Chemosphere 282 (2021) 131052

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Air quality biomonitoring through *Olea europaea* L.: The study case of "Land of pyres"

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ARTICLE INFO

Handling Editor: A. Gies

Keywords:
Air biomonitoring
Olive trees
Land of pyres (fires) area
PTE
Enrichment factors

ABSTRACT

The "Land of pyres", namely "La Terra dei Fuochi", is an area of Campania region (South-Italy), highly inhabited and comprises between the Provinces of Naples and Caserta, sadly known worldwide for the criminal activities related to the illegal waste disposal and burning. These fires, concomitantly with traffic emissions, might be the source of potential toxic element (PTE) dangerous for the human health and causing pathologies. In the framework of Correlation Health–Environment project, funded by the Campania region, eight municipalities (of area "Land of pyres") and three remote sites have been bio-monitored using the olive (*Olea europaea* L.) plants as biomonitors. Leaves of olive plants were collected in each assayed municipality and the concentration of 11 metal(loid)s was evaluated by means of ICP-OES. Our findings revealed that the air of these municipalities was limitedly contaminated by PTE; in fact, only Sb, Al and Mn were detected in the olive leaves collected in some of the assayed municipalities and showed a high enrichment factors (EC) manly due, probably, to the vehicular traffic emissions. Furthermore, the concentrations of the other assayed PTEs were lower than those of Sb, Al and Mn. For these reasons we suppose that their emissions in the troposphere have been and are limited, and they mainly have a crustal origin. Even if our data are very comforting for those urban area, regarded by many as one of the most contaminated one in Italy, a great environment care, in any case, is always needed.

1. Introduction

Air pollution has been recognized as one of the major threats to human health and environment, up to become as the main world's top topic in many strategic environmental policies (Tan et al., 2021). In the recent Anthropocene era, the industrialization, urbanization and advances in technology have provided an ever-increasing and needful range of goods and services, but at the same time they have contributed to the introduction of different contaminants into the environment (Sage, 2020). The air is enriched, mainly in industrial and urban areas, by a wide array of pollutants, including nitrogen and sulphur gaseous compounds, and particulate matter, forming a complex mixture which may contain, among others, even the potentially toxic elements (PTE; Nematollahi et al., 2020; Ali et al., 2019). The latter can be ubiquitous substances and/or naturally occur, even if only few PTE are released from natural sources (such as volcanic eruptions and forest fires, or weathering of parent materials). Nevertheless, the large part of PTE come from a variety of human activities, including the burning of fossil fuels, transports, metal processing and smelting, industrial emissions (Chen et al., 2019; Beck and Birch, 2012; Škrbić et al., 2018) and farming. PTE can be transported in various forms through the exchanges among different ecosystems; they are substantially accumulated in recent years mainly in soils and sediments, but, at the same time, they are highly mobile in air and water (Hadjipanagiotou et al., 2020). For their environment persistence and biotoxicity, the PTE are posing serious risks to the ecosystem and human health due to long-term exposure even at very low concentrations (Khanam et al., 2020; Antoniadis et al., 2017). Monitoring of toxic air pollutants is needed to understand their spatial and temporal distribution, but also to try to establish a correlation with human health status and minimize their harmful effects. Different conceptual approaches to air quality monitoring are currently available and include direct physical and chemical methods, ground stations of monitoring networks, satellite telemonitoring and the application of biomonitoring (Liu et al., 2020;

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https://doi.org/10.1016/j.chemosphere.2021.131052
Received 8 April 2021; Received in revised form 26 May 2021; Accepted 27 May 2021
Available online 1 June 2021

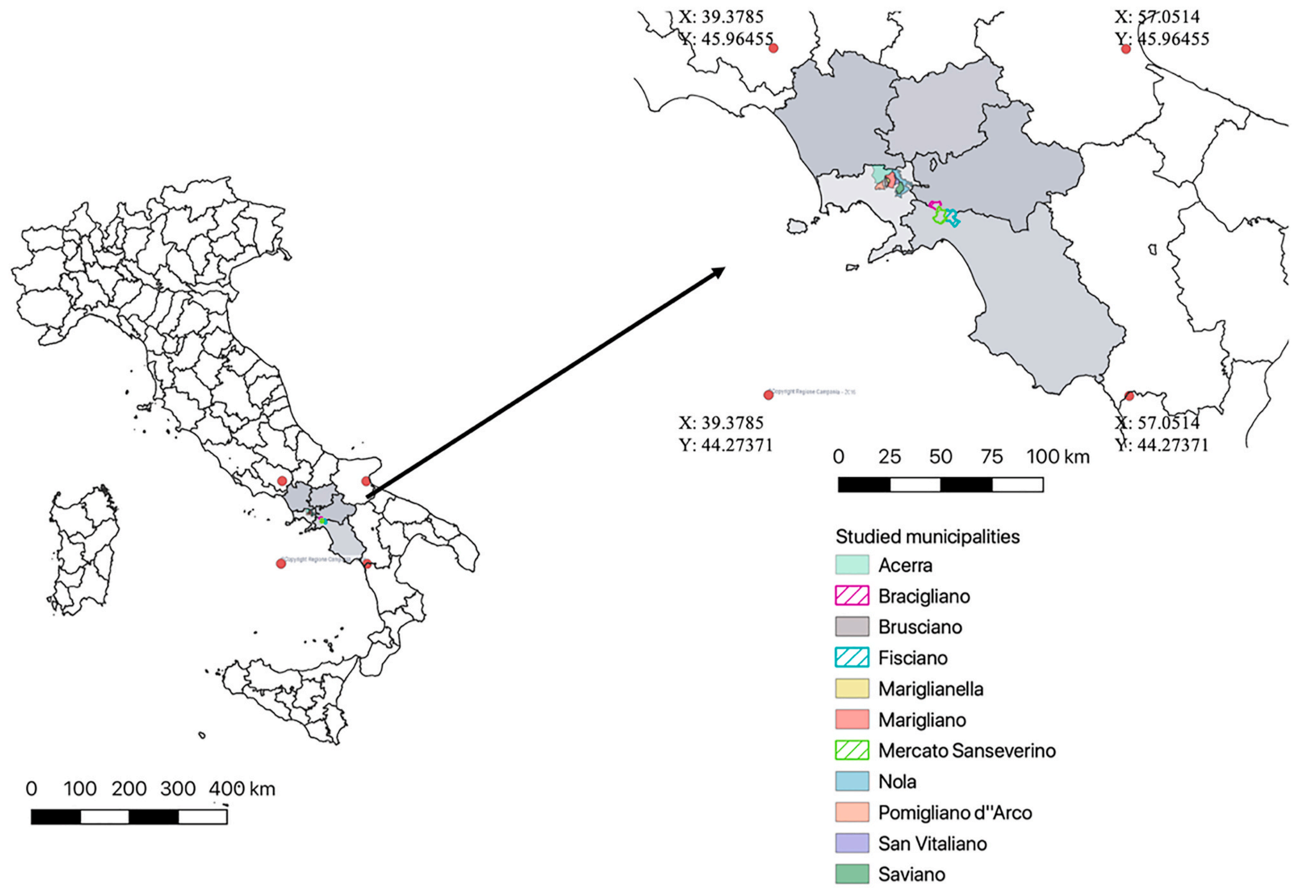

Fig. 1. Overview of the studied area. In grey the Campania region and its Provinces. Coordinate in WGS 84 UTM33 N.

Table 1
PTE contents of the leaves at each collection site (mean ± SD, mg kg^{-1} dry weight); ND indicates Not Detectable concentrations.

Site	Ni	Cu	Cr	Pb	Sb	Al	Cd	Hg	Mn	Ba	B	As
Acerra	1.76 ± 0.51	5.19 ± 1.38	1.69 ± 0.30	0.89 ± 0.40	181.43 ± 79.34	207.17 ± 116.77	1.18 ± 0.81	0.39 ± 0.21	24.34 ± 4.94	5.91 ± 2.36	13.49 ± 6.42	ND
Brusciano	1.44 ± 0.59	6.43 ± 1.12	1.47 ± 1.37	0.43 ± 0.12	129.25 ± 43.20	157.74 ± 71.26	0.50 ± 0.41	0.94 ± 0.58	14.30 ± 1.71	4.08 ± 1.45	29.50 ± 7.51	ND
Mariglianella	1.58 ± 0.70	5.43 ± 1.19	1.01 ± 0.43	0.54 ± 0.17	92.11 ± 67.93	146.46 ± 92.83	0.36 ± 0.06	0.47 ± 0.25	13.67 ± 3.90	5.53 ± 1.69	30.25 ± 9.11	ND
Marigliano	1.85 ± 0.96	5.09 ± 0.96	1.32 ± 0.52	0.45 ± 0.09	303.08 ± 124.54	116.97 ± 40.51	0.11 ± 0.02	1.94 ± 0.72	21.13 ± 7.40	4.04 ± 1.52	8.62 ± 5.37	ND
Nola	1.62 ± 0.46	5.50 ± 0.86	0.46 ± 0.29	0.33 ± 0.14	ND	125.40 ± 22.21	2.82 ± 0.03		17.21 ± 2.55	3.24 ± 1.97	17.63 ± 10.47	ND
Pomigliano d'Arco	4.00 ± 2.36	6.54 ± 4.21	1.10 ± 0.23	0.69 ± 0.17	211.49 ± 81.10	135.88 ± 28.34	0.16 ± 0.01	2.67 ± 2.20	15.23 ± 3.17	6.14 ± 1.51	29.79 ± 4.00	ND
San Vitaliano	3.18 ± 1.97	6.24 ± 1.50	1.24 ± 0.34	0.72 ± 0.56	377.88 ± 223.67	182.40 ± 102.81	0.15 ± 0.08	1.62 ± 1.15	15.30 ± 2.32	5.47 ± 1.68	25.78 ± 4.94	ND
Saviano	2.01 ± 0.95	9.81 ± 13.99	0.59 ± 0.15	0.55 ± 0.31	ND	75.14 ± 43.11	0.55 ± 0.21	0.29 ± 0.03	11.84 ± 10.01	4.37 ± 1.68	12.08 ± 2.03	ND
Bracigliano	1.35 ± 0.70	65.75 ± 91.68	0.43 ± 0.15	1.22 ± 1.41	ND	99.92 ± 35.03	0.43 ± 0.23	2.67 ± 1.77	17.52 ± 8.99	15.26 ± 13.92	16.26 ± 5.60	ND
Fisciano	2.26 ± 1.15	ND	1.45 ± 0.14	0.98 ± 0.01	ND	133.44 ± 47.31	0.82 ± 0.01	ND	26.85 ± 4.68	8.03 ± 0.68	31.15 ± 4.24	ND
Mercato San Severino	1.43 ± 1.20	4.91 ± 1.19	1.10 ± 0.25	0.71 ± 0.24	ND	130.84 ± 55.71	2.66 ± 0.75	ND	20.43 ± 8.50	5.89 ± 3.69	25.07 ± 9.01	ND

Morawska et al., 2018; Kim et al., 2020). Some approaches foresee the direct measurement of pollutants, by means of precipitation and total deposit, and are mainly focused on quantitative surveys at local, short-range, medium-range or global transport of pollutants. Then, these methods require continuous sampling on a long period and at many sites in order to ensure the temporal and spatial representativeness of the measurements. Otherwise, the biomonitoring approach (Ram et al., 2015; Abas, 2021) is a non-expensive and reliable method for air quality status assessment in a specific site. Some biological indicators accumulate the pollutants, providing, in this way, a measure of a long exposure over the time to those pollutants present in the air; this allows to improve the analytical accessibility and reduce the measurement

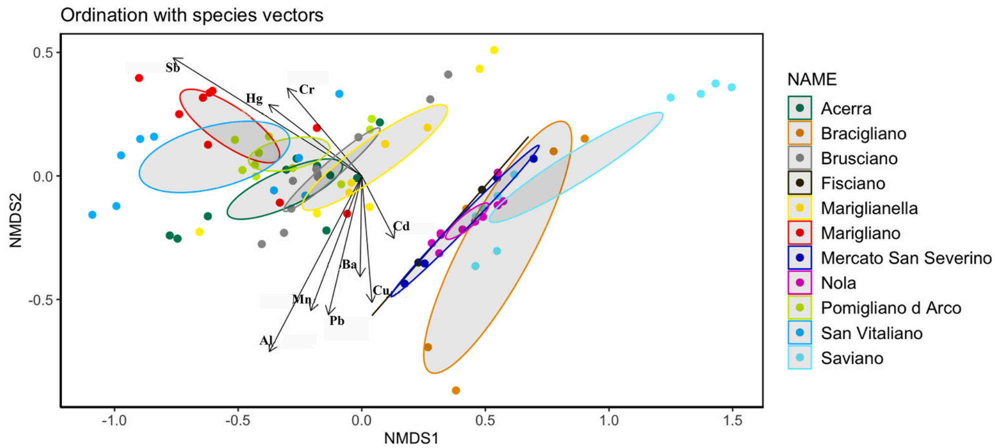

Fig. 2. NMDS biplot with the superimposition of confidence ellipses (for α = 0.05) showing the differentiation among the municipalities as a function of the leaf PTE concentrations in each sampling site within each municipality. For interpretation of the references to colour in this figure legend. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

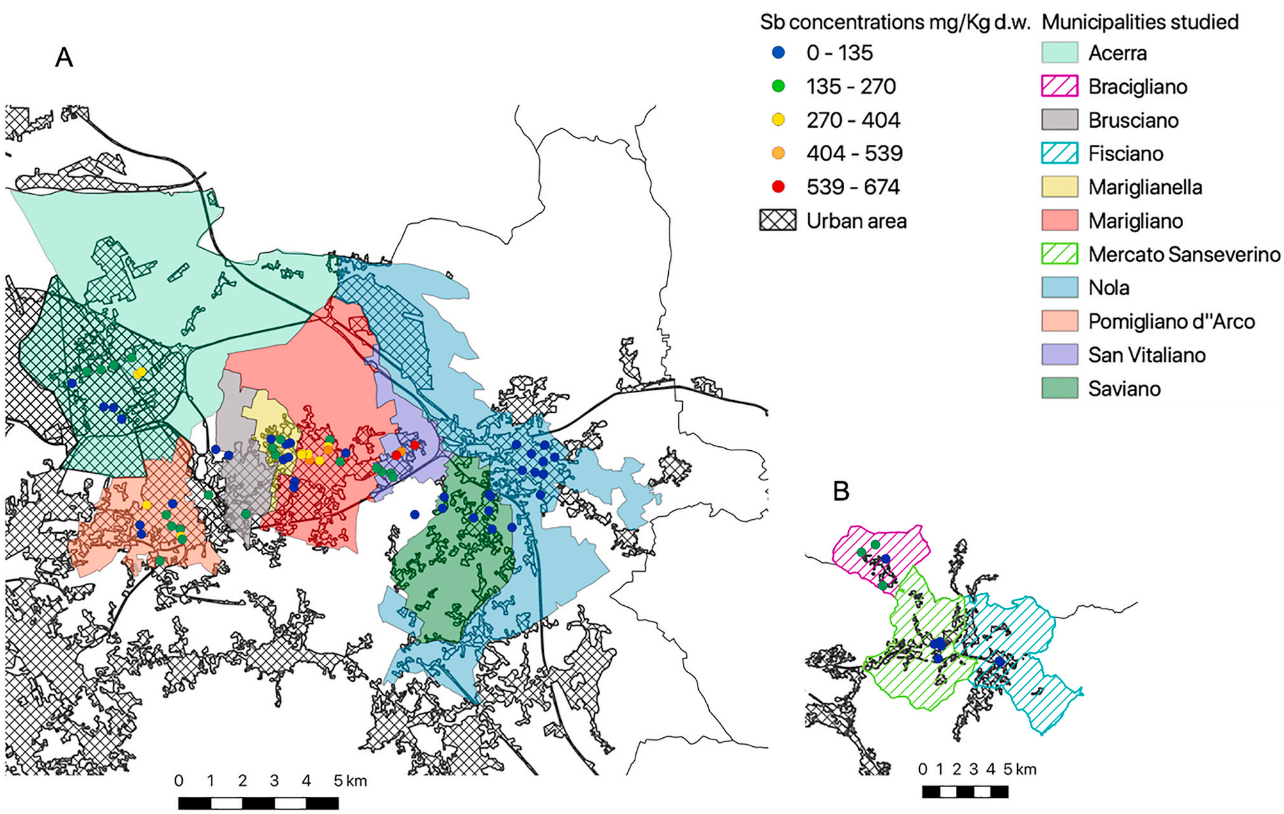

Fig. 3. An overview of the eight municipalities (solid colour) included in the "Land of pyres" (A), located in the Province of Naples, and of the three (colour texture) corresponding to the remote sites (B). The different colours of the points are referred to the diverse range of the Sb concentrations. With black texture are indicated the urban areas. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

uncertainty. Since plants are sessile organism constantly exposed to air, they are the primary pollutant receptors present in the atmosphere, including PTE (Ram et al., 2015; Tarricone et al., 2015). Based on plant species considered, it has been reported a high susceptibility or high tolerance to PTE. The capability of plants to accumulate contaminants in the different organs or tissues (roots, fruits, leaves or barks) has been exploited worldwide since the sixties of last century. Plant accumulator, mainly trees, exploit physiological, biochemical, and/or morphological mechanisms to increase their ability to survive in highly polluted sites for several years (Sawidis et al., 2011; Baldantoni et al., 2020; Maisto et al., 2004); at the same time, they are able to accumulate toxic elements in the organs, as in the case of air PTE that can be adsorbed and/or deposited on the leaves (Solgi et al., 2020; Memoli et al., 2020; Molnar et al., 2020). This aspect is particularly true and suitable in the case of evergreen trees (*e.g.*, olive, holm oak, etc. - Dolegowska et al., 2021). For these reasons, leaves have been used as bioindicators of environmental pollution to assess the air suitability (Maisto et al., 2004; Tomasevic et al., 2005), and even to draw conclusions about specific pollutant sources or contamination distribution comparing the area of interest with a similar one (from the point of view of pedoclimatic conditions), but less affected by anthropic pressure (background sites) (Maisto et al., 2004; Çelik et al., 2005; Gratani et al., 2008). Among the

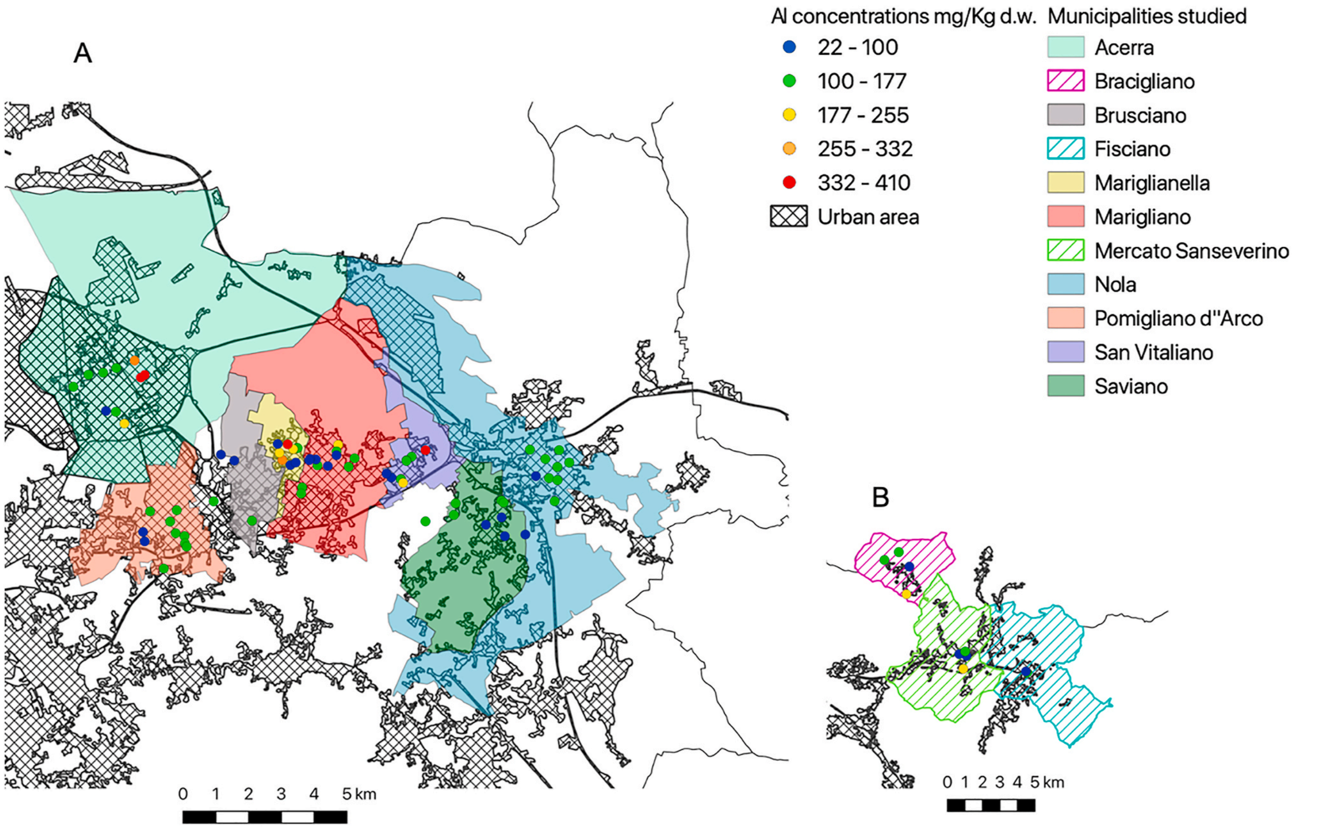

Fig. 4. An overview of the eight municipalities (solid colour) included in the "Land of pyres" (A), located in the Province of Naples, and of the three (colour texture) corresponding to the remote sites (B). The different colours of the points are referred to the diverse range of the Al concentrations. With black texture are indicated the urban areas. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

evergreen species, olive tree (*Olea europaea* L.) can be elected to chosen species for biomonitoring (Madejon et al., 2006; Higueras et al., 2012; Turan et al., 2011) due to several reasons: they are indigenous especially in the Mediterranean countries; they can live, probably, over 500/600 years; they are often used as ornamental trees in the urban areas (public parks, gardens, roundabouts, etc.).

The present work was established in the framework of Correlation Health – Environment project (Correlazione Salute e Ambiente; Co.S.A.) aimed at the assessment of links between the environmental risk factors and their impact on human health. Although increasing evidences are revealing the impact of environmental pollution on human health, a strong knowledge is as yet weak, probably due to the complexity and the number of variables (environmental degradation, local and cultural factors, socioeconomic deprivation) and, last but not least, to the quality and management of several kind of data.

In the light of what written above, this work has focused on the evaluation of air quality in an interesting study area of the Campania Region (Napoli province) named "Land of pyres". Some zones in that area, highly inhabited, have been affected, for several years, by extensive illegal dumping of mixed waste of urban and/or industrial origin, and even exposed to fires in the open of waste (Diletti et al., 2005; Esposito et al., 2014; Giovannini et al., 2020). These illegal practices resulted in a concurrent release of organic and inorganic chemical contaminants in the air, which may have had a detrimental impact on local people. Then, with the aim to detect PTE pollution across different areas differing in population density and urbanization, the present research investigated the concentrations of 12 PTE (Ni, Cr, Pb, Sb, Al, Cd, Hg, Mn, B, Ba, Cu, As) in eight municipalities comprised in the "Land of pyres" area and in three municipalities far away considered as remote background sites using the olive trees as air pollutant bioaccumulators.

2. Materials and methods

2.1. Study area

The study area is located in the North of the Campania Region (Fig. 1), along the province of Naples (NA-Italy). Campania region is situated on the south-western portion of the Italian Peninsula.

On the basis of the last general population census of 2018, the region has a population of around 5′820′000 people, making it the third-most-populous region in the country, and Naples' urban area the 7th-most populous one of the European Union, with its 3,019,343 inhabitants. The region is home to 10 of the 55 UNESCO sites in Italy, such as: Pompeii and Herculaneum, the Royal Palace of Caserta, the Amalfi Coast, the Historic Centre of Naples and more. Furthermore, Mount Vesuvius is part of the UNESCO World Network of Biosphere Reserves. Unfortunately, in 1994, Campania formally declared a state of emergency for the waste management, ending in 2008; however, the crisis has caused negative impacts on the environment of region, as well as those linked to human health, specifically in an area that became known as the "Triangle of death". Due to the burning of accumulated toxic wastes in overfilled landfills and streets, Naples and the surrounding areas became known as the "Land of pyres" (Terra dei Fuochi). This area is characterized by a Mediterranean climate, with an average annual temperature of 17.2 °C and an annual rainfall amount of 1200 mm, mostly concentrated at the end of the summer (Xoplaki et al., 2004; Ulbrich et al., 2013). In that study area, eight urban areas (Acerra, Brusciano, Pomigliano d'Arco, Marignanella, Marigliano, Nola, San Vitaliano, Saviano) have been chosen for the sampling of leaves from olive trees, whilst three remote sites in the Salerno province in a not urbanized area (Bracigliano, Fisciano, Mercato San Severino) have been considered for the sampling. Based on Google Maps Traffic (Figure SI 1)

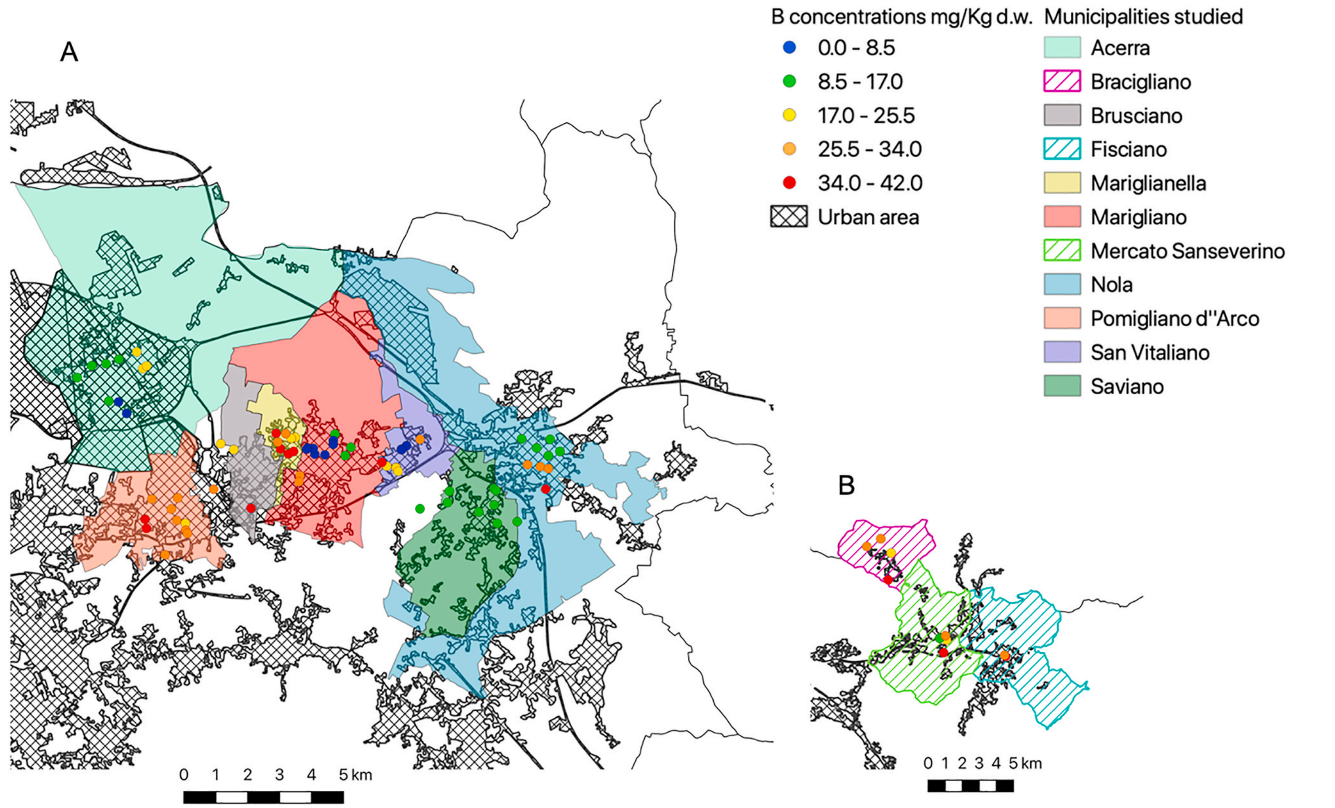

Fig. 5. An overview of the eight municipalities (solid colour) included in the "Land of pyres" (A), located in the Province of Naples, and of the three (colour texture) corresponding to the remote sites (B). The different colours of the points are referred to the diverse range of the B concentrations. With black texture are indicated the urban areas. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

some collection sites were located in traffic areas with the presence of urban congested local transportation vehicles and private cars, while in remote sites, the vehicular traffic is very scarce and is mainly due to circulation of private or agriculture vehicles.

2.2. Leaf sampling and PTE determination

From each site, 50 leaves of the same age were sampled uniformly around the crown of olive trees (from 25 to 40 cm diameter at breast height) according to their availability in the sampling chosen area. Leaves were carefully inspected to avoid selecting those unsuitable (insect infestation, bird dropping, chlorosis or necrosis, etc.) for the PTE determination. The collected leaves were unwashed before the PTE determination to evaluate the capability of the olives to reflect the PTE deposition of atmospheric origin. All samples were dried (75 °C to constant weight) and processed in triplicate, manually pulverized (in mortars, using liquid nitrogen), and PTE (Ni, Cr, Pb, Sb, Al, Cd, Hg, Mn, B, Ba, Cu) concentrations were determined as reported in De Agostini et al. (2020). For As, aliquots of leaves were dried at room temperature and As concentration was estimated by means of hydride generation atomic absorption spectrometry (PerkinElmer 4110 ZL) equipped with an electrode-less discharge lamp (As EDL) as reported in Guarino et al. (2020). The method precision, calculated as relative standard deviation, based on n = 9 sequential measurements of the same sample for each element, ranged from 2% to 10%, depending on the element.

2.3. Distribution maps of the elements and statistical analyses

The sources of data used for this study include:

- Administrative Map of the study area showing local boundaries obtained from the Campania Region GIS platform (https://sit2.regione.campania.it/node);
- Campania Street Map;
- Additional information was gleaned from other sources such as academic journals, gazettes, brochures, Internet and statistical publications of the Environmental Protection Agency (EPA);
- Pollution data and survey information were sourced from air quality monitoring survey and air quality reports.

The PTE concentration data and the UTM coordinates of the sample collection sites were employed to generate concentration distribution maps in QuantumGis 3.10 LTR. Statistical analyses were performed in RStudio (Version February 1, 5033) and in particular by means of "ade 4", "stats", "lme4″ "vegan", "emmeans" "corrplot", (https://cran.r-project.org/web/packages/available_packages_by_name.html).

The differentiation among the sampling sites as a function of the PTE concentration pattern in olive leaves was evaluated by a non-metric multidimensional scaling (NMDS) based on two axes and the Manhattan distance metric, with the superimposition of the confidence ellipses (for $\alpha = 0.05$). Finally, we used the distance-matrices to perform a pairwise correlation test among them using the Mantel test choosing 100,000 permutations and a minimum significance level of $\alpha = 0.05$.

2.4. Enrichment factor

To evaluate the relative contribution of anthropic sources to air elemental concentrations, the enrichment factor (EF) was estimated. Enrichment factor is defined as the concentration ratio of a given metal, used as standard, normalized to the same concentration ratio characteristic of the upper continental crust (*i.e.,* the composition of the continental crust). According to Chen et al. (2019) in this study, Al was

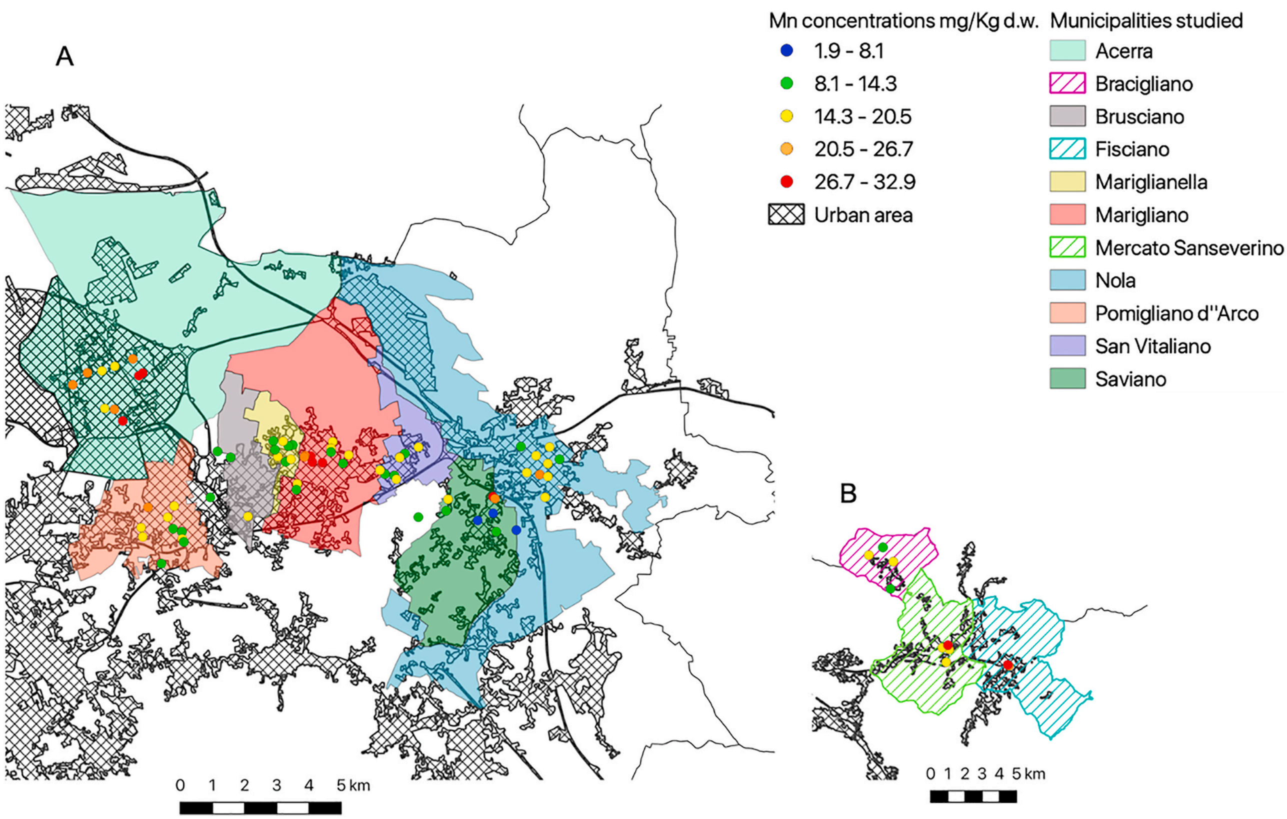

Fig. 6. An overview of the eight municipalities (solid colour) included in the "Land of pyres" (A), located in the Province of Naples, and of the three (colour texture) corresponding to the remote sites (B). The different colours of the points are referred to the diverse range of the Mn concentrations. With black texture are indicated the urban areas. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

adopted as reference because it is one of the largest components of soil, while Cu was used for EF calculation of Al. The EF is calculated by Eq. (1) (Xu et al., 2004):

EF = [Element (sample)/Al (sample)]/[Element (UC)/Al (UC)] where UC refers to upper continental crust concentrations. Crustal composition data is obtained from the study of Rudnick and Gao (2003).

3. Results

3.1. Trace element concentrations in olive leaves

The mean values of PTE measured in leaves of olive trees collected in all municipalities objective of study are reported in Table 1. Only the As concentrations were very low and even undetectable in all the leaves collected for our study. The highest PTE concentrations followed this order Sb, Al, B, Mn, Cu (similar to Ba), while Ni, Cr, Pb and Hg concentrations were low.

It is noteworthy that the standard deviations (Table 1), within each municipality, were very high for some of them because of the high PTE concentration variability.

The NMDS analysis was employed to detect the relationships among all PTE and all municipalities, and the results were statistically validated. The biplot (Fig. 2) showed a clear separation of the confidence ellipses related to the collection sites and to the remote ones, as a function of leaf PTE concentrations. In particular, the remote sites, in addition to Saviano and Nola ones, were characterized by a higher concentrations of Cd and Cu respect to the other examined municipalities, while the remaining collection sites were mostly characterized by relatively high concentrations of Cr, Sb and Hg.

In addition, to establish a possible and significant correlation between PTE and specific geographic areas of sampling, the PTE concentrations were imported in GIS environment and a statistical analysis was performed (Mantel Test). In general, the analysis showed that the PTE concentrations have a considerable spatial diversity not only among the studied areas, but even within each municipality. The results relative to the concentration and distribution of different PTE are reported in Fig. 2.

3.2. Distribution maps of PTE

The PTE concentrations were imported in GIS environment in order to establish a possible correlation with the geographic areas. In general, the analysis showed that the PTE concentrations were reliable within each municipality or within a specific geographic area.

3.2.1. Antimony

The Antimony (Sb) was the main contaminants detected on olive leaves sampled. The highest concentrations (Fig. 3) were estimated in the municipalities of San Vitaliano and Marigliano, and mainly along the road via *Nazionale delle Puglie* that connects the towns of this area of the Naples province. In particular, the concentrations detected in the municipality of San Vitaliano ranged between 147 and 675 mg Kg^{-1} D.W. and the consecutive collection sites SV1, SV2, SV3 and SV4 showed concentrations comprised between 550 and 675 mg Kg^{-1} D.W. Similarly, Marigliano was characterized by Sb concentrations from 87 to 498 mg Kg^{-1} D.W., but the large part of the collection sites (from MA4 to MA10) revealed concentrations comprised between 312 and 498 mg Kg^{-1} D.W. Even in Pomigliano d'Arco, six collection sites with Sb concentrations comprised between 245 and 319 mg Kg^{-1} D.W. were found. In the case of Acerra, once again, some collection sites from AC4 to AC10, showed the highest concentrations of this element in the analysed area and they ranged between 130 and 301 mg Kg^{-1} D.W. The other municipalities and remote sites showed the lowest Sb concentrations ever lower than 112 mg Kg^{-1} D.W., as in the case of some collection sites of Brusciano, Mariglianella, Pomigliano and Acerra. The statistical

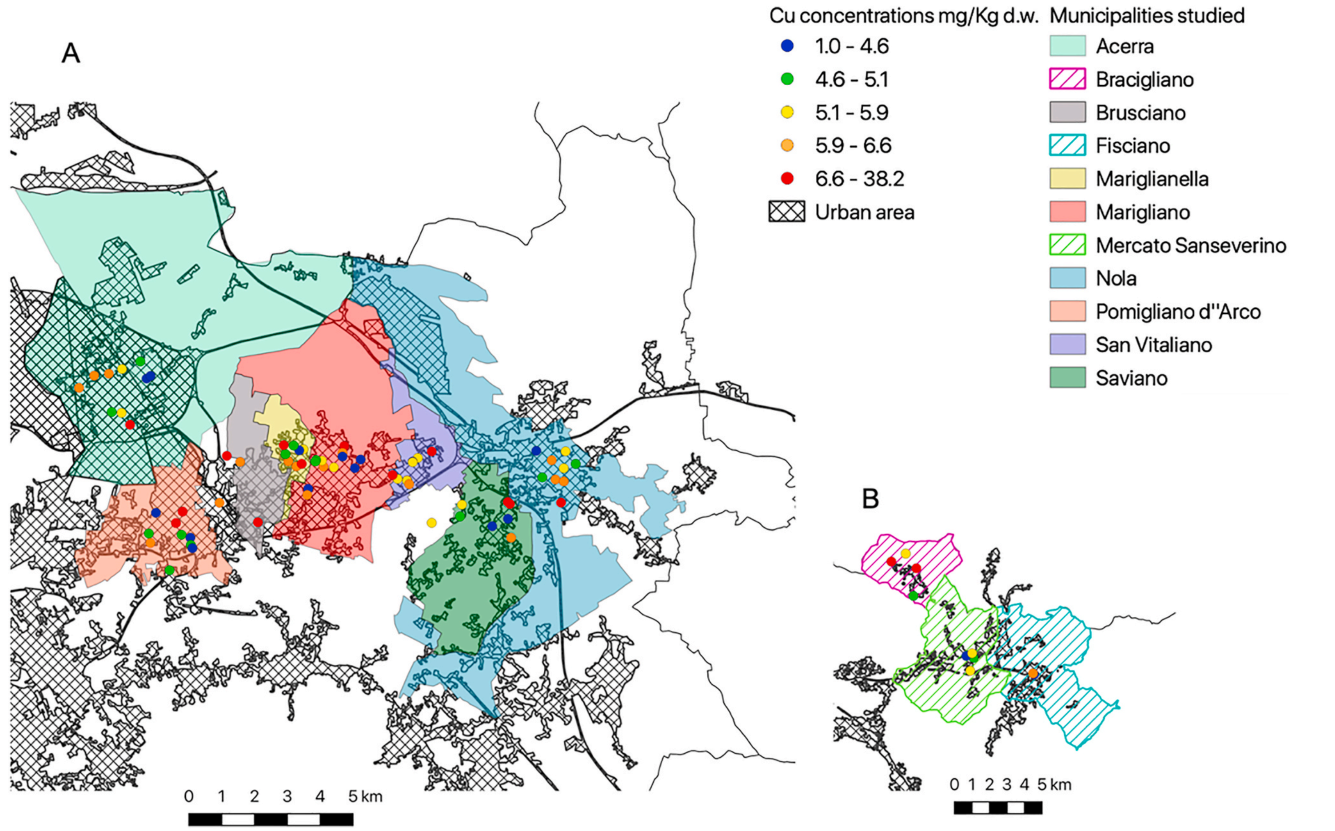

Fig. 7. An overview of the eight municipalities (solid colour) included in the "Land of pyres" (A), located in the Province of Naples, and of the three (colour texture) corresponding to the remote sites (B). The different colours of the points are referred to the diverse range of the Cu concentrations. With black texture are indicated the urban areas. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

analyses carried out to investigate a possible association between the geographic position and Sb concentrations revealed that, within some municipalities, the correlation was strong and statistically significant as in the case of Acerra ($r = 0.61$; $p < 0.05$), Marigliano ($r = 0.03$; $p < 0.05$), Pomigliano d'Arco ($r = 0.3$; $p < 0.05$) and San Vitaliano ($r = 0.69$; $p < 0.05$).

3.2.2. Aluminium

In the case of Aluminium (Al) the highest concentrations were observed in Acerra (Fig. 4). Even in the municipalities of Mariglianella, Brusciano and San Vitaliano, some Al *hot spots* were found and characterized by concentrations over 300 mg Kg^{-1} D.W. (AC4, AC5, SV1, SV2, ML4 showed 396, 410, 375, 347, 359 mg Kg^{-1} D.W., respectively). However, the large part of the collected samples (81 out of 90) showed Al concentration under 200 mg Kg^{-1} D.W., including the remote sites.

Even in this case, the Mantel Test highlighted statistically significant association between Al concentration and the collection sites within some specific municipalities, as in the case of Acerra ($r = 0.42$; $p < 0.05$), Pomigliano d'Arco ($r = 0.44$; $p < 0.05$) and San Vitaliano ($r = 0.79$; $p < 0.05$).

3.2.3. Boron

In the case of Boron (B; Fig. 5), the samples collected in Mariglianella and Brusciano municipalities showed the highest concentrations among the municipalities assayed. In Mariglianella (ML7 and ML 6) concentrations of 42.5 and 41 mg Kg^{-1} D.W. were detected, and a quite similar value in Brusciano (BR1 - 39.3 mg Kg^{-1} D.W.). However, alike B concentration was found also in the remote sites: 39.4 mg Kg^{-1} D.W. in Bracigliano (BRA5), 36.44 mg Kg^{-1} D.W. in Mercato San Severino (MS1) and 34.15 in Fisciano (CS1). On the contrary, the lowest values were scored in the *"Land of pyres"* as in the case of Marigliano (MA5, MA4 and MA3 with B concentrations equal to 1.99, 5.75 and 8.65 mg Kg^{-1} D.W., respectively), Acerra (in AC1, AC2 and AC10 showing B concentrations equal to 3.15, 7.47 and 9.79 mg Kg^{-1} D.W., respectively), Nola (where the B concentration of 4 collection sites ranged between 8.71 and 9.89 mg Kg^{-1} D.W.), and Saviano (where SA10 and SA9 the B concentrations were 8.79 and 9.93 mg Kg^{-1} D.W., respectively).

In the case of B, the Mantel test highlighted a strong and statistically significant correlation in the case of Acerra ($r = 0.49$; $p < 0.05$), Bracigliano ($r = 0.69$; $p < 0.05$), Marigliano ($r = 0.65$; $p < 0.05$) and Pomigliano d'Arco ($r = 0.3$; $p < 0.05$).

3.2.4. Manganese

In the case of Mn (Fig. 6), the concentrations estimated in all the studied municipalities, located in the *"Land of pyres"* and outside from this area (remote site), were included in the same range between 8.0 and 32.0 mg Kg^{-1} D.W. Its highest concentrations were reached on the central and busy street of Marigliano, and in Acerra, where 8 sites out of the 10 collected, showed a concentration range between 20.0 and 31.0 mg Kg^{-1} D.W. Only in four sites located in the municipality of Saviano the concentrations were lower than 8.0 mg Kg^{-1} D.W. This value was in the same range of those found in the municipality of the remote sites.

Nevertheless, the Mantel Test revealed the statistically significant correlation between the concentrations estimated in some municipalities and the geographic position of the collection sites as in the case of Marigliano ($r = 0.29$; $p < 0.05$) and Pomigliano d'Arco ($r = 0.45$; $p < 0.05$).

3.2.5. Copper

The Cu concentrations (Fig. 7), estimated in almost all the analysed municipalities, were in the range between 1.0 and 10.0 mg Kg^{-1} D.W. Just in the case of two sites of Bracigliano (remote sites BRA1 and BRA2)

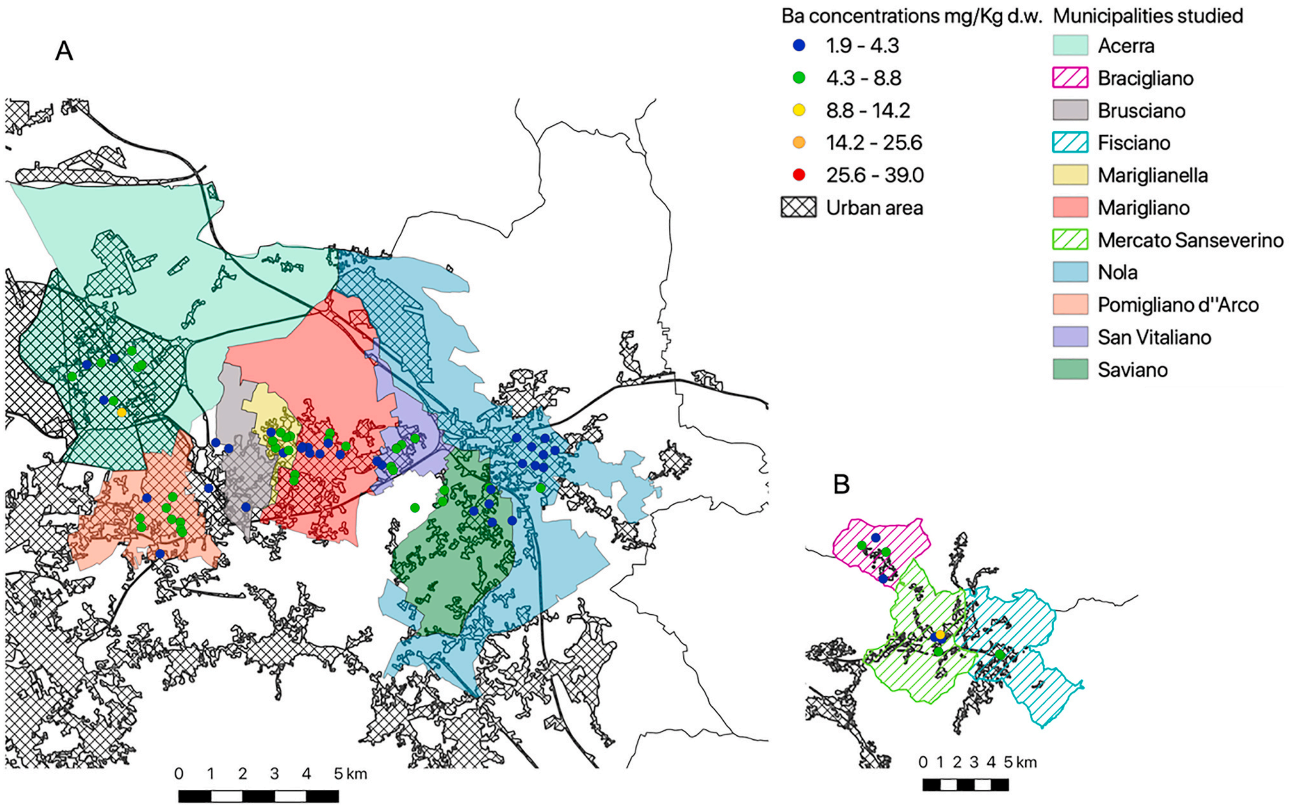

Fig. 8. An overview of the eight municipalities (solid colour) included in the "Land of pyres" (A), located in the Province of Naples, and of the three (colour texture) corresponding to the remote sites (B). The different colours of the points are referred to the diverse range of the Ba concentrations. With black texture are indicated the urban areas. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Cu concentration was comprised between c. a. 100 and 210 mg Kg^{-1} D. W., as well as in other collection sites of Saviano and Pomigliano d'Arco.

The Mantel Test indicated that the Cu concentrations and geographic positions of the collection sites were not statistically correlated, with the only exception for Acerra ($r = 0.32$; $p < 0.05$).

3.2.6. Barium

Barium (Ba) concentrations (Fig. 8) were comparable in all the collected sites in the *"Land of pyres"* and even in the remote sites. In fact, the large part of samples showed concentrations comprised between 1.90 and 4.42 mg Kg^{-1} D.W. (41 samples), or between 4.43 and 8.76 mg Kg^{-1} D.W. (44 samples). Just in one case of Bracigliano municipality (remote site) BRA1 the Ba concentration reached the 39.0 mg Kg^{-1} D. W., whilst all the other samples had concentrations comprised between 8.9 and 14.2 mg Kg^{-1} D.W.

However, the Mantel Test revealed, in general, that the Ba concentrations and geographic positions of the collection sites were correlated ($r = 0.2$; $p < 0.05$). In particular, a significant statistically correlation was found also in the case of Marigliano ($r = 0.31$; $p < 0.05$), Pomigliano d'Arco ($r = 0.35$, $p < 0.05$) and San Vitaliano ($r = 0.37$; $p < 0.05$).

3.2.7. Nickel

In the case of Ni (Fig. 9), the highest values were reached in the municipality of Pomigliano d'Arco. In the collection sites PO8, PO9 and PO10 the concentrations ranged between 7.1 and 9.3 mg Kg^{-1} D.W. In addition, the collection sites SV3, SV7 and SV8 located in San Vitaliano showed Ni concentrations between 4.86 and 6.49 mg Kg^{-1} D.W. However, Pomigliano d'Arco showed the highest number of collection sites associated with Ni concentration greater than 2.7 mg Kg^{-1} D.W. On the contrary, in the case of the remote sites, including Fisciano, Mercato San Severino and Bracigliano, as well as in the case of the other investigated municipalities, the Ni concentration ranged between 0.5 and 2.7 mg Kg^{-1} D.W.

In the case of Ni concentrations, the Mantel test highlighted a significant correlation with the distance matrix in the case of Marigliano ($r = 0.6$; $p < 0.05$), Pomigliano d'Arco ($r = 0.55$; $p < 0.05$), Saviano ($r = 0.45$, $p < 0.05$) and San Vitaliano ($r = 0.3$; $p < 0.05$).

3.2.8. Chromium

In the case of Cr (Fig. 10), the highest concentration values were scored in Brusciano at the collection sites BR8 and BR9, where the Cr concentrations reached the maximum value of 4.52 and 3.25 mg Kg^{-1} D. W., respectively. However, this appeared as a spot/punctual variation given that, in the other collection sites of Brusciano, the Cr concentration was lower than 1.5 mg Kg^{-1} D.W. On the contrary, Acerra municipality had the greatest number of collection sites characterized by the concentration range of 1.5–3.0 mg Kg^{-1} D.W. (7 sites on 10). In the remaining municipalities, including the remote sites, the Cr concentrations ranged between 0 and 1.5 mg Kg^{-1} D.W., with the exceptions of punctual overruns as in the case of SV1 (1.77 mg Kg^{-1} D.W.), SV6 (1.69 mg Kg^{-1} D.W.), MA1 (2.73 mg Kg^{-1} D.W.) and ML7 (1.96 mg Kg^{-1} D. W.).

However, the Mantel test performed within each municipality highlighted that, just in the case of Saviano, the collection site (geographic position) was statistically associated with the Cr concentration ($r = 0.36$; $p < 0.05$).

3.2.9. Lead

In the case of Pb (Fig. 11), a large part of the collection sites showed Pb concentrations lower than 0.7 mg Kg^{-1} D.W., just in the case of Acerra and Pomigliano d'Arco five and six collection sites, respectively, showed Pb concentrations comprised between 0.7 and 1.5 mg Kg^{-1} D. W., or 0.7 and 0.9 mg Kg^{-1} D.W., respectively. The concentration value of 1.5 mg Kg^{-1} D.W. was overrun in the case of sites SV1 and SV2 in

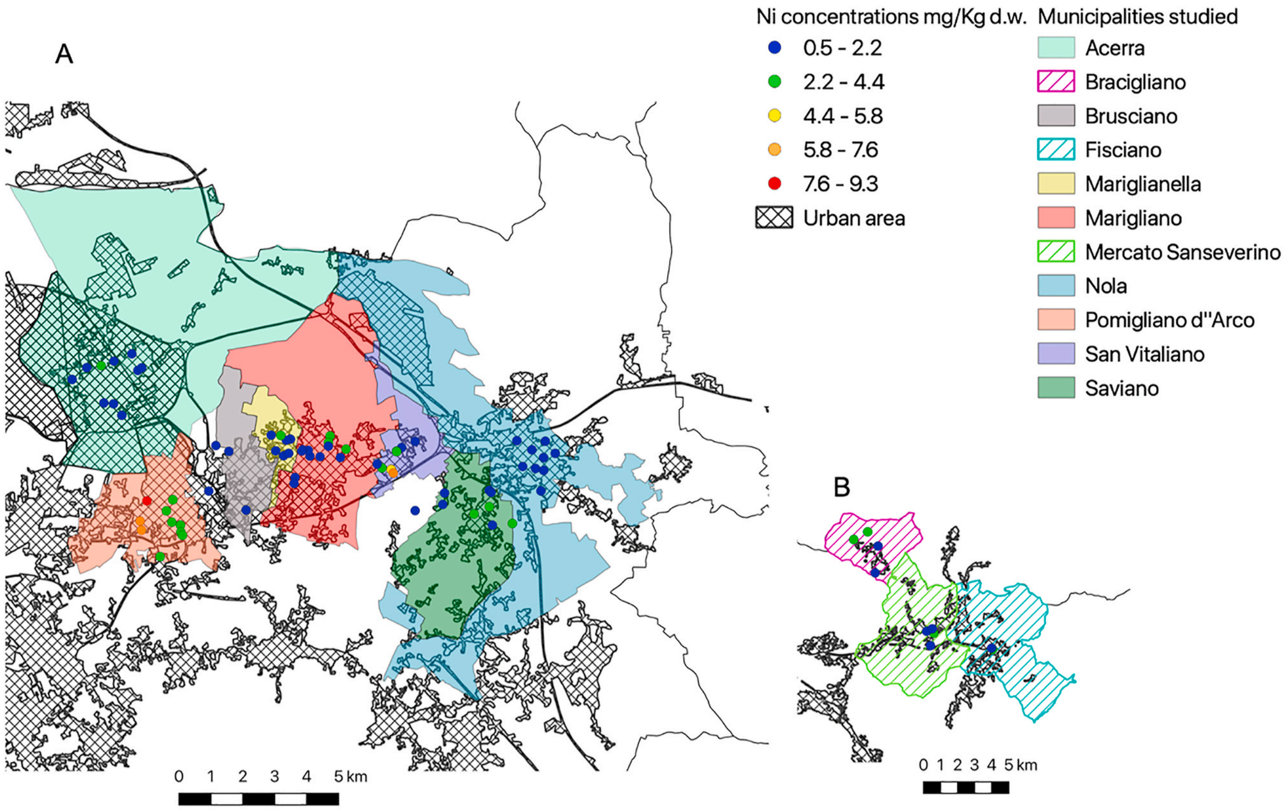

Fig. 9. An overview of the eight municipalities (solid colour) included in the "Land of pyres" (A), located in the Province of Naples, and of the three (colour texture) corresponding to the remote sites (B). The different colours of the points are referred to the diverse range of the Ni concentrations. With black texture are indicated the urban areas. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Saviano municipality. Contrarily to the other elements, the highest Pb concentration was found in the remote site of Bracigliano (BRA1), where the concentration was equal to 3.39 mg Kg^{-1} D.W., although the Pb concentration in leaves collected in BRA2 site, only at 20 m far from BRA1, was lower than10 times.

In general, the Mantel test revealed a statistically significant association between geographic positions and Pb concentrations ($r = 0.17$; $p < 0.05$). Even when the statistical analyses were performed analysing the concentrations within each single municipality, statistically strong correlations were found in the case of Acerra (0.52; $p < 0.05$), Pomigliano d'Arco ($r = 0.45$; $p < 0.05$), Saviano ($r = 0.48$, $p < 0.05$) and San Vitaliano ($r = 0.72$; $p < 0.05$). On the contrary, in the other municipalities, including the remote ones, the association between Pb concentrations and geographic position was not statistically significant.

3.2.10. Cadmium

In the case of Cd (Fig. 12), the highest concentrations were found in the municipality of Mercato San Severino (MS1, MS2, MS3 and MS4 showing the Cd concentrations of 3,03, 3,47, 1,76 and 2,38, respectively). In the other remote sites (Bracigliano and Fisciano), the Cd concentration was under 1 mg Kg^{-1} D.W., or even under the limit of detection. In the area of *"Land of pyres"*, Acerra had the highest number (three) of collection sites with a concentration over 1 mg Kg^{-1} D.W., and again associated to the sites AC6, AC7 and AC8. In the remaining municipalities, Cd concentration was lower than 0.87 mg Kg^{-1} D.W.

In the case of Cd, a general statistically significant association between this PTE concentration and geographic position was found ($r = 0.31$; $p < 0.05$). Furthermore, performing the Mantel Test for each municipality a statistically significant correlation was highlighted in the case of Marigliano ($r = 0.02$; $p < 0.05$).

3.2.11. Mercury

In the case of Hg (Fig. 13), the large part of the samples (66 out of the 90 sampled olive trees), including the remote sites, showed concentrations under 1.5 mg Kg^{-1} D.W. Its highest concentrations were scored in Pomigliano d'Arco municipality, in the collection sites from PO1 to PO6 that showed a concentration range from 7.44 (PO1) to 2.2 mg Kg^{-1} D.W. (PO6). Interestingly in the sites from PO1 to PO6, a concentration gradient was also revealed.

The municipality with the highest number of collection sites showing Hg concentrations over 2.0 mg Kg^{-1} D.W. was Marigliano (7 collection sites out of the 10 sampled); in these cases, the values were comparable and ranged between 2.07 (MA10) and 2.85 (MA5). Even in the case of San Vitaliano municipality, four collection sites with a Hg concentration higher than 2.0 mg Kg^{-1} D.W. were observed. In particular this happened in the case of SV3 (2.5 mg Kg^{-1} D.W.), SV5 (3.1 mg Kg^{-1} D.W.), SV6 (3.3 mg Kg^{-1} D.W.) and SV8 (2.2 mg Kg^{-1} D.W.).

The correlation analyses performed through the Mantel Test highlighted a statistically significant association between geographic position of the collection sites within each single municipality and the Hg concentrations; in particular, statistically significant correlations were found in the case of Acerra ($r = 0.5$; $p < 0.05$), Marigliano ($r = 0.38$; $p < 0.05$) and San Vitaliano ($r = 0.3$; $p < 0.05$).

3.3. Enrichment factors and correlation analysis

The EFs for all PTE were calculated with respect to their natural abundance in the continental crust using a reference element. On the basis of EF values, different ranges are generally recognized: $EF \leq 1$ no effect; $1 < EF < 5$ slight/moderate; $5 = EF < 20$ significant; $20 = EF < 40$ strong and $EF \geq 40$ extremely strong anthropogenic effect (Chen et al., 2019).

The low EF values (<of 10; Table 2) for Ni, Cu, Cr, Pb, Cd, Hg, Ba and

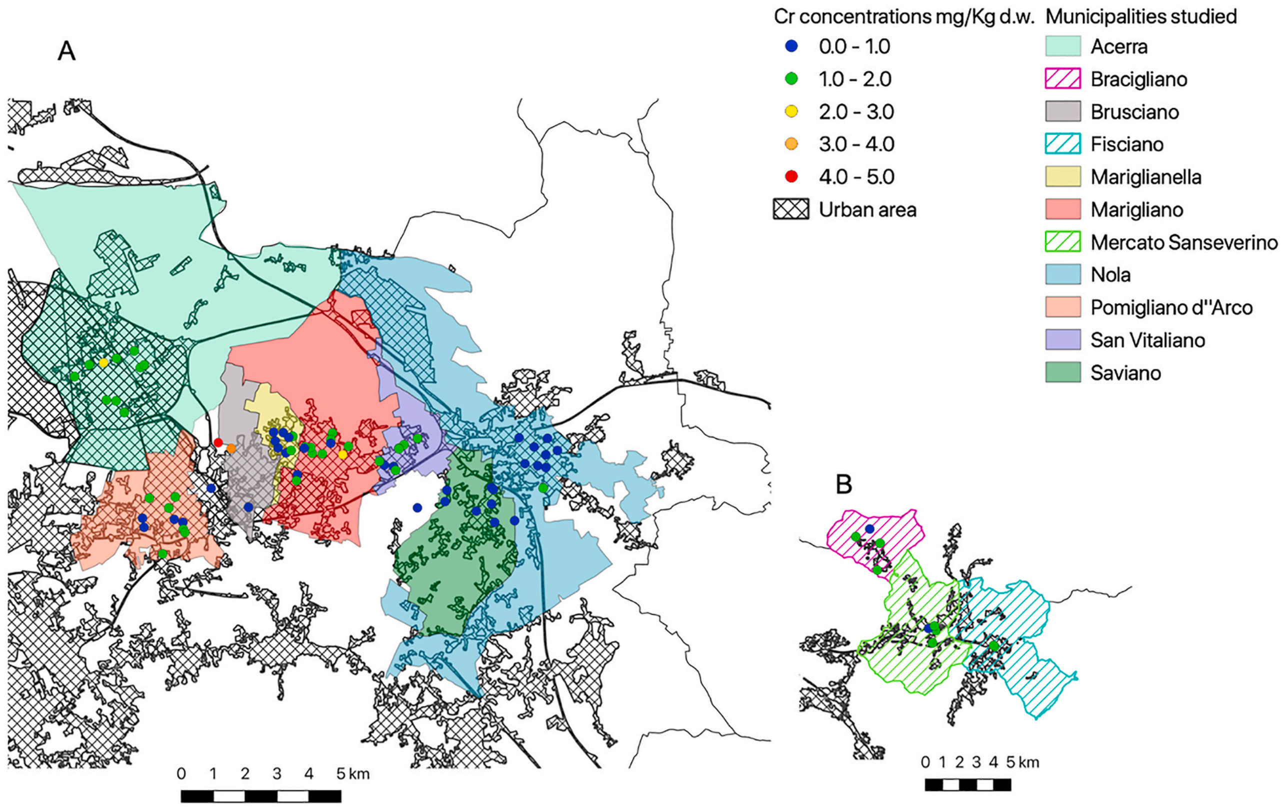

Fig. 10. An overview of the eight municipalities (solid colour) included in the "Land of pyres" (A), located in the Province of Naples, and of the three (colour texture) corresponding to the remote sites (B). The different colours of the points are referred to the diverse range of the Cr concentrations. With black texture are indicated the urban areas. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

B indicated that the air of all studied municipalities were likely not enriched of these elements by non-crustal sources; while the EF values relative to Mn, Sb and Al are significantly larger than 10, indicating an important contribution due to anthropogenic emission in the air. The EF mean for Mn in all municipalities was within the 23 to 26 range, indicating that the Mn air concentration was affected by strong enrichment. In the case of Sb and Al, the EF mean values revealed that some municipalities were greater enriched than others.

Correlations among PTE concentrations were estimated for each municipality (data not shown) in order to hypothesize information about putative sources and pathways of PTE. For some sampling locations the correlations were very low or not statistically significant, while in the case of Acerra, Brusciano, Pomigliano d'Arco, Mariglianella, Marigliano and Pomigliano d'Arco municipalities, the three most abundant PTE, as Sb, Al and Mn, showed a very significant correlation, mainly positive, with each other (at $p < 0.01$ or $p < 0.001$).

4. Discussion

The rapid urbanization and transportation system around the world caused the traffic-related air pollution. Traffic exhaust fumes and, in addition, brake, tire and road pavement wears, as well as resuspension of road dust (non-exhaust traffic emissions), have been recognized as a crucial pollution source of heavy metals, metalloids and PTE (Wang et al., 2021; Jose and Srimuruganandam, 2020). In general, traffic-related air pollutants became commonly distributed in the air, soil and water, and, making them ubiquitous and, consequently, in close contact with biota and living beings, including human. A recent review (De Silva et al., 2021), focused on the effects of PTE, mainly due to vehicular traffic, on the global roadside environment and soil microbiota, and in addition on plants and animals (vertebrates and invertebrates) adjacent to roads. A meta-analysis of the literature allowed the authors to evaluate the PTE pathways from vehicle emissions to soil and into the organisms, and the consequences of their impacts on biological functioning, and the risk of biomagnification through the food chain. The authors demonstrated an increase in the concentrations of Cd, Pb, Zn and platinum group elements (Pt, Pd and Rh) in roadside soils compared to the mean global crustal concentrations. The meta-analysis of the global literature carried out by De Silva et al. (2021) demonstrated that the mean concentration of Pb in plants and vertebrates adjacent to roads is above WHO guidelines, and the concentrations of Cd and Zn were also found, in some plants, above these guidelines. Moreover, they also highlighted the gaps in current knowledge in terms of vehicular emitted PTE and effect on living beings. However, the direct exposition of air PTE are representing a serious public health damage (Anwar et al., 2013). In fact, it was reported that the human exposure to metals and PTE can cause not only deleterious effects on nervous, endocrine and respiratory systems, kidney function, but also cardiovascular diseases at low level of exposure (Brucker et al., 2020).

Since leaf and bark of trees grown in urban sites are tools for assessing the effects of the PTE pollution and monitoring the environmental air quality, our study, developed in the framework of the Co.S.A. project, has been conducted in some municipalities of the Campania region, differing in population density and urbanization, and located in the "Land of pyres".

Some zones of this area, highly inhabited, have been affected, for several years, by extensive illegal dumping of mixed waste of urban and/or industrial origin, and even exposed to fires in the open of waste (Giovannini et al., 2020). Although increasing evidence is revealing the impact of environmental pollution on human health, Esposito et al. (2018) reported that, although around 30% of vegetable and fruit samples, collected in the "Land of pyres" area, showed quantifiable levels of chemicals, no significant difference emerged among the potentially polluted area and the nearby control cities (limitedly

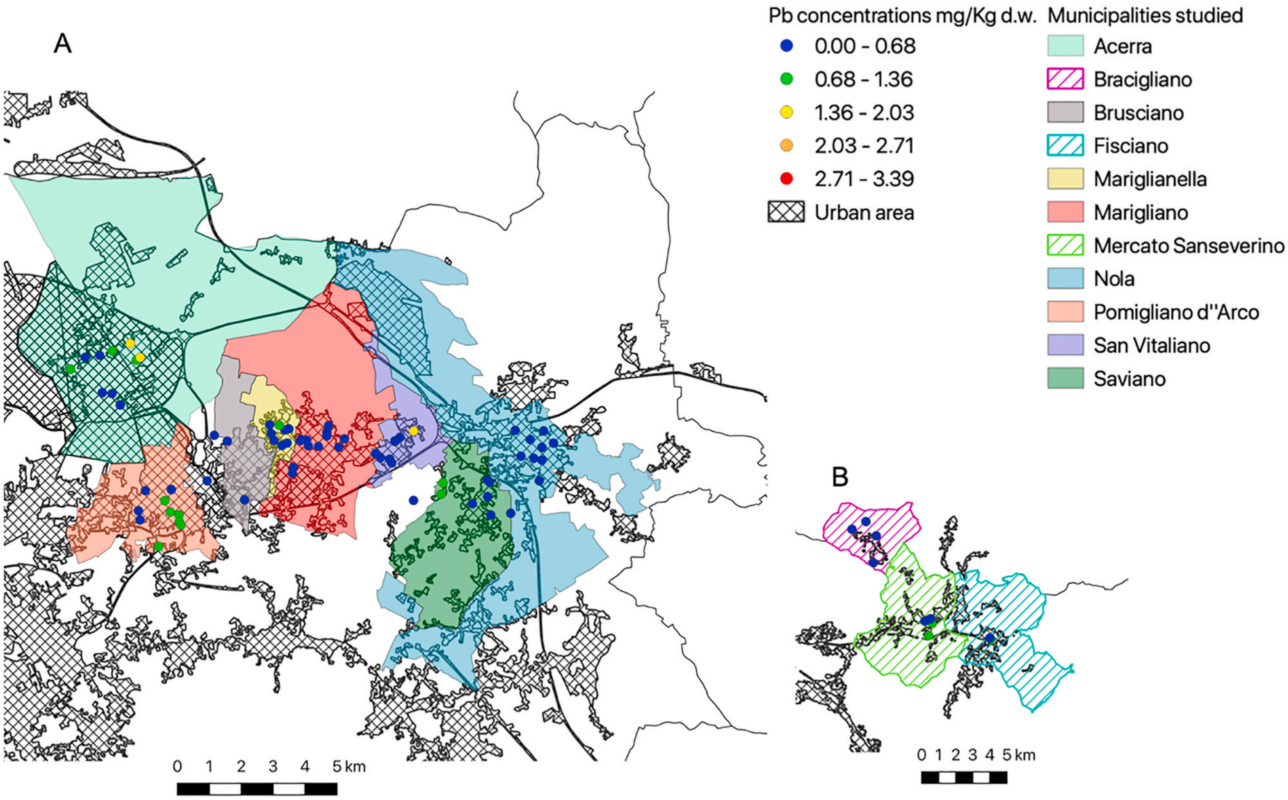

Fig. 11. An overview of the eight municipalities (solid colour) included in the "Land of pyres" (A), located in the Province of Naples, and of the three (colour texture) corresponding to the remote sites (B). The different colours of the points are referred to the diverse range of the Pb concentrations. With black texture are indicated the urban areas. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

polluted). It is note of worthy that the "Land of pyres" is one of the most urbanized and also high traffic areas, contributing at a strong air contamination. The concentrations of 12 PTE have been determined in leaf samples of olive trees collected in urban sites and compared with the background sites (remote site). Although leaves of deciduous or evergreen trees are recognized as useful air pollution biomonitors for trace elements (Dolegowska et al., 2021), many difficulties arise when comparing data among studies, not only due to the use of different plant species with specific characteristics, but also from the application of different experimental approaches (washed vs unwashed leaves). In general, the element content in tree leaves may originate from the soil by uptake via roots and/or by atmospheric deposition of particles on vegetation, and thus foliar uptake. When the biomonitoring using higher plants is performed, it is not easy to distinguish the contribution of these two contaminant sources to the total leaf element content. Then, an atmospheric origin of the elements in leaves must be assumed.

In the present study, olive trees, thanks to their widespread and abundant presence in the study area, resulted exploitable and useful as biomonitor. A general trend for PTE in the leaves was in this order of magnitude Sb > Al > B > Mn > Cu (similar to Ba), while Ni, Cr, Pb, As and Hg concentrations were very low, or even undetectable in almost all the sampled sites. In general, our results indicate that the PTE concentrations are lower than those reported in other studies, using as biomonitors both olive trees and the other un-deciduous species (*e.g.*, holm oak). A substantial loading of some elements, like Sb, Al and Mn on the olive leaves was recorded in different collection sites of the cities, and it has been widely accepted that these elements have anthropogenic origins and broadly present in urban areas with a relevant vehicular traffic (Liu et al., 2020). Tree leaves, collected in sampling sites with relatively higher traffic density as in Acerra, Pomigliano d'Arco, San Vitaliano, Brusciano, Marigliano and Mariglianella, generally show the highest concentrations of PTE. On the contrary, collection sites interested by a lower vehicular traffic volume are characterized by lowest concentrations of PTE, although some exceptions have been identified as in the case of Cu and Ba. This trend has also been confirmed by the estimated EF values. For the majority of the PTE, the EF values were less than 10, not exhibiting enrichment due to anthropogenic activities. However, Mn showed slight enrichment in all municipalities, whereas Sb and Al were highly enriched in almost all collection sites with very high EF values in some of them. In addition, strong correlations between Sb, Al and Mn, detected in some of the assayed municipalities (Acerra, Brusciano, Pomigliano d'Arco, Marignanella, Marigliano and Saviano) indicated that they share one or few dominant sources of emissions.

The distribution map of Sb reveals high concentrations of this element in several collection sites of Acerra, Marigliano, Mariglianella, Pomigliano d'Arco and San Vitaliano municipalities; while it results undetectable in the remote sites, Nola and Saviano. Antimony is a metalloid and occurs naturally as trace element in the environment (mainly in soil - Sanchez-Rodas et al., 2017; Wilson et al., 2010), however in the last decades anthropogenic activities determined an increase of its concentrations in urban and industrial areas (Li et al., 2018; He et al., 2019; Hu et al., 2015). In particular, the Sb, released in the environmental matrices (air, soil and water), is attributable to an high exploitation and overuse of the Sb containing products (*e.g.*, catalytic converters, batteries, raw material for flame retardants, semi-conductors, fossil fuels, timber preservatives, etc.). In relation to its presence in the air, the main recognized source is the traffic associated with the consumption of some vehicle parts containing Sb alloys and other Sb compounds (Hu et al., 2015; Sanchez-Rodas et al., 2017). It is noteworthy that the Sb pollution primarily depends not only by the local traffic intensity, but also by seasonal period characterized, for instance, by different temperatures, precipitations, winds, etc. Recently, in a study conducted in the city of Granada (Spain) and its metropolitan area (Parviainen et al., 2020), Sb has been reported as a clear tracer of brake

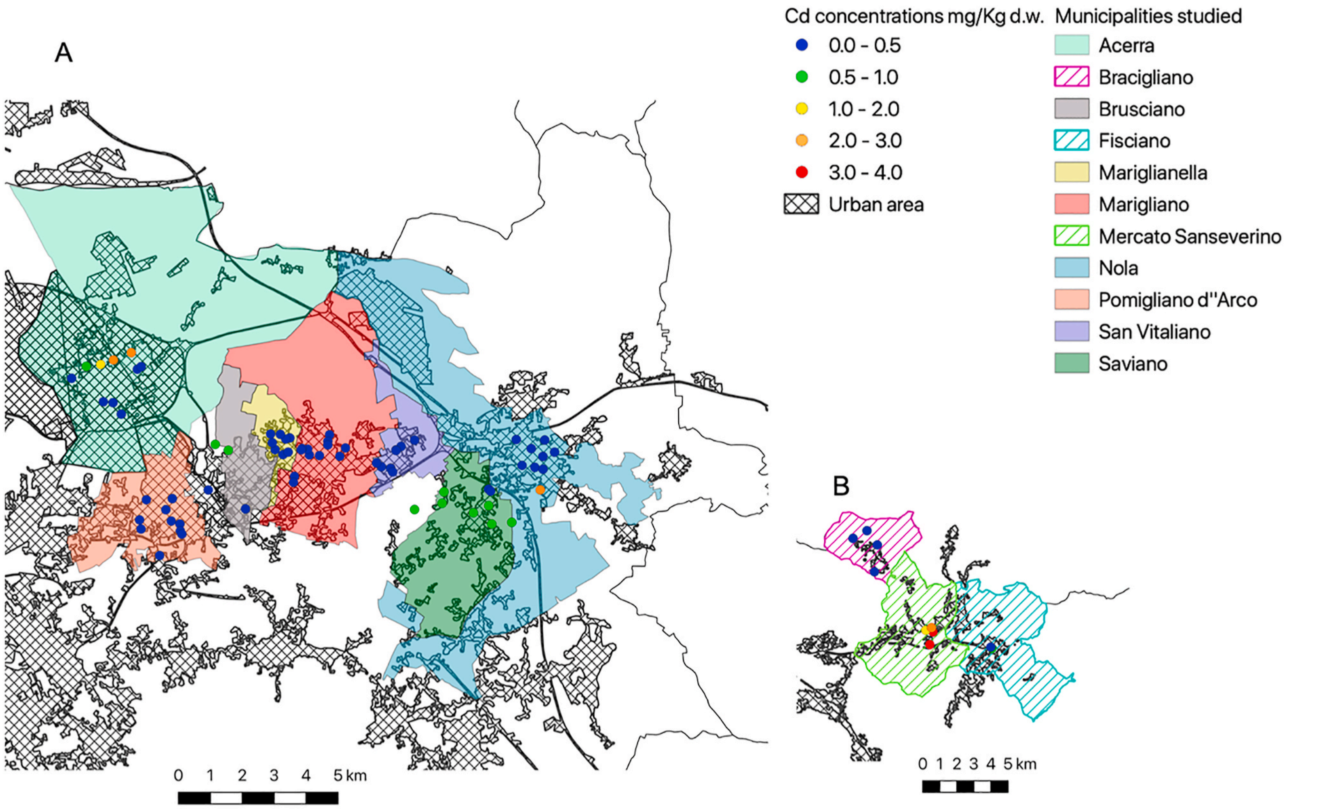

Fig. 12. An overview of the eight municipalities (solid colour) included in the "Land of pyres" (A), located in the Province of Naples, and of the three (colour texture) corresponding to the remote sites (B). The different colours of the points are referred to the diverse range of the Cd concentrations. With black texture are indicated the urban areas. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

wear. The lichen *Xanthoria parietina* (L.) Th. Fr., used as a bioindicator, revealed a high enrichment for Sb concentrations especially in those collection sites located at close distance to the highway and at the main accesses to the city, locations characterized by a high vehicular traffic. In addition, the same authors (Parviainen et al., 2020) revealed a low Cu/Sb ratio in particulate matter, proposing that non-exhaust traffic emissions can be the potential sources of Sb pollution, principally derived from brake wear (Sternbeck et al., 2002; Varrica et al., 2013). In our study, a very low Cu/Sb ratio in the olive leaves collected in most sites of Acerra, Pomigliano d'Arco and San Vitaliano municipalities is estimated suggesting that, even in these locations, a severe brake wear, due to the vehicular traffic, can be its pollution source.

Since Al and Mn are typical crust elements, their high concentrations, that we observed in the olive tree leaves, suggest that the resuspension of soil particles contributes to their aerosol abundance at the sampling sites. The Al concentrations in the leaves were higher in several collection sites in Acerra and San Vitaliano, as well as in other sampling sites of Brusciano and Mariglianella municipalities; however, its values were within the range found in rural, urban and industrial areas (Aksu, 2015), and this is probably due to its prominence as one of the major constituents of the earth's crust, and, consequently, naturally released into the environmental matrices as air and water. In addition, anthropogenic sources can contribute to Al or its constituent release. In fact, Al is used in several human activities, including several industrial products (*e.g.*, building materials, automobiles, paintings, explosives, metal alloys, etc.), or applications (*e.g.*, water purification, pharmacological, glass processing, aerospace, etc.), which, along with vehicle emission and decay of vehicle parts, could contribute to the high concentrations of this element in the air of some sites (Ali et al., 2017; Polizzi et al., 2007).

In our study, the mean Mn concentration observed in the olive leaves ranged from 10 to 27 mg Kg^{-1} D.W. in all the analysed municipalities without significant Mn spots. The major sources of air Mn are or have been the burning of diesel fuel, or of added leaded gasoline, where Mn was used as an anti-knock compound, or in industrial processes (*e.g.*, component of ferroalloy, or welding). Manganese concentrations in the air tend to be lowest in remote locations (about 0.5–14 ng m^{-3}, on average), higher in rural areas (40 ng m^{-3}, on average), and still higher in urban areas (about 65–166 ng m^{-3}, on average), or where important sources are present (*e.g.*, WHO, 1999 - https://apps.who.int/iris/handle/10665/107335).

It surprised positively in our study that As and Pb concentrations were undetectable, or very low in all collection sites. Arsenic is considered as a hyper-toxic element and emitted during the use of fossil fuels and by brake wear in motor vehicles. Single vehicle car may emit small amounts of As in the short term, both in the road soils and in the air, however combined emissions due to intense traffic over time could be relevant. The As abundance in the Earth's crust is around 4.8 mg kg^{-1} (Rudnick, 2003) and the minimal values we detected on the olive leaves suggest a minimal As enrichment in the air.

It is clear that Pb emissions started to decline since the use of Pb in the gasoline was banned in many countries (Byrd et al., 1983), even if some studies found high Pb concentrations in the soils near industrial plants (Baldantoni et al., 2011), or in bioindicators or accumulators (Forbes et al., 2009), indicating that the presence of historical Pb pollution are persisting again in the environment.

The concentrations of the remaining PTE were lower than those observed for Sb, Al and Mn in all municipalities we surveyed, therefore we suppose that anthropogenic air emissions have been and are still limited. However, it is interesting to note that, even if the low Hg concentrations we detected in Pomigliano d'Arco, they follow an increasing concentration gradient along the sites from PO1 to PO6. Nevertheless, at present, it is unclear which factors contribute most significantly to the variability in spatial range of Hg concentrations in this area.

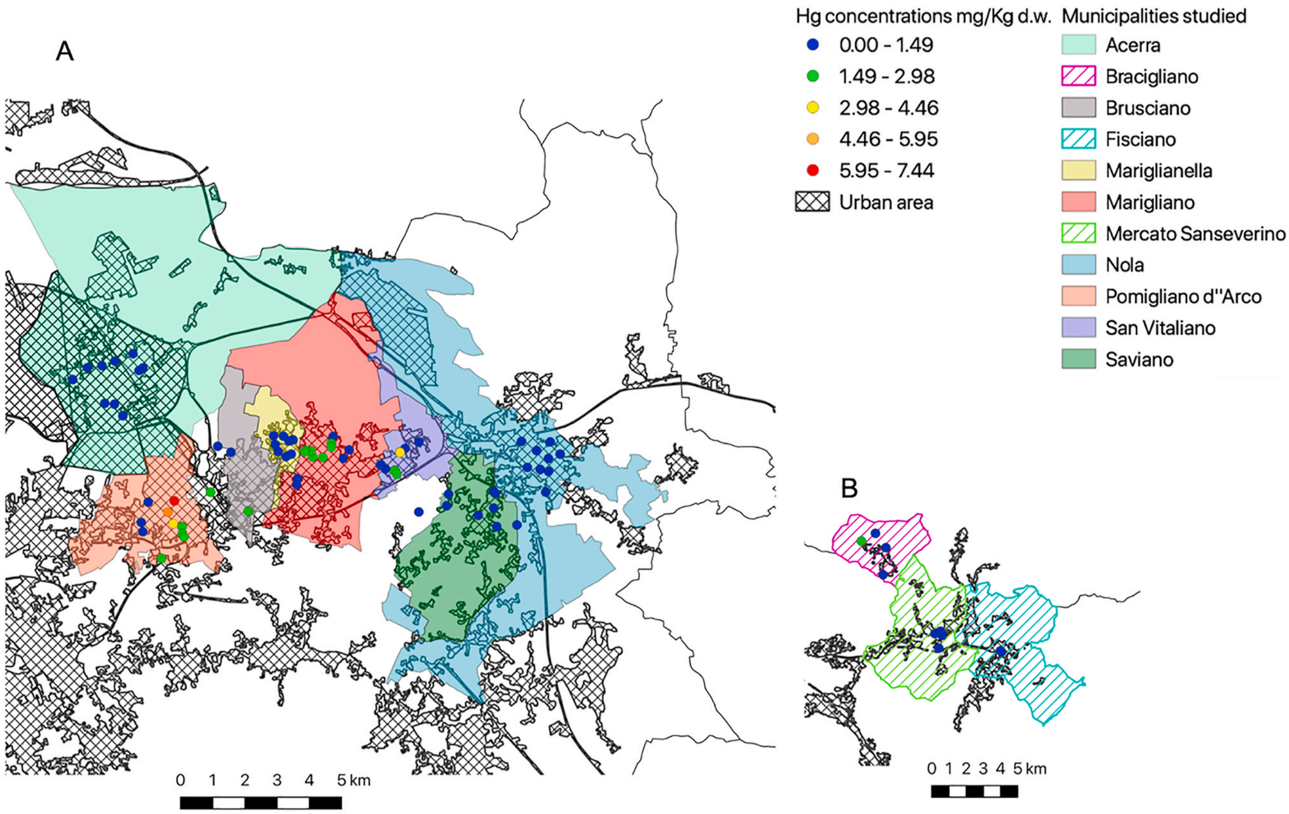

Fig. 13. An overview of the eight municipalities (solid colour) included in the "Land of pyres" (A), located in the Province of Naples, and of the three (colour texture) corresponding to the remote sites (B). The different colours of the points are referred to the diverse range of the Hg concentrations. With black texture are indicated the urban areas. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 2
Mean values of enrichment factors of PTEs per each municipality.

Site	Enrichment Factor									
	Ni	Cu	Cr	Pb	Sb	Al	Cd	Hg	Mn	Ba	B
Acerra	0.004	0.021	0.002	0.004	44.816	80.272	0.931	0.578	23.212	0.001	0.066
Brusciano	0.005	0.179	0.002	0.007	38.745	72.743	1.021	1.367	24.808	0.001	0.083
Mariglianella	0.005	0.186	0.002	0.007	27.047	33.388	1.213	1.626	25.921	0.002	0.114
Marigliano	0.006	0.183	0.002	0.007	30.532	49.105	1.172	1.303	25.362	0.002	0.100
Nola	0.006	0.187	0.001	0.006	25.904	27.635	0.781	2.080	25.685	0.002	0.139
Pomigliano d'Arco	0.014	0.188	0.001	0.006	24.512	26.682	0.577	2.273	25.329	0.002	0.149
San Vitaliano	0.022	0.190	0.001	0.006	24.569	25.087	0.447	2.150	25.117	0.002	0.161
Saviano	0.010	0.189	0.001	0.006	23.798	28.199	0.395	2.072	23.256	0.002	0.172
Bracigliano	0.006	0.066	0.002	0.006	42.158	76.366	0.974	1.386	23.634	0.001	0.075
Fisciano	0.007	0.180	0.002	0.007	33.875	72.035	1.096	1.339	23.982	0.002	0.088
Mercato San Severino	0.006	0.187	0.002	0.007	27.960	27.246	1.070	1.901	26.147	0.002	0.130

Furthermore, in the remote site of Bracigliano city, and, in particular, at BRA1 site, moderate levels of Cu and Ba were detected, suggesting a possible air deposition or absorption from the soils of these elements. The remote site of Bracigliano is an agricultural area, and possibly the contamination sources, other than due to vehicular traffic (very limited), might be the agro-chemicals employed for the olive tree cure, in synergy, of course, with the influence of the winds that can take these elements over long distances. Although the causes for the high concentrations Cu and Ba detected in BRA1 site have not been clearly identified in our study, nevertheless, it highlights, at the same time, that significant PTE, or metal contaminations are possible in seemingly unexpected locations.

5. Conclusions

Our findings reveal that the air of the studied cities/municipalities, located in the "Land of pyres" was limitedly contaminated by PTE or metals; in fact, only Sb, Al and Mn were detected at high level in the olive tree leaves collected in some of the surveyed municipalities and they were likely related to vehicular traffic emissions (*e.g.,* SV4, SV5, MA7, MA7, etc.). To determine the emission sources of these elements, in further works, it would be useful to perform a more detailed and comprehensive study and obtain detailed measurements from traffic monitoring sites and also meteorological (*e.g.,* rains, wind transportation, etc.) and seasonal data able to affect the PTE air spread. However, it is also note of worthy the fact that the concentrations of the other assayed PTEs were lower than those observed for Sb, Al and Mn, therefore, we suppose that their emissions in the atmosphere have been and are still limited, and, probably, have a natural source.

When PTE or metals are released into the atmosphere, they can pass through water and soil, and then taken by living organisms via ingestion, inhalation, and skin absorption causing some environmental and health problems. However, Esposito et al. (2018) demonstrated that "no statistically significant difference emerged between the concentrations of PTE found in fruit and vegetables harvested in the "Land of pyres" and non-"Land of pyres" areas with the majority of the samples showing concentrations below the limit of quantification". In agreement with those results, our data are very comforting and and suggest that the contribution to the pollution of the "Land of pyres" area due to anthropogenic activities is very limited and comparable to the remote site. Anyway a great environment care is, for sure, needed.

Funding

This work was supported by the Campania Region, grant to project "CO.S.A.-CORRELAZIONE SALUTE AMBIENTE", in the frame of call "PROGETTI DI TRASFERIMENTO TECNOLOGICO E DI PRIMA INDUSTRIALIZZAZIONE PER LE IMPRESE INNOVATIVE AD ALTO POTENZIALE PER LA LOTTA ALLE PATOLOGIE ONCOLOGICHE - CAMPANIA TERRA DEL BUONO" CUP B43D18000170007.

Credit author statement

Conceptualization: AC, SC. Methodology: FG, AC. Formal analysis: FG, AC. Investigation: FG, AC, SC. Resources: MT, GI, SC. Writing - Original Draft: FG, AC, SC, MT and GI; Writing – review & editing FG, AC, SC; Supervision SC, AC, MT.

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.

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