by either Mod. A or Mod. B (explanatory variables) and the element concentrations (EC) or enrichment factors (EF) values (response variables) derived for samples of one lichen species only (F: *Flavoparmelia caperata,* n = 29; X: *Xanthoria parietina,* n = 18) or both (F + X; *n* = 47). Empty spaces refers to non-significant GRMs

	Al	As	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe	Hg	Mn	Pb	Tl	V	Zn
Mod. A																
EC																
$F+X^{L}$								0.088								
$F+X^{Log}$								0.043								
$F+X^{P}$								0.157								
F^{L}		0.129						0.297								
F^{Log}								0.120								
F^{P}								0.365								
X^{L}																
X^{Log}						0.074							0.244			
X^{P}																
EF																
$F+X^{L}$								0.142					0.155		0.320	0.047
$F+X^{Log}$								0.061					0.084		0.252	
$F+X^{P}$								0.459					0.232		0.326	
F^{L}								0.428					0.415		0.455	
F^{Log}								0.242					0.315		0.359	
F^{P}								0.664					0.418		0.457	
X^{L}						0.402										
X^{Log}						0.237										
X^{P}						0.663										
Mod. B																
EC																
$F+X^{L}$			0.118			0.097		0.088								0.154
$F+X^{Log}$			0.117			0.105		0.077								0.122
$F+X^{P}$																0.175
F^{L}		0.190	0.130			0.136		0.173								
F^{Log}		0.214	0.150			0.146		0.211								
F^{P}		0.191														
X^{L}																
X^{Log}																
X^{P}																0.435
EF																
$F+X^{L}$						0.093		0.081								
$F+X^{Log}$						0.092		0.067								
$F+X^{P}$																
F^{L}								0.142								
F^{Log}								0.138								
F^{P}																
X^{L}																
X^{Log}																
X^{P}						0.344										

sampled lichen material". In bioaccumulation phenomena, on the contrary, it is important, if not fundamental, to critically consider the exposure time of the analysed material (Monaci et al. 2000). With transplants, this coincides with the duration of the exposure, which is generally comprised between 1 and 3 months, max. 6 (Tretiach et al. 2007). More problematic is to

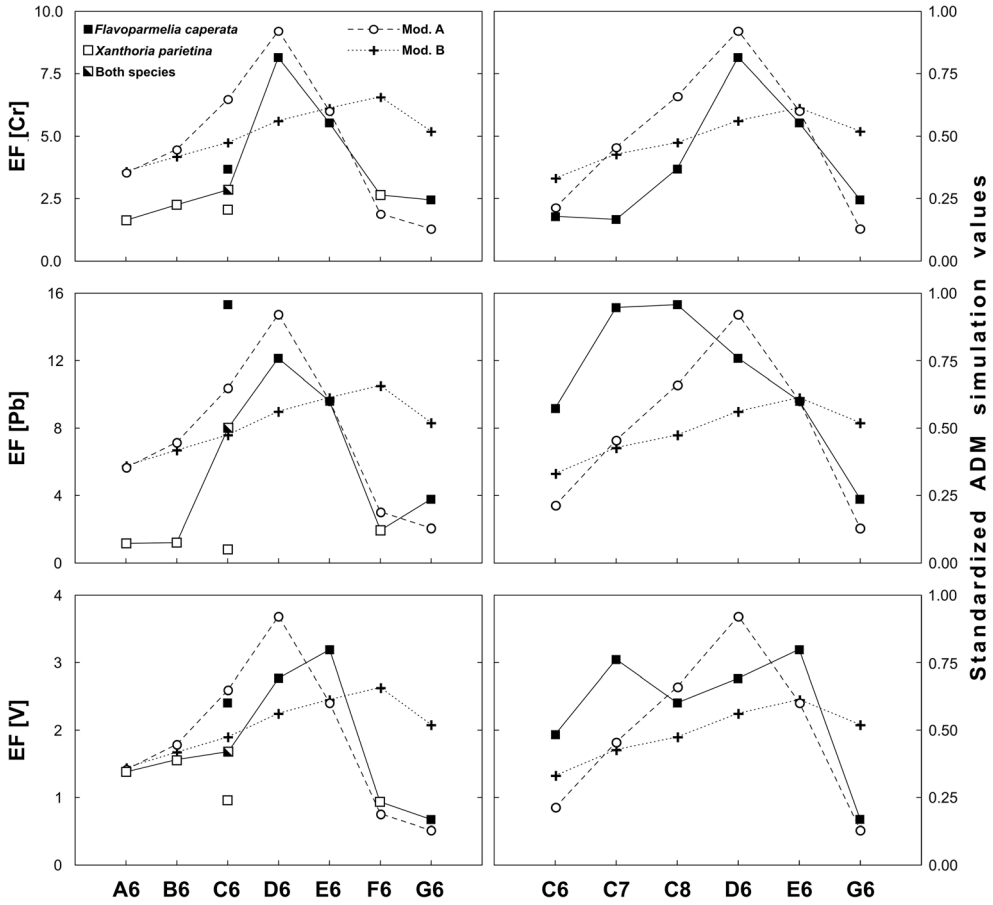


Fig. 4 Trends of Cr, Pb and V enrichment factors (EFs) observed in samples of *Flavoparmelia caperata* (filled squares), *Xanthoria parietina* (empty squares) or in both species (half-filled squares) collected along two wind-based transects, namely T1 (PSUs A6, B6, C6, D6,E6, F6, G6; left panel) and T2 (PSUs C8, C7, C6, D6, E6, G6; right panel) where samples of both species or *F. caperata* only have been collected, respectively. The TSP concentration values of Mod. A (dashed lines with open circles) and Mod. B (dotted lines with crosses) were reported as standardized values included between 0 and 1

define the exposure time of native organisms, if these do not have a seasonal growth, possibly marked by discrete, easily recognized portions. In the past, many authors bypassed this problem by sampling the whole thalli, under the assumption that the whole body reflects the mean air composition (e.g. Bennett and Wetmore 1999; Freitas et al. 1999). Unfortunately, this is not certainly true for most foliose lichens, in which the younger, peripheral lobes have lower concentrations of airborne trace elements with respect to the old, central portion of the thallus (Bargagli et al. 1987; Nimis et al. 2001). For this reason, we purposely selected the average age estimated for *F. caperata* (i.e. the most abundant and homogeneously distributed species sampled in this LBS, covering 75% of the study area) as the best proxy to define the temporal domain of one of the two alternative ADM simulations presented here, i.e. Mod. A. This simulation predicted the spatial distribution of TPS deposition released by the coal power plant according to the meteorological conditions occurred in the last 6months before lichen sampling, approximately corresponding to the age of the collected material. Mod. A was alternative to Mod. B, which was a canonical 1-year long ADM based on the arbitrarily defined "exemplificative year" 2005, when the weather conditions were those "typical" for the area, and a complete series of meteorological data were available.

The high environmental heterogeneity of the study area (Fig. 1a-b), well reflected by the allopatric distribution of the two target lichens, certainly partially affected the validation analysis at spatial level. However, our methodological approach allowed to minimize at least the side effects related to soil dust re-suspension phenomena that are generally recognized as a source of trace elements emissions, especially in agricultural areas (Nimis et al. 2000), well represented in the study area (Fig. 1a). By computing the element EFs according to Bargagli (1995), the elemental composition of the three soil classes C, D and E of Fig. 1b was used as a proxy of the average elemental contribution of different soil types in the respective lichen sampling sites. *F. caperata* and *X. parietina* seem to have different bioaccumulation capabilities for the selected elements, likely due to the different chemical composition of their cell walls which can play a decisive role in covalently binding ionic metals. For example, the mycobiont cell wall of *F. caperata*, but not of *X. parietina*, is rich in oxalates deposits, which enhances the immobilization of bivalent cations, consistent to our results (Fig. 3a). Furthermore, the collected samples of *X. parietina* were evidently too scarce to give a spatially consistent match to the outcomes of both models. Conversely, the bioaccumulation data of *F. caperata* resulted temporally and spatially consistent with both ADM simulations, in particular to Mod. A. Indeed, the validation

analyses based on a PCA approach and the implementation of GRMs clearly indicated that only Cr, Pb and V EFs of *F. caperata* were highly and significantly related ($R^2 > 0.40$; p value <0.05) with the outcomes of Mod. A according to a polynomial trend (Fig. 3; Table 2). Cr, Pb and V are frequently encountered in the particulate matter emissions of coal-fired power plants (Vejahati et al. 2010). The trace element concentrations of coal combustion emissions strongly depend on the mineral composition of coal (Vassilev et al. 1995), as well as on the segregation processes during the formation of combustion residuals, i.e. fly ashes and slag (Querol et al. 1995). Cr, Pb and V usually occur in the finest fraction of particulate emissions (0.3–10 μm) and their concentration increases with decreasing particle size (Xu et al. 2004). The coal fired power plant at the centre of this LBS is equipped with BAT for the abatement of particulate emissions such as an electrostatic precipitator (ESP) and a wet scrubber flue gas desulphurization (FGD) system. However, despite its high efficiency (>99.9%), the ESP system is not able to remove particles of 0.5–1.5 μm in diameter, whereas the FGD system may actually increase heavy metal concentrations downstream to the particulate abatement systems (Vejahati et al. 2010). Although the plant fully respected the emission limits defined by the Italian regulations (ARPA 2014), on the basis of the results of the bioaccumulation classes as well as those presented in Figs. 3 and 4, the plant itself must be considered as the first potential source of the three elements accumulated in *F. caperata* thalli. Supplementary, totally independent data actually fully support this conclusion, at least for Cr: in spring and summer 2014, the local environmental agency ARPA FVG carried out an air particulate matter sampling campaign in two arbitrarily selected sampling points when the power plant was fully active (for 41 days of sampling) and inactive (for 58 days of sampling). The concentration of most elements in atmospheric PM_{10} samples did not differ significantly between the two periods, with the exception of Cr, which increased when the coal burning groups of the plant were active, passing from 9.6 (inactive) to 41.1 ng m^{-3} (active). ARPA FVG (2014, 2015) interpreted this increase as a mere instrumental anomaly (sic), not related to the power plant activity, but this conclusion should now critically be re-evaluated in function of the results of Fig. 4.

Although the PCA analysis of Fig. 3 clearly associated Pb and V to Cr, it must be underlined that along the transect T2, the maximum EFs of Pb and V did not perfectly coincide with the maximum TSP concentration values predicted by Mod. A, as conversely seen for Cr (Fig. 4). Also, the ARPA FVG (2014, 2015) study did not actually have evidence on increasing the Pb and V concentration in the air when the power plant was active. Therefore, the spatial distribution of Pb and V in the study area might reflect a diffusive pollution scenario in which several point and non-point sources contribute to their total load, eventually obscuring the emission pattern of the power plant – the elemental composition of lichen samples certainly reflecting all trace element emissions present in an area (Wolterbeek and Verburg 2002). Actually, the highest concentrations of Pb and V (but also Cr) were observed in several sites classified as urban and/or industrial (Figs. 1 and 2a). V can be released by unrelated sources, all present in the study area: vehicular traffic (Adamo et al. 2011), galvanisation (Van Caneghem et al. 2010) and oxy-fuel welding and cutting (Topham et al. 2011). The latter processes related to the shipbuilding activities, which are concentrated in the vast, open-air shipyards located in the harbour area, at the rear of the power plant, are particularly important for V (Moldanová et al. 2009). Concerning Pb, the partial inconsistency between Pb content in lichen samples and the values of ADM simulations might be related to shipbuilding industry and to naval traffic too, since the high concentration of heavy metals in coastal sediments has been referred to these activities (Luo 2013). On the other hand, the influence of vehicular traffic emissions cannot be excluded. Indeed, more than 20 years ago, most of the European countries banned this element as gasoline additive (as tetraethyl Pb) in automobile engines (Ilyin et al. 2007; Monaci et al. 2000). Nevertheless, throughout the twentieth century, the deposition of atmospheric Pb has massively accumulated in urban and forest soils (Nriagu and Pacyna 1988; Kaste et al. 2003) so that soil re-suspension phenomena are considered as an important source of Pb emission in the atmosphere (Laidlaw et al. 2012). In this study the elemental composition of lichen samples was normalized with that of reference soil samples (i.e. collected in stands of semi-natural vegetation), but it cannot be excluded that lichens sampled in urban and agricultural sites had been enriched by soil particulate with a higher Pb concentration than that of the reference soil samples. Finally, it must be taken in consideration that aviation traffic is still considered as an important source of Pb emissions (Carr et al. 2011) because the fuels currently used in aviation still contains tetraethyl Pb. Therefore, the regional airport present within the study area might concur to explain the partial inconsistency between Pb EFs and ADM simulation values.

Conclusions

Although our experimental work cannot give fully conclusive evidences for the complex environmental conditions of the study area and the relatively high number of possible alternative sources of TSP release, we can conclude that lichen bioaccumulation data can profitably be used to validate TPS models, if these are developed for a time frame which correspond as much as possible to the average age of the sampled material (c. 7-month-old in our case). Less clear results are obtained for TPS models that refer to a purportedly

"exemplificative" period of time, typically 1 year, often quite faraway in time (c. 10 years in our case).

Certainly different element data can be used in different environmental contexts to validate different TSP simulations. In this study, Cr seems to be a good local tracer of the coal power plant emissions, although these are relatively low and confused by many others, of disparate origin, as it typically occurs in highly anthropized, mixed land use areas. Finally, *F. caperata* seems to be more effective than *X. parietina* as trace element biomonitor, but this might be related to the facts that in our case study **i** the number of samples of *X. parietina* was too low to give solid information, and **ii** Mod. A was built on the basis of the growth rate of the former species.

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