Environmental Pollution xxx (xxxx) 114482

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: http://ees.elsevier.com

Antimony as a tracer of non-exhaust traffic emissions in air pollution in Granada (S Spain) using lichen bioindicators☆

Annika Parviainen [a,*], Evgenia Maria Papaslioti [a], Manuel Casares-Porcel [b], Carlos J. Garrido [a]

[a] Instituto Andaluz de Ciencias de la Tierra (IACT), CSIC-UGR, Avda. de las Palmeras 4, E-18100, Armilla, Granada, Spain
[b] Departamento de Botánica, Universidad de Granada, Campus Universitario de Cartuja, E-18071, Granada, Spain

ARTICLE INFO

Article history:
Received 25 Febraury 2020
Received in revised form 22 March 2020
Accepted 26 March 2020
Available online xxx

Keywords
Metal(loid) air pollution
Lichen Xanthoria parietina
Antimony
Non-exhaust emissions
Brake wear

ABSTRACT

We have studied the metal air pollution trends in a medium-sized Spanish city suffering from traffic emission using *in-situ* lichen *Xanthoria parietina* as a bioindicator. The large scale sampling included 97 samples from urban, metropolitan and remote control areas of Granada that were analyzed by Inductively Coupled Plasma-Mass Spectrometry. Enrichment factor of Sb exhibited severe anthropogenic enrichment, whereas Cu and Sb showed significantly higher median values in the urban areas with respect to metropolitan areas. Additionally, bioaccumulation ratios of V, Cr, Ni, Cu, Zn, Cd, Sb, and Pb —associated to exhaust and non-exhaust traffic emissions— enabled us to delineate hot spots of metal(loid) accumulation in the main accesses to the city, characterized by dense traffic and copious traffic jams. To distinguish non-exhaust emissions, we studied the spatial distribution of the Cu:Sb ratio —a tracer of brake wear— highlighting the surroundings of the highway and the main traffic accesses to the city likely due to sudden hard braking and acceleration during frequent traffic jams. Our study shows that the metal(loid) contents in lichens are excellent proxies for non-exhaust traffic emissions and that their contribution to the metal(loid) air pollution in Granada is more significant than previously thought.

1. Introduction

Airborne particulate matter (PM) – aerosols – form part of the atmosphere. At the global level, the majority of the PM is of natural origin (∼98%) as opposed to anthropogenic origin (∼2%) (Gieré and Querol, 2010). However, the portion of anthropogenic PM significantly increases in urban areas and the chemical signature of anthropogenic PM is distinct from the natural PM, which has a negative impact on air quality and, subsequently, on human health (Grobéty et al., 2010). The fine fractions of PM (<10 μm and <2.5 μm) tend to be concentrated in anthropogenic pollutants posing higher toxicity, and they are also more harmful to human beings as they may reach the lungs and deposit in the trachea-bronchial or alveolar region (Oberdörster et al., 2005; Pope and Dockery, 2006; Schlesinger et al., 2006; Valavanidis et al., 2008; Zereini et al., 2012). For instance, the World Health Organization (WHO) acknowledges atmospheric pollution as the major source of pollution exposure to humans (WHO, 2018), and the International Agency for Research on Cancer (IARC) of WHO classifies outdoor air pollution as carcinogenic to humans (Group 1) (IARC, 2013). Typical trace elements in polluted air, such as Cd, Cr, Pb, and Hg, are known to be toxic to humans (Tchounwou et al., 2012), As, Be, Cd, Ni, and Cr (VI) are classified as carcinogenic, and Sb_2O_2 as potentially carcinogenic (Group 2 B) according to IARC (IARC, 1989; 2012). Furthermore, a recent publication alerts on the short-term mortality attributed to the PM pollution in Spain (Ortiz et al., 2017). These authors call for urgent implementation of measures designed to reduce PM concentrations of anthropic origin in cities where the principal emission source is road traffic.

Anthropogenic PM may derive from diverse sources, including construction and demolition actions, traffic, industrial and mining activities, metal smelting, waste incineration, and combustion of fossil fuels and biomass (Gieré and Querol, 2010). Traffic emissions are one of the major sources of PM in urban environments. Traffic exhaust fumes have been recognized as a pollution source and are well-contemplated in the environmental legislation, but research interest in non-exhaust emissions is growing fast. The contribution of brake wear, tire wear, and road pavement wear, as well as re-suspension of road dust (non-exhaust traffic emissions), to the atmospheric PM accounts for equally as much as exhaust emissions and their share is estimated to increase in the future (Amato et al., 2014; Grigoratos and Martini, 2015; Pant and Harrison, 2013).

The epiphytic lichens are commonly used as bioindicators of atmospheric metal pollution because they are long-lived perennial organisms

☆ This paper has been recommended for acceptance by Pavlos Kassomenos

* Corresponding author.
E-mail addresses: aparviainen@iact.ugr-csic.es (A. Parviainen); empapaslioti@correo.ugr.es (E.M. Papaslioti); mcasares@ugr.es (M. Casares-Porcel); carlos.garrido@csic.es (C.J. Garrido)

https://doi.org/10.1016/j.envpol.2020.114482
0269-7491/© 2020.

where photobionts and fungi live in a delicate balance that makes them sensitive to environmental variations. Their prolonged exposure time to environmental factors, lack of cuticles or stomata and the absence of mechanisms of excretion make them behave like aerosol bioaccumulators, particularly of metals (Hale, 1979; 1983). The amount of the metals accumulated in the lichen thallus proportionally represents their presence in the atmosphere. In the case of epiphytic species, the thallus acts as a vehicle for transmitting the particles by direct deposition from the air —specifically from the fog, rainwater, gaseous adsorption, or from various types of aerosols. Hence, they serve as valid instruments and proxies to assess the air quality and the potential contamination sources of metals (Conti and Cecchetti, 2001; Brunialti and Frati, 2014). Lichens have been successfully used in the evaluation of metal pollution in urban areas in many countries (Brunialti and Frati, 2007; Giordano et al., 2013; Demiray et al., 2012; Salo et al., 2012; Scerbo et al., 1999, 2002; Vannini et al., 2019). Despite the frequent use of lichens as bioindicators of air pollution around the world, studies of the trace elements in lichens as pollution biomonitors are rare in Spain.

Larger Spanish cities, such as Madrid, Barcelona, and Bilbao, frequently suffer from low air quality but occasionally also medium-sized cities like Granada surpass the national air quality guidelines (Ministry for Ecological Transition, 2019). A “beret of pollution” —as the locals call the pollution layer— due to traffic emissions is often observed covering the city of Granada. The present study focuses on the assessment of the air pollution by metal(loid)s (Al, V, Cr, Mn, Co, Ni, Cu, Zn, Rb, Sr, As, Cd, Sn, Sb, Ba, Tl, Pb, Th, U) in the urban areas of Granada. There is no previous data on the distribution of metal(loid) air pollution over the city and the surrounding metropolitan area, hence this study is complementary to the national air quality monitoring. We present the results of a large scale study of metal(loid)s concentration in the *Xanthoria parietina* in urban and semiurban areas of the city Granada. *X. parietina* is one of the few nitrophilic and toxitolerant lichen species compatible with the atmosphere of the interior of cities and hence suitable for bioaccumulation-based monitoring of traffic emissions in an urban environment. Our study also shows the usefulness of lichens to monitor the impact of non-exhaust emissions on the metal(loid) distribution in an urban environment and to unveil hot spots of exhaust and non-exhaust traffic contamination.

2. Materials and methods

2.1. Description of the study area

The city of Granada is located in a sedimentary basin composed of neogenic-quaternary sediments surrounded by mountains of the Cordillera Bética. The geographical location of the city in a depression and generally slow wind speed hinders the renewal of air and enhances the effect of thermic inversion during the winter season. This geography prolongs the effect of atmospheric aerosol sources, which makes Granada one of the Spanish cities with the highest levels of air pollution. Mediterranean pluviseasonal-oceanic climate prevails in Granada and is characterized by a mean annual temperature of 15.7 °C and mean annual precipitation of 352 mm (www.aemet.es). The night frosts are frequent during the cold winters, and summers are typically dry and very hot with maximum temperatures exceeding 40 °C. Southerly wind direction prevails in the city though it varies along the day. Bioclimatically, the city is located on the upper mesomediterranean, low dry, belt (Rivas-Martínez and Rivas-Sáenz, 2018).

Sierra de Huétor (roughly 10 km from Granada), Valle de Lecrín (20 km), and Río Cacín (30 km) were selected as control areas as they preserve a good state of conservation far-off from traffic pollution. Sierra de Huétor, also part of Cordillera Bética, is mainly composed of limestones of the Alpujárride complex and part of the Maláguide complex. The Sierra de Huétor was declared a Natural Park by the Junta de Andalucía in 1989, and the park is part of the Natura 2000 Network under the designation of Special Conservation Area (ZEC) and Special Protection Area for Birds (ZEPA). In Valle de Lecrín micaschist and calcareous micaschist dominate, whereas the basement of the Río Cacín is composed of sandy limestone.

With ca. 232.000 inhabitants and little over half a million when considering the whole metropolitan area, Granada is a relatively small city in comparison to other Spanish cities. There are no large industries, metal mining or smelting activities near the city of Granada. The ceased Montevives and the active Escúzar mines of celestite ($SrSO_4$) are located 10 and 20 km Southwest of the city of Granada, respectively.

The national air quality monitoring network in Granada consists of three urban observation stations (Granada—North, Congress Palace—center and Armilla—periurban station; Fig. 1). Additionally, there is

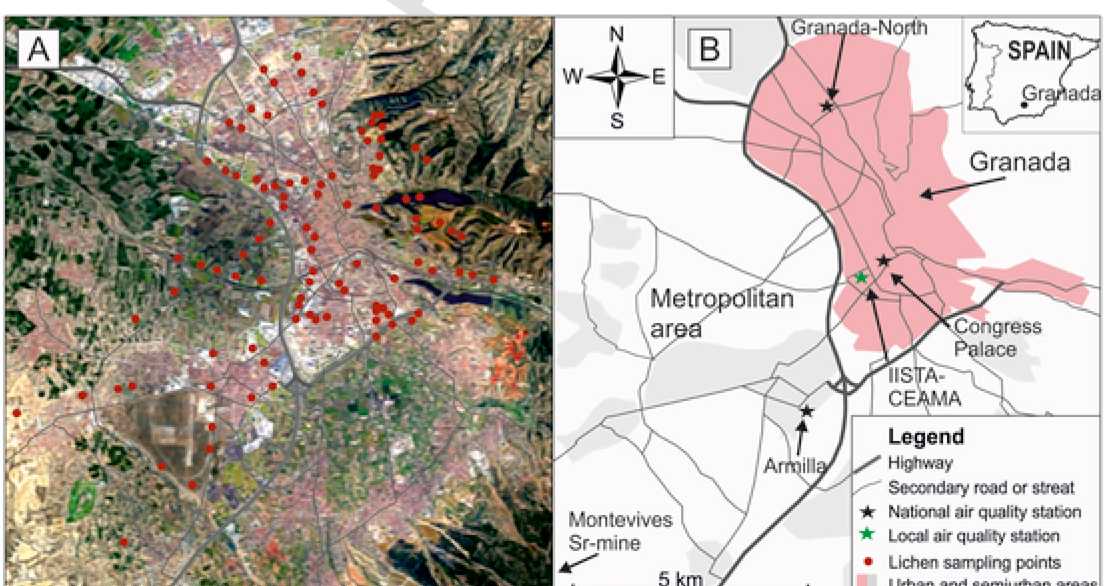

Fig. 1. A) Google Earth© image (November 2019) of the city of Granada and its metropolitan area. Red dots show lichen sampling locations. B) Schematic map of Granada city (red area) and its metropolitan area (grey), showing the location of the air quality stations (stars), and the main highways, secondary roads, and streets. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.).

one monitoring station maintained by the University of Granada at the Instituto Interuniversitario de Investigación del Sistema Tierra en Andalucía (IISTA-CEAMA).

2.2. Sampling

In this contribution, we will refer to the city of Granada and its metropolitan area as the urban and semiurban areas, respectively. We collected 94 lichen samples in green areas, public parks, playgrounds and bike lanes from the urban and semiurban areas (Fig. 1A, Supplementary Table S1). In an urban environment a regular sampling grid is not feasible. We surveyed all green areas of the city as potential sampling sites, and care was taken to obtain as dense and representative sampling as possible. As control samples, we collected lichen composite samples in three remote areas (Sierra de Huétor, Río Cacín, and Valle de Lecrín) located >10 km from Granada. Small villages and roads are located close to these control sites. The approximate distances of sampling sites to the streets, secondary roads and highway are provided in Supplementary Table S1.

As in most cities, there are low abundance and diversity of eligible epiphytic lichen species in the city of Granada (Muñoz-Ibáñez, 2001). We chose *Xanthoria parietina* because it is a ubiquitous, easy to sample, and a toxitolerant species with a large surface that captures and accumulates high quantities of atmospheric pollutants. The whole thalli of lichens were carefully removed from the tree trunks using plastic knife and gloves and collected in metal-free plastic vials. Depending on the availability, we sampled one to six lichen thalli from the same tree trunk to assure enough sample material. In a few cases, we collected lichens in adjacent trees where lichens were scarce. Lichen sampling was challenging in the center of the Granada urban area where green areas are small and scarce. In most cases, lichen samples were collected >1.5 m above the ground to avoid potential influence of soil contamination, and a few were taken between 1 and 1.5 m due to the absence of lichens in the upper parts of the trunk.

2.3. Sample preparation and analysis

Prior to the analysis, the samples were cleaned manually, and dried at 55 °C in an oven for 24 h, then ground and homogenized with a pestle in an agate mortar. Subsequently, they were frozen at −28 °C, re-ground until attaining an optimal grain size reduction and lyophilized using a Telstar LyoQuest. The sample digestion and analyses followed the procedure described elsewhere (Parviainen et al., 2019). Briefly, 50 mg of lichen powder were digested in a mixture of HNO_3 and HF acids (tri-distilled using a Savillex DS-1000 distiller) in closed Anton-Paar high pressure bombs during 20 h, and then slowly evaporated (<60 °C) in metal-free graphite hot plates within ISO-5 vertical flow cabins at the Andalchron ultra-clean lab facilities of the Instituto Andaluz de Ciencias de la Tierra (Granada, Spain). The concentration of Al, V, Cr, Mn, Co, Ni, Cu, Zn, Rb, Sr, As, Cd, Sn, Sb, Ba, Tl, Pb, Th, and U, were measured in diluted nitric acid solutions by Inductively Coupled Plasma-Mass Spectrometry using an Agilent 8800 ICP-MS/MS at the Andalchron facilities (Instituto Andaluz de Ciencias de la Tierra, Granada) by external calibration using standard solutions traceable to NIST. Chemical blanks were used to monitor the elemental contributions during the digestion and analytical procedure. For quality control, we analyzed aliquots of CRM BCR-482 (Lichen; Institute for Reference Material and Measurements of the European Commission) and IAEA-336 (Lichen; International Atomic Energy Agency). The results of analyses of these two CRMs are provided in the Supplementary Table S2 and demonstrate an excellent accuracy and reproducibility of certified values for most metal(loid)s, including Sb.

2.4. Statistical analysis and maps

The statistical analysis of the lichen data was performed using the software IBM SPSS Statistics (v. 24). Normality of the dataset was evaluated by the Kolmogorov-Smirnov test. Based on this test, non-parametrical statistical tools were used, including Spearman's correlation and Mann-Whitney *U* test (significance level $\alpha = 0.05$). For the statistical analysis, outliers for Cr, Co, Ba, and Pb in the sample GL83 were eliminated because they were anomalously high.

The Enrichment Factor (EF) was calculated to evaluate the terrigenous vs. anthropogenic origin of metal(loid)s in lichens by using concentrations of the elements of interest (E) and the proposed value for Aluminum (Al) in the Earth's crust (Rudnick and Gao, 2003):

$$EF = \frac{[E]_{Lichen}/[Al]_{Lichen}}{[E]_{Crust}/[Al]_{Crust}}$$

EF values < 10 are considered as terrigenous, whereas EF values > 10 are considered to be impacted by anthropogenic activity. The bioaccumulation ratio (B-ratio) for each element in lichens was calculated after Cecconi et al. (2019) by dividing the measured element concentrations (alteration) by the median concentrations of the lichen control samples (naturality). Considering that the control samples consist only of three samples (Sierra de Huétor, Valle de Lecrín, and Río Cacín) and there are no Spanish national databases of lichens, we made also an evaluation of the B-ratio using the species-specific background element concentrations (BECs) for *X. parietina* in Italy (Cecconi et al., 2019) and for comparison we also used the minimum value measured in our dataset. The Italian BECs for Cr, Ni, Cu, Zn, As, Cd, and Pb were obtained using the peripheral parts of the thalli. Following Cecconi et al. (2019), we used a five-class scale for the interpretation of the pollution level using B-ratios based on the percentile thresholds (25th, 75th, 90th and 95th): Class 1 (Absence of bioaccumulation); Class 2 (Low bioaccumulation); Class 3 (Moderate bioaccumulation); Class 4 (High bioaccumulation); and Class 5 (Severe bioaccumulation). We used the ArcMap (v. 10.5) software for the drawing of the elemental distribution maps

3. Results

3.1. Trace element concentrations in lichens

For the evaluation of the results, we classified lichen samples into urban (city of Granada), semiurban (Metropolitan area), and control areas (remote areas > 10 km). The full chemical data set is provided in the Supplementary Table S3; Table 1 summarizes the data from the different investigated areas, whereas Fig. 2 presents boxplots for the whole data set. The highest maximum concentrations of all measured elements are observed in the urban and semiurban areas. The urban areas host the maximum values of almost all elements except for Sr and Tl that have the highest maximum values in the semiurban area. Similarly, the highest mean and median values of nearly all elements were encountered in the urban and semiurban areas, except for Mn and Cd that display the higher values in the control areas. Moreover, according to the Mann Whitney *U* test, the difference was significant for Cr, Co, Ni, Zn, Sr, Sn, Sb, and Th. When comparing the urban and semiurban areas, Cu, Sn, Sb, and Tl were significantly higher in the urban core.

The EF values of the majority of the elements analyzed in lichens in urban and semiurban areas did not exhibited anthropogenic enrichment (<10). However, Ni, Zn, Cd, and Pb exhibited enrichment in few samples, whereas Sb was the only element that exhibited exceptionally high enrichment with EF values up to >300 in the urban environment (Supplementary Fig. S1).

Our study shows that the highest trace element concentrations in *X. parietina* are found in the urban core and close to the highway — near

Table 1
Summary table of lichen chemistry (mg/kg) with Min., Max., Mean, Median, Standard deviation (SD) for Al, V, Cr, Mn, Co, Ni, Cu, Zn, Rb, Sr, As, Cd, Sn, Sb, Ba, Tl, Pb, Th, and U for urban, semiurban and control areas.

		Al	V	Cr	Mn	Co	Ni	Cu	Zn	Rb	Sr	As	Cd	Sn	Sb	Ba	Tl	Pb	Th	U
Urban area	Min	559	2.1	3.1	29	0.28	1.9	6.2	28	5.0	5.6	0.45	0.035	0.032	0.11	12	0.018	1.2	0.27	0.080
	Max	13,400	26	53	192	3.2	193	97	187	28	186	6.0	0.52	13	42	91	0.14	308	2.4	0.93
	Mean	4200	12	13	74	1.4	12	24	63	14	57	1.6	0.12	2.3	7.2	46	0.065	20	0.85	0.40
	Median	3460	11	11	63	1.4	6.4	19	60	14	52	1.5	0.073	1.8	2.0	43	0.061	13	0.69	0.37
	SD	2450	5.0	7.6	34	0.65	26	15	25	4.7	32	0.79	0.12	2.0	12	17	0.026	37	0.42	0.19
Semiurban area	Min	1080	7.2	5.3	43	0.92	4.0	11	41	6.0	24	1.1	0.036	0.017	0.15	26	0.047	4.0	0.35	0.25
	Max	7220	19	15	170	2.4	11	21	97	21	377	2.8	0.23	3.2	33	69	0.15	24	1.6	0.67
	Mean	3960	12	10	75	1.4	6.7	16	57	14	70	1.7	0.088	1.0	4.0	44	0.088	12	0.88	0.41
	Median	3860	12	10	69	1.5	6.7	16	52	13	45	1.6	0.067	1.1	1.1	44	0.084	12	0.83	0.39
	SD	1840	3.6	2.3	32	0.35	1.5	3.0	14	3.7	78	0.41	0.054	0.93	10	12	0.029	5.6	0.29	0.12
Control area	Min	1030	5.0	4.6	36	0.63	2.1	7.5	29	7.4	12	0.62	0.042	0.16	0.10	20	0.031	3.1	0.36	0.14
	Max	1450	9.4	6.8	115	1.0	4.9	18	42	11	20	1.5	0.25	0.34	0.37	26	0.056	22	0.47	0.29
	Mean	1240	7.2	5.7	75	0.83	3.5	13	35	9.3	16	1.0	0.15	0.25	0.24	23	0.044	12	0.41	0.22
	Median	1240	7.2	5.7	75	0.83	3.5	13	35	9.3	16	1.0	0.15	0.25	0.24	23	0.044	12	0.41	0.22
	SD	298	3.1	1.5	56	0.29	2.0	7.6	9.1	2.7	6.0	0.59	0.15	0.13	0.19	4.0	0.018	13	0.076	0.11

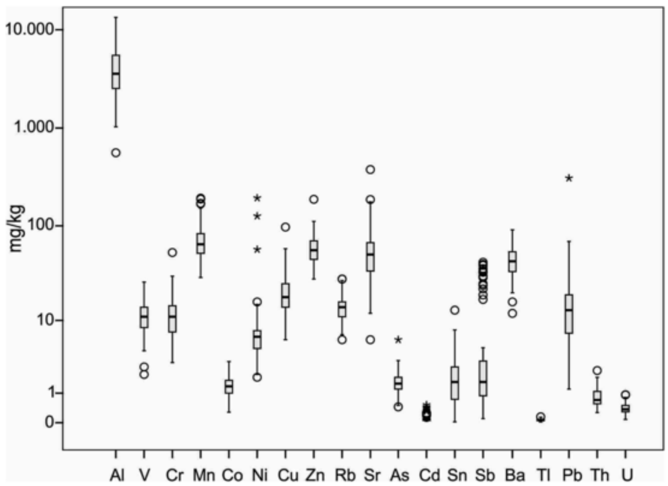

Fig. 2. Boxplots in a logarithmic scale for the analyzed elements in lichen *X. parietina* in Granada.

the main accesses to the city of Granada— where daily dense traffic and copious traffic jams occur (Fig. 3). Spearman's correlations exhibit that the Sb concentrations in *X. parietina* in Granada have a positive and good correlation with Cr and Cu (>0.63), whereas V, Cr, Ni, As, Ba, and Pb are wellcorrelated (>~0.70) (Table 2). Elements such as Co, Tl, Th, and U —with relatively low concentrations— also correlate well with the last group of trace elements (especially, with V, Cr, and As). On the other hand, concentrations of Zn, Sr, Cd, and Sn do not exhibit correlation with other analyzed trace elements in our study. Based on these observations and the potential toxicity of some of the elements, we chose V, Cr, Ni, Cu, Zn, Sr, As, Cd, Sn, Sb, and Pb for further evaluation of bioaccumulation of trace elements in lichens. Some of these elements can also be used as tracers of metal(loid) pollution (Iijima et al., 2008; Pant and Harrison, 2013; Sternbeck et al., 2002; Thorpe and Harrison, 2008; Varrica et al., 2013).

3.2. Bioaccumulation of trace elements

The comparison of B-ratios based on the median of the control samples, minimum value of our dataset and the Italian BECs, confirmed that the results were very similar, showing the same trace element accumulation tendencies only with slight variation in some points from one class to another. Hence, we used the median of the control samples for calculation of the B-ratios (Fig. 3).

The B-ratios for *X. parietina* revealed that the areas suffering from moderate, high, and severe trace element bioaccumulation are found in the urban area, whereas, with a few exceptions, the semiurban areas have B-ratios representing low or absence of bioaccumulation (Fig. 3). However, there is no specific pattern in the trace element distribution in the urban core, but the B-ratios reveal hot spots with metal bioaccumulation in lichens (Fig. 3). Two central samples, one near the Congress Palace National air quality station and another ca. 1 km to the northeast, exhibit moderate to severe bioaccumulation for all metal(loid)s. In Fig. 3, hot spots are surrounded by ellipses to display the spatial distribution of bioaccumulation tendencies. The B-ratios of Sb exhibit high and severe bioaccumulation close to the highway bordering the Granada urban areas and moderate bioaccumulation in the urban core. Vanadium, Cr, Ni, Cu, and Zn exhibit moderate to severe bioaccumulation in the main accesses and the city center, whereas As and Pb have slightly more dispersed distribution. Cadmium presents the highest B-ratios in the southern parts of the Granada urban areas. Strontium exhibits severe bioaccumulation in two sampling points in the semiurban areas, although high and severe B-ratios are also observed in the urban core.

4. Discussion

4.1. Distribution and sources of metal(loid) air pollution in Granada

The air quality in Spain is evaluated according to European Commission Directives for NO_2, SO_2, CO, O_3, benzene (C_6H_6), PM_{10}, $PM_{2.5}$, Pb, Ni, As, Cd, and polycyclic aromatic hydrocarbons (Directive). In Granada, nitrogen oxides (NO, NO_2, NO_x), O_3, and PM (PM_{10} and $PM_{2.5}$) constitute the most significant pollutants, whereas the concentrations of metal(loid)s evaluated in PM remain below threshold values (20, 6, 5, and 0.5 ng/m^3 for Ni, As, Cd, and Pb, respectively) (Ayuntamiento de Granada, 2017; Ceballos et al., 2018; Ministry for Ecological Transition, 2019). According to the annual reports of the air quality in Granada, the Granada-North monitoring station (Fig. 1B) records the highest levels of NO_2 and PM (Ayuntamiento de Granada, 2017; Ministry for Ecological Transition, 2019). The predominant wind direction from South may transport airborne PM from southern parts of the city and the metropolitan area to the northern parts of the city of Granada.

Principal sources of NO_2 are domestic heating and exhaust fumes of traffic emission (Ministry for Ecological Transition, 2019). Further, domestic heating, dense traffic, road dust, re-suspension of cortical material, and air masses —which transport suspended dust from the Saharan desert— are the primary sources of PM impacting the air quality of Granada (Titos et al., 2014). Traffic emissions from direct exhaust fumes and non-exhaust PM, derived from brake and tire wear and resuspension of road dust, are the major contributions to PM in Granada (Titos et al., 2014). In recent years, traffic restrictions to private car circulation and reorganization of the public transport system in the center of the city of Granada have reduced traffic emissions. According to Titos al. (2015), black carbon emissions and PM_{10} decreased significantly in the urban core in 2014 as a consequence of the new public transport organization. However, the air quality of Granada is still very low compared to other Spanish cities with similar environmental characteristics because the geography of Granada —located in a confined basin and depression surrounded by mountains— hinders the renewal of the air masses over the city. This geography enhances the accumulation of air pollution derived from the sources mentioned above.

Several studies have identified different sources of air pollution based on PM chemistry. The sources of non-exhaust traffic emissions can be divided into those caused by abrasion of brakes (Cr, Cu, Ba, Sb, Zn, and Pb pollution), tires (Cu, Cd, Ba, Zn and Pb), and street and road pavements abrasion (Fe, Ti, Li, Ni, Rb and Sr) (Horemans et al., 2011; Pant and Harrison, 2013 and references therein; Sternbeck et al., 2002; Thorpe and Harrison, 2008 and references therein; Titos et al., 2014; Querol et al., 2007). Although the metal composition of brake lining and tires may substantially vary according to the manufacturer, Cu and Sb are considered reliable tracers of brake wear contamination, whereas Zn is associated with tire wear (Iijima et al., 2008; Sternbeck et al., 2002; Thorpe and Harrison, 2008; Varrica et al., 2013; Querol et al., 2007). Diverse metal composition, including Fe, Cr, Cu, Zn, Mn, Pb, Ni, Ba and Cd, is also associated with exhaust emissions from diesel combustion (Agarwal et al., 2011; Coufalík et al., 2019; Shukla et al., 2017). Additionally, V and Ni concentrations are commonly ascribed to fuel oil (Querol et al., 2007; Turunen et al., 1995). In Granada, V and Ni are attributed to diesel combustion emissions (Horemans et al., 2011), but they are also related to regional re-circulation pollution (Titos et al., 2014). Furthermore, according to Titos et al. (2014), Sr, sulfate and crustal elements (mainly Ca and Mg) are attributed to the celestite mines. It is therefore apparent that many metal(loid)s in PM originate from multiple sources, and fingerpointing a reliable and definite source of pollution based on the metal(loid) content may be challenging.

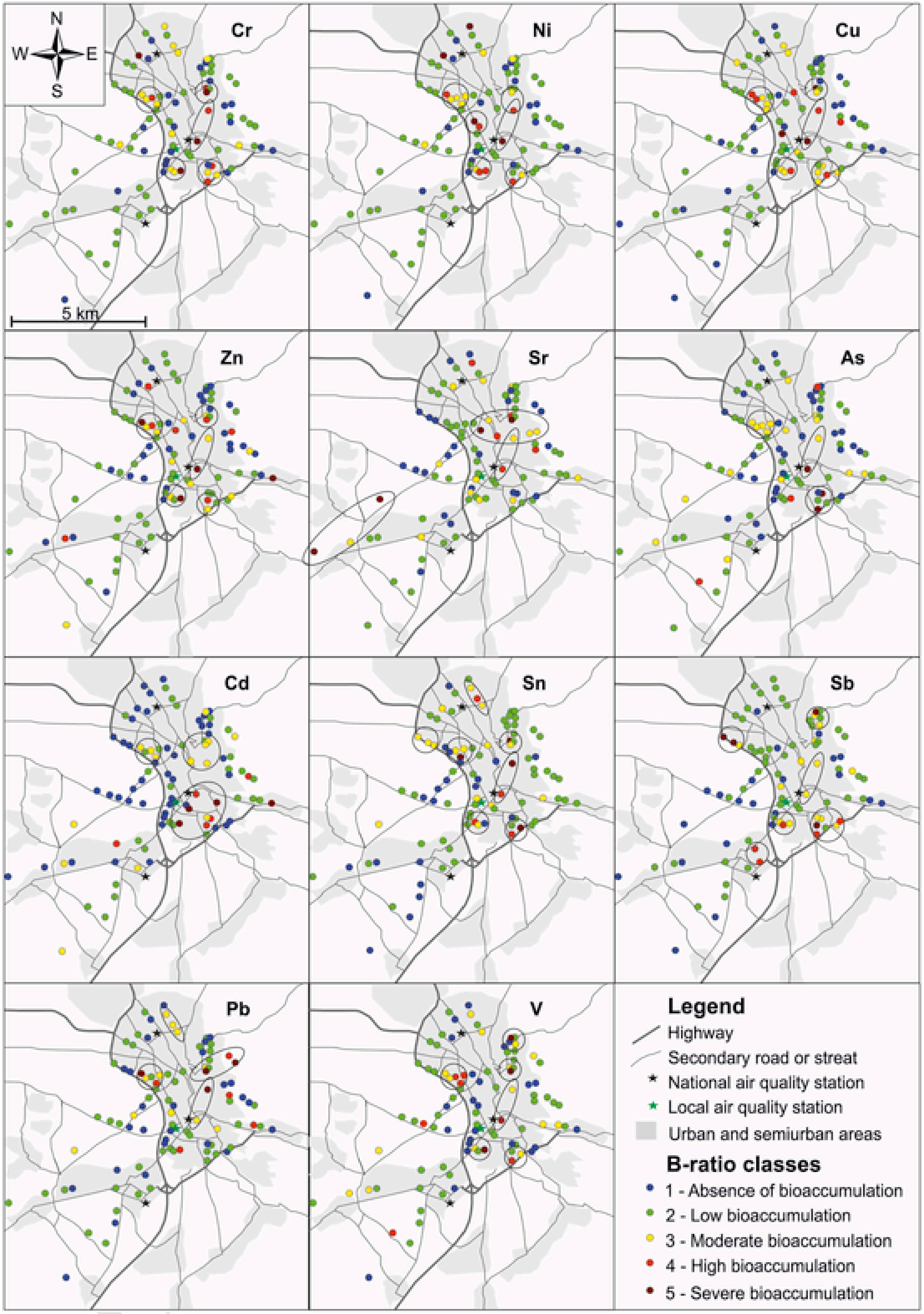

Fig. 3. Bioaccumulation ratios (B-ratios) of *X. parietina* samples for Cr, Ni, Cu, Zn, Sr, As, Cd, Sn, Sb, Pb, and V in the urban and semiurban areas of Granada. The ellipses indicate hot spots of metal bioaccumulation.

The B-ratios of *X. parietina* exhibit different distribution patterns for trace elements in Granada but several systematic trends can be inferred. The B-ratios of V, Cr, Ni, Cu, Zn, As, Cd are moderate to severe in main accesses to the urban areas. In Fig. 3, we have delineated these areas, which are characterized by high traffic density, suffering from copious traffic jams. The sampling sites have a close distance to the streets (>10–50 m), whereas the distance to the circular highway may vary up to several hundred meters. Cadmium differs from this distribution pattern and has particularly high B-ratios in the southern parts of the city. Lead also has a more dispersed distribution pattern

Table 2
Spearman's correlation for concentrations of Al, V, Cr, Mn, Co, Ni, Cu, Zn, Rb, Sr, As, Cd, Sn, Sb, Ba, Tl, Pb, Th, and U in *X. parietina*.

	Al	V	Cr	Mn	Co	Ni	Cu	Zn	Rb	Sr	As	Cd	Sn	Sb	Ba	Tl	Pb	Th	U
Al	1.000																		
V	0.377	1.000																	
Cr	0.482	0.811	1.000																
Mn	0.514	0.565	0.554	1.000															
Co	0.480	0.865	0.862	0.648	1.000														
Ni	0.303	0.674	0.795	0.510	0.744	1.000													
Cu	0.435	0.543	0.730	0.398	0.688	0.574	1.000												
Zn	0.222	0.455	0.517	0.422	0.555	0.495	0.551	1.000											
Rb	0.507	0.567	0.486	0.504	0.541	0.477	0.299	0.385	1.000										
Sr	0.234	0.213	0.144	0.268	0.237	0.116	0.257	0.355	0.179	1.000									
As	0.343	0.824	0.728	0.553	0.765	0.579	0.553	0.597	0.459	0.314	1.000								
Cd	0.211	0.584	0.419	0.315	0.538	0.300	0.354	0.578	0.431	0.243	0.553	1.000							
Sn	0.249	0.298	0.449	0.348	0.349	0.340	0.439	0.242	−0.008	0.179	0.288	0.050	1.000						
Sb	0.468	0.374	0.629	0.321	0.587	0.436	0.632	0.441	0.212	−0.023	0.311	0.272	0.476	1.000					
Ba	0.652	0.738	0.780	0.685	0.819	0.634	0.707	0.451	0.500	0.416	0.673	0.314	0.393	0.486	1.000				
Tl	0.461	0.815	0.693	0.568	0.838	0.606	0.428	0.372	0.606	0.198	0.687	0.516	0.122	0.348	0.687	1.000			
Pb	0.300	0.693	0.563	0.385	0.595	0.440	0.493	0.306	0.361	0.295	0.561	0.501	0.224	0.315	0.591	0.554	1.000		
Th	0.734	0.745	0.708	0.637	0.709	0.538	0.504	0.376	0.606	0.286	0.672	0.373	0.269	0.361	0.795	0.693	0.583	1.000	
U	0.349	0.789	0.633	0.550	0.696	0.547	0.540	0.493	0.399	0.436	0.842	0.438	0.348	0.254	0.716	0.604	0.652	0.716	1.000

and may be affected by the long-term Pb pollution and its recirculation in the PM. As mentioned earlier, V, Cr, Cu, Zn, Ni, Cd, and Pb, are all ascribed to exhaust and non-exhaust traffic emissions. Therefore, evaluating the source of these metals in lichens is challenging, but based on these observations hot spots of traffic emissions can be identified. The severe bioaccumulation of Sr in the semi-urban areas may occur due to the vicinity (2–3 km) of the Montevives celestite mine, even though high and severe B-ratios are also observed in urban areas of Granada.

Considering that V, Cr, Cu, Zn, Ni, Cd, and Pb have multiple sources from both exhaust and non-exhaust traffic emissions, Sb as a clear tracer of brake wear is discussed in more detail. The B-ratios of Sn and Sb rise near the highway and the main accesses to the city, and Sb locally exhibits bioaccumulation in the NE part of the city. The lichen samples with moderate to severe B-ratios of Sb are again located close to the streets (>10–50 m). The high EF values of Sb in the urban areas (Fig. S1) indicate anthropogenic enrichment and the elevated B-ratios suggest that non-exhaust traffic emissions are the potential sources of Sb pollution, principally derived from brake wear (Iijima et al., 2008; Sternbeck et al., 2002; Thorpe and Harrison, 2008; Varrica et al., 2013). We investigated the distribution of Cu:Sb ratio in *X. parietina* as a potential proxy for non-exhaust pollution due to brake wear. Low Cu:Sb in PM is considered as non-exhaust pollution indicator with values of 5:1 —much lower than the natural ratio of 125:1 in the Earth's crust— indicating severe brake wear pollution (Sternbeck et al., 2002; Thorpe and Harrison, 2008). The Cu:Sb ratios for the mean concentrations of PM in the local air quality station of the University of Granada (IISTA-CEAMA) are 7:1 and 8:1 for PM_{1-10} and PM_1, respectively (Titos et al., 2014). These ratios are similar to those calculated for lichen samples in the northern and southern parts of Granada that are in close distance from the highway and in the main accesses to the city indicating hot spots of dense traffic (Fig. 4). The distribution of Sb may depend on traffic density, as well asdriving habits including speed and braking intensity. Low Cu:Sb ratios are also detected in the NE Granada, an urban area with steep streets. As this area does not suffer from dense traffic, the low Cu:Sb ratios may be due to frequent hard braking during circulation in steep streets. The impact of tire wear cannot be evaluated in detail due to the disperse sources of metals characteristic (Cd, Cu, Zn, and Pb) of tire composition. Nevertheless, the high B-ratios of Zn imply the highest tire wear in the main accesses and the city center.

There are numerous sampling points in the urban areas that show absence or low bioaccumulation of the analyzed metal(loid)s. The sampling distance to the streets may influence on the low B-ratios, even though most of the samples were collected to less than 10–50 m from the streets (only 9 samples had 60–80 m distance). Additionally, traffic density is assumed to play an important role in the metal(loid) bioaccumulation. The absence or low bioaccumulation may also be due to the percentile-based classes according to which merely ca. 9 samples out of 94 are classified as suffering from high or severe bioaccumulation. For instance, compared with the maximum Sb concentration of 3.5 mg/kg (mean 0.18 mg/kg) ascribed to traffic emissions in Izmir (Turkey; Yenisoy-Karakaş and Tuncel, 2004), in our study the values ranging from 0.11 to 3.3 mg/kg are ranked in the categories of absence or low of bioaccumulation. Hence, the R-ratios give a relative indication of the severity of metal bioaccumulation.

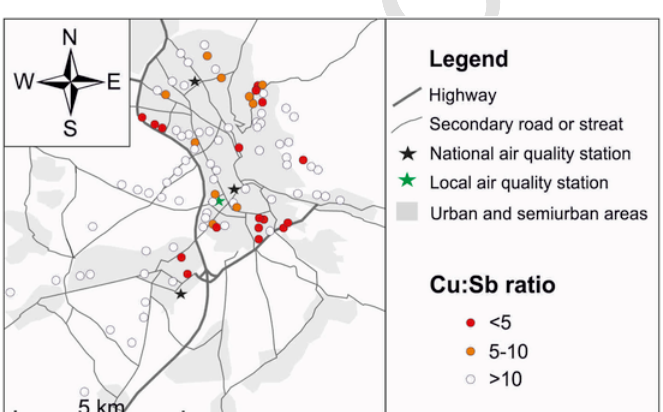

Fig. 4. Cu:Sb ratio of 5:1 in PM is used as an indicator of brake wear. Here the division was made for Cu:Sb < 5:1, 5:1 to 10:1 and < 10:1 for lichen samples.

These findings may be of interest to the decision makers. Local government has recently reduced the speed limit of the circular highway from 100 to 90 km/h in order to reduce air pollution. This measure may work for reducing NO_2 emissions but to reduce metal(loid) air pollution other measures ought to be explored. Based on the results of our study, metal(loid) air pollution is partially derived from non-exhaust emissions and subsequent generation of PM in the air. Reducing traffic jams and moderating the harsh driving style may be partial solutions to decreasing non-exhaust traffic metal(loid) air pollution in PM in Granada and the metropolitan area.

4.2. Comparison of lichen chemistry in other urban areas

Previous studies using lichens as bioindicators in urban areas have identified metal accumulation (*e.g.* Cr, Cu, Ni, Zn, Pb) due to traffic air pollution. For instance, elevated Zn and Pb concentrations in transplanted lichen *Pseudovernia furfuracea* in Viterbo, Italy, are associated to traffic emission (Guidotti et al., 2009), whereas Cu and Pb concentrations in *P. furfuracea* are ascribed to vehicle emissions in urban areas of Naples, Italy (Sorbo et al., 2008). Here we compare the concentrations of traffic-related metal(loid)s in *X. parietina* elsewhere to samples in our study. In urban areas of the Livorno and Pisa provinces (Italy), *X. parietina* samples (peripheral parts) exhibit the highest concentrations for Cr (1.2–102 mg/kg, mean 10 mg/kg in Livorno), Ni (0.9–75 mg/kg, mean 7.4 mg/kg), Zn (11–206 mg/kg, mean 42 mg/kg), and Pb (1.1–8.6 mg/kg, mean 7.4 mg/kg) due to traffic emission pollution without direct impact of industrial activity (Scerbo et al., 1999, 2002). These authors reported lower values for V (0.1–8.3 mg/kg, mean 3.1 mg/kg), As (0.12–14 mg/kg, mean 1.7 mg/kg), and Cd (0.037–0.31 mg/kg, mean 0.10 mg/kg) in Livorno (Scerbo et al., 1999). The mean concentrations of V, Cr, Ni, Zn, and Pb in these Italian urban areas are lower than in urban areas of Granada in our study, whereas As and Cd have similar mean values. *X. parietina* in the urban areas of Kocaeli Province (Turkey) —with mixed influence of traffic and industrial emissions— contains V (3.0–15 mg/kg), As (0.60–3.4 mg/kg), Cd (0.18–1.2 mg/kg), Cu (8.0–26 mg/kg), Pb (8.0–132 mg/kg) (Demiray et al., 2012). The contents of V, Cu, Ni, As, Pb in Kocaeli are lower than those in Granada, while their Zn content shows relatively higher maximum value.

Although Sb is a highly toxic and potentially carcinogenic trace element, it is rarely reported in studies of lichens as pollution bioindicators and only a few studies highlight that Sb is a traffic-related pollutant. According to Yenisoy-Karakaş and Tuncel (2004), traffic emissions are the main contributors to the bioaccumulation of Sb (0.031–3.5 mg/kg, mean 0.18 mg/kg) and Pb (0.28–170 mg/kg, 4.2 mg/kg) in *X. parietina* in the city of Izmir, Turkey. These values are much lower than those we report in *X. parietina* from Granada. Furthermore, Cr (mean 1.4 mg/kg), Cu (7.6 mg/kg), Sb (0.52 mg/kg), and Zn (42 mg/kg) in *Punctelia borreri* in Siena, Italy, are ascribed to traffic pollution (Paoli et al., 2013). However, these concentrations are not comparable to our results due to the different species studied. Transplanted *Evernia prunastri* in Siena showed enrichments in Cu, Cd, and Sb due to traffic-related metal pollution nearby a busy road (Vannini et al., 2019). Surprisingly, *X. parietina* in Granada has more elevated Sb concentrations than those in *X. parietina* in the highly industrialized city of Huelva, Spain (0.29–34 mg/kg, 3.6 mg/kg) (Parviainen et al., 2019). The advantage of Sb lies in that it allows the discrimination of brake wear as a pollution source, whereas other traffic related metals (*e.g.* Cr, Cu, Ni, Zn, Pb) have multiple sources from both exhaust and non-exhaust traffic emissions.

5. Conclusions

According to national air quality monitoring and other previous PM studies, the city of Granada is one of the most air polluted cities in Spain where the main pollutants, NO_2 and PM, are mainly derived from outdated domestic heating and exhaust fumes of traffic. Our study describing metal(loid)s in lichen *X. parietina* in urban and semiurban areas of the city of Granada shows that the lichen chemistry is a valid proxy for biomonitoring of traffic pollution —particularly non-exhaust pollution— that provides a large-scale spatial coverage and is complementary to air quality monitoring stations. Our study clearly shows that metal(loid) concentrations in lichens in the urban core are significantly higher than in the metropolitan area due to higher traffic density. The B-ratios reveal, as well, the hot spots of metal emissions in places with frequent traffic jams. Compared with similar studies of *X. parietina* in urban areas affected by traffic-related pollution elsewhere, *X. parietina* in Granada exhibits higher concentrations of V, Cr, Cu, Ni, As, Sb, and Pb. Our study highlights the bioaccumulation of Cr, Cu, Ni, Zn, Cd, Pb —associated with traffic emissions in general— and Sb —associated with non-exhaust traffic emissions— in lichens in urban areas near high-traffic streets. Antimony is especially enriched in close distance to the highway and the main accesses to the city with dense traffic and exhibits low Cu:Sb ratios indicating brake wear as a major source of metal(loid) pollution. The habit of speeding up and braking in traffic jams in these locations may be the reason for low Cu:Sb ratios. Hence, in order to improve the air quality and to reduce metal(loid) air pollution, the non-exhaust emissions should as well be taken into consideration in the decision making of traffic regulations. We encourage more large-scale biomonitoring studies in other Spanish cities suffering from traffic emissions to establish general guidelines to minimize exhaust and non-exhaust metal(loid) air pollution.

Uncited reference

Directive 2008/50/EC, 2008.

CRediT authorship contribution statement

Annika Parviainen: Conceptualization, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing - original draft, Writing - review & editing. **Evgenia Maria Papaslioti:** Investigation, Validation, Writing - original draft, Writing - review & editing. **Manuel Casares-Porcel:** Investigation, Methodology, Writing - review & editing. **Carlos J. Garrido:** Conceptualization, Funding acquisition, Methodology, Resources, Supervision, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

We acknowledge Ms. I. Martínez Segura and Mr. M.J. Roman Alpiste for their assistance in laboratory work. Dr. A. Parviainen acknowledges the 'Juan de la Cierva —Incorporación' (IJCI-2016-27412) Fellowship funded by the Spanish Ministry of Economy, Industry, and Competitiveness (MEIC). C.J. Garrido received funding from the "Junta de Andalucía" research grant RNM-131. Fellowships, research and infrastructure grants supporting this research have been (co)funded by the European Regional Development Fund (ERFD) and the European Social Fund (ESF) of the European Commission.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2020.114482.

Uncited references

Directive 2004/107/EC, 2005; .

References

Agarwal, A K, Gupta, T, Kothari, A, 2011. Particulate emissions from biodiesel vs diesel fuelled compression ignition engine. Renew. Sustain. Energy Rev. 15, 3278–3300.
Amato, F, Cassee, F R, Denier van der Gon, H A C, Gehrig, R, Gustafsson, M, Hafner, W, Harrison, R M, Jozwicka, M, Kelly, F J, Moreno, T, Prevot, A S, Schaap, M, Sunyer, J, Querol, X, 2014. Urban air quality: the challenge of traffic non-exhaust emissions. J. Hazard Mater. 275, 31–36.
Ayuntamiento de Granada, 2017. Plan de mejora de calidad de aire. Ayuntamiento de Granada, p. 250 (in Spanish).
Brunialti, G, Frati, L, 2007. Biomonitoring of nine elements by the lichen Xanthoria parietina in Adriatic Italy: a retrospective study over a 7-year time span. Sci. Total Environ. 387, 289–300.
Brunialti, G, Frati, L, 2014. Bioaccumulation with lichens: the Italian experience. Int. J. Environ. Stud. 71 (1), 15–26. doi:10.1080/00207233.2014.880996.
Ceballos, M A, Segura, P, Gutierrez, E, Gracia, J C, Ramos, P, Reano, M, Garcia, B, Villeta, C, Garcia, M, Marin, B, Prima, H, Aranda, J A, Veiras, X, Barcena, J, Belmonte, P, Luengo, P, Navascues, E, Hernandez, K, Cabo, J, 2018. La calidad del aire en el Estado español durante 2018. Ecologistas en Acción. https://www.ecologistasenaccion.org/?p = 96516. (Accessed 23 October 2019) (In Spanish.
Cecconi, E, Fortuna, L, Benesperi, R, Bianchi, E, Brunialti, G, Contardo, T, Di Nuzzo, L, Frati, L, Monaci, F, Munzi, S, Nascimbene, J, Paoli, L, Ravera, S, Vannini, A, Giordani, P, Loppi, S, Tretiach, M, 2019. New interpretative scales for lichen bioaccumulation data: the Italian proposal. Atmos 10 (3), 136. doi:10.3390/atmos10030136.
Conti, M E, Cecchetti, G, 2001. Biological monitoring: lichens as bioindicators of air pollution assessmentda review. Environ. Pollut. 114, 471–492.
Coufalík, P, Matoušek, T, Křůmal, K, Vojtíšek-Lom, M, Beránek, V, Mikuška, P, 2019. Content of metals in emissions from gasoline, diesel, and alternative mixed biofuels. Environ. Sci. Pollut. Res. 26, 29012–29019.
Demiray, A D, Yolcubal, I, Akyol, N H, Çobanoğlu, G, 2012. Biomonitoring of airborne metals using the lichen Xanthoria parietina in Kocaeli province, Turkey. Ecol. Indicat. 18, 632–643.
Directive 2004/107/EC, 2005. the European Parliament and of the Council of 15 December 2004 relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air. Orkesterjournalen L 23 (26.1.2005), 3–16.
Directive 2008/50/EC, 2008. the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe. Orkesterjournalen L 152 (11.6.2008), 1–44.
Gieré, R, Querol, X, 2010. Solid particulate matter in the atmosphere. Elements 6 (4), 215—222.
Giordano, S, Adamo, P, Spagnuolo, V, Tretiach, M, Bargagli, R, 2013. Accumulation of airborne trace elements in mosses, lichens and synthetic materials exposed at urban monitoring stations: towards a harmonization of the moss-bag techniques. Chemosphere 90, 292—299.
Grigoratos, T, Martini, G, 2015. Brake wear particle emissions: a review. Environ. Sci. Pollut. Res. 22, 2491–2504.
Grobéty, B, Gieré, R, Dietze, V, Stille, P, 2010. Airborne particles in the urban environment. Elements 6 (4), 229—234.
Guidotti, M, Stella, D, Dominici, C, Blasi, G, Owczarek, Vitali, M, Protano, C, 2009. Monitoring of traffic-related pollution in a province of central Italy with transplanted lichen Pseudovernia furfuracea. Bull. Environ. Contam. Toxicol. 83 (6), 852—858. doi:10.1007/s00128-009-9792-7.
Hale, M E, 1979. How to Know the Lichens. Wm. C. Brown Company Publishers, Dubuque, Iowa, p. 246.
Hale, M E, 1983. In: The Biology of Lichens, 13. Hodder Arnold H&S, London, pp. 978–713128673 200.
Horemans, B, Cardell, C, Bencs, L, Kontozova-Deutsch, V, De Wael, K, Van Grieken, R, 2011. Evaluation of airborne particles at the Alhambra monument in Granada, Spain. Microchem. J. 99, 429–438.
International Agency for Research on Cancer (IARC), 1989. Some organic solvents, resin monomers and related compounds. In: Pigments and Occupational Exposures in Paint Manufacture and Painting. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, 47. p. 291 Lyon, France.
International Agency for Research on Cancer (IARC, 2012. In: Arsenic, Metals, Fibres, and Dusts. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, 100C. p. 501 Lyon, France.
International Agency for Research on Cancer (IARC), 2013. Outdoor Air Pollution a Leading Environmental Cause of Cancer Deaths. The International Agency for

Research on Cancer (IARC) Press release N 221. https://www.iarc.fr/wp-content/uploads/2018/07/pr221_E.pdf. (Accessed 12 October 2019).
Iijima, A, Sato, K, Yano, K, Kato, M, Kozawa, K, Furuta, N, 2008. Emission factor for Antimony in brake abrasion dusts as one of the major atmospheric Antimony sources. Environ. Sci. Technol. 42 (8), 2937–2942.
Ministry for Ecological Transition, 2019. Evaluación de la calidad del aire en España 2018. p. 208 (in Spanish). https://www.miteco.gob.es/es/calidad-y-evaluacion-ambiental/temas/atmosfera-y-calidad-del-aire/informeevaluacioncalidadaireespana2018_tcm30-498764.pdf. (Accessed 27 October 2019).
Muñoz-Ibáñez, A, 2001. Líquenes como bioindicadores de contaminación atmosférica en el área metropolitana de Granada. Bachelor degree work at the University of Granada, In Spanish.
Oberdörster, G, Maynard, A, Donaldson, K, Castranova, V, Fitzpatrick, J, Ausman, K, Carter, J, Karn, B, Kreyling, W, Lai, D, Olin, S, Monteiro-Riviere, N, Warheit, D, Yang, H, 2005. Principles for characterizing the potential human health effects from exposure to nanomaterials: elements of a screening strategy. Part. Fibre Toxicol. 6, 2–8.
Ortiz, C, Linares, C, Carmona, R, Díaz, J, 2017. Evaluation of short-term mortality attributable to particulate matter pollution in Spain. Environ. Pollut. 224, 541–551.
Pant, P, Harrison, R M, 2013. Estimation of the contribution of road traffic emissions to particulate matter concentrations from field measurements: a review. Atmos. Environ. 77, 78–97.
Paoli, L, Munzi, S, Fiorini, E, Gaggi, C, Loppi, S, 2013. Influence of angular exposure and proximity to vehicular traffic on the diversity of epiphytic lichens and the bioaccumulation of traffic-related elements. Environ. Sci. Pollut. Res. 20, 250–259.
Parviainen, A, Casares-Porcel, M, Marchesi, C, Garrido, C J, 2019. Lichens as a spatial record of metal air pollution in the industrialized city of Huelva (SW Spain). Environ. Pollut. 253, 918–929.
Pope, C A, Dockery, D W, 2006. Health effects of fine particulate air pollution: lines that connect. J. Air Waste Manag. Assoc. 56 (6), 709–742. doi:10.1080/10473289.2006.10464485.
Querol, X, Viana, M, Alastuey, A, Amato, F, Moreno, T, Castillo, S, Pey, J, de la Rosa, J, Sánchez de la Campa, A, Artiñano, B, Salvador, P, García dos Santos, S, Fernández Patier, R, Moreno Grau, S, Negral, L, Minguillón, M C, Monfort, E, Gil, J I, Inza, A, Ortega, L A, Santamaría, J M, Zabalza, J, 2007. Source origin of trace elements in PM from regional background, urban and industrial sites of Spain. Atmos. Environ. 41 (34), 7219–7231.
Rivas-Martínez, S, Rivas-Sáenz, S, 2018. Worldwide Bioclimatic Classification System, 1996-2018. Phytosociological Research Center, Spain. http://www.globalbioclimatics.org.
Rudnick, R L, Gao, S, 2003. 3, pp. 1-64. . Composition of the Continental Crust, 3. Treatise on Geochemistry, pp. 1–64, https://doi.org/10.1016/B0-08-043751-6/03016-4.
Salo, H, Bu_cko, Ms, Vaahtovuo, E, Limo, J, Mäkinen, J, Pesonen, L J, 2012. Biomonitoring of air pollution in SW Finland by magnetic and chemical measurements of moss bags and lichens. J. Geochem. Explor. 115, 69–81.
Scerbo, R, Possenti, L, Lampugnani, L, Ristori, T, Barale, R, Barghigiani, C, 1999. Lichen (*Xanthoria parietina*) biomonitoring of trace element contamination and air quality assessment in Livorno Province (Tuscany, Italy). Sci. Total Environ. 241, 91–106.
Scerbo, R, Ristori, T, Possenti, L, Lampugnani, L, Barale, R, Barghigiani, C, 2002. Lichen (*Xanthoria parietina*) biomonitoring of trace element contamination and air quality assessment in Pisa Province (Tuscany, Italy). Sci. Total Environ. 286, 27–40.
Schlesinger, R B, Kunzli, N, Hidy, G M, Gotschi, T, Jerrett, M, 2006. The health relevance of ambient particulate matter characteristics: coherence of toxicological and epidemiological inferences. Inhal. Toxicol. 18 (2), 95–125.
Shukla, P C, Gupta, T, Labhsetwar, N K, Agarwal, A K, 2017. Trace metals and ions in particulates emitted by biodiesel fuelled engine. Fuel 188, 603–609.
Sorbo, S, Aprile, G, Strumia, S, Castaldo Cobianchi, R, Leone, A, Basile, A, 2008. Trace element accumulation in Pseudevernia furfuracea (L.) Zopf exposed in Italy's so called Triangle of Death. Sci. Total Environ. 407, 647–654.
Sternbeck, J, Sjödin, Å, Andréasson, K, 2002. Metal emissions from road traffic and the influence of resuspension—results from two tunnel studies. Atmos. Environ. 36, 4735–4744.
Tchounwou, P B, Yedjou, C G, Patlolla, A K, Sutton, D J, 2012. Heavy metal toxicity and the environment. In: Luch, A (Ed.), Molecular, Clinical and Environmental Toxicology. Experientia Supplementum, 101. Springer, Basel, pp. 133–164. doi:10.1007/978-3-7643-8340-4_6.
Thorpe, A, Harrison, R M, 2008. Sources and properties of non-exhaust particulate matter from road traffic: a Review. Sci. Total Environ. 400, 270–282.
Titos, G, Lyamani, H, Pandolfi, M, Alastuey, A, Alados-Arboledas, L, 2014. Identification of fine (PM1) and coarse (PM10-1) sources of particulate matter in an urban environment. Atmos. Environ. 89, 593–602.
Titos, G, Lyamani, H, Drinovec, L, Olmo, F J, Močnik, G, Alados-Arboledas, L, 2015. Evaluation of the impact of transportation changes on air quality. Atmos. Environ. 114, 19–31.
Turunen, M, Peräniemi, S, Ahlgrén, M, Westerholm, H, 1995. Determination of trace elements in heavy oil samples by graphite furnace and cold vapour atomic absorption spectrometry after acid digestion. Anal. Chim. Acta 311 (1), 85–91.
Valavanidis, A, Fiotakis, K, Vlachogianni, T, 2008. Airborne particulate matter and human health: toxicological assessment and importance of size and composition of particles for oxidative damage and carcinogenic mechanisms. J. Environ. Sci. Health. Part C 26 (4), 339–362 10.1080/10590500802494538..
Vannini, A, Paoli, L, Russo, A, Loppi, L, 2019. Contribution of submicronic (PM1) and coarse (PM > 1) particulate matter deposition to the heavy metal load of lichens transplanted along a busy road. Chemosphere 231, 121–125.
Varrica, D, Bardelli, F, Dongarrà, G, Tamburo, E, 2013. Speciation of Sb in airborne particulate matter, vehicle brake linings, and brake pad wear residues. Atmos. Environ. 64, 18–24.
World Health Organization (WHO), 2018. Press Release: 9 Out of 10 People Worldwide Breathe Polluted Air, but More Countries Are Taking Action. https://www.who.int/news-room/detail/02-05-2018-9-out-of-10-people-worldwide-breathe-polluted-air-but-more-countries-are-taking-action. (Accessed 13 October 2019).
Yenisoy-Karakaş, S, Tuncel, S G, 2004. Geographic patterns of elemental deposition in the Aegean region of Turkey indicated by the lichen, Xanthoria parietina (L.) Th. Fr. Sci. Total Environ. 329, 43–60.
Zereini, F, Wiseman, C L S, Püttmann, W, 2012. In vitro investigations of platinum, palladium, and rhodium mobility in urban airborne particulate matter (PM10, PM2.5, and PM1) using simulated lung fluids. Environ. Sci. Technol. 46, 10326–10333.