

Article

Evaluation of the Efficiency of *Arundo donax* L. Leaves as Biomonitors for Atmospheric Element Concentrations in an Urban and Industrial Area of Central Italy

Martina Ristorini ^{1,2}, Maria Luisa Astolfi ³, Maria Agostina Frezzini ³, Silvia Canepari ³ and Lorenzo Massimi ^{3,*}

¹ Department of Bioscience and Territory, Università del Molise, 86090 Pesche (IS), Italy

² Institute of Terrestrial Ecosystem research – Council of National research (IRET-CNR) Via G. Marconi 2, 05010 Porano (TR), Italy

³ Department of Chemistry, Sapienza University of Rome, Rome, 00185, Italy

* Correspondence: l.massimi@uniroma1.it; Tel.: +39-0649913742 or +39-3703022703

Received: 29 November 2019; Accepted: 22 February 2020; Published: 26 February 2020

Abstract: Washed and unwashed *Arundo donax* L. (*A. donax*) leaves were analyzed for elements, and results were compared with element concentrations detected in river water and particulate matter (PM) Samples were collected along a river in an urban and industrial hot spot of Central Italy, where element concentrations show relevant spatial gradients both in air and river water. The aim of this study is to identify the role of the two environmental matrices on leaves composition. Element concentrations of washed and unwashed leaves were compared to differentiate between the superficial deposition and the uptake into leaf tissues of elements. Water-soluble and -insoluble element concentrations were measured in PM₁₀ samples collected on membrane filters by using innovative high spatial resolution samplers. The comparison among leaf and atmospheric concentrations of PM₁₀ elements showed a similar trend for Ni, Mo, Cr, Ti, and Fe, which are reliable tracers of the PM₁₀ contribution by steel plant and vehicular traffic. Soluble species appeared to be mainly bounded into leaf tissues, while insoluble species were deposited on their surface. On the other hand, element concentrations detected in washed *A. donax* leaves were poorly correlated with those measured in river water samples. The obtained results proved that *A. donax* leaves can be used as reliable biomonitors for the evaluation of the atmospheric concentrations of some PM₁₀ elemental components.

Keywords: air quality; biomonitoring; particulate matter; leaf deposition; source tracer

1. Introduction

Arundo donax L., commonly known as giant reed, is a tall perennial grass of the family *Poaceae*, typical of riparian areas and characterized by great productivity, growing up to 10 cm per day in optimal conditions [1,2]. Numerous studies had underlined the potential of this species for the phytoremediation of contaminated waters and soils due to its tolerance to high concentrations of heavy metals, such as Cd, Cr, and Ni [3], and to its ability to absorb and bioaccumulate contaminants. In particular, *A. donax* turns out to be characterized by a root > leaf > stem translocation pattern [4], with the belowground biomass (roots and rhizomes) as the main bioaccumulation organs [5–7]. These characteristics make this species suitable to be used as bioindicator of heavy metal pollution of water and soil. Therefore, *A. donax* provides an alternative to the traditional sampling and analytical procedures applied to this task [8].

On the other hand, numerous studies underlined the potential of biomonitoring to assess airborne particulate matter (PM) pollution [9–11]. In this context, urban trees and shrubs leaves are often proposed as efficient and low-cost passive biomonitors for PM [12–14], since they are able to affect dispersion and deposition of airborne particles [15]. In particular, the evaluation of chemical and physical characteristics of particles deposited on leaves can be used to achieve information about the role and the impact of anthropogenic PM emission sources [16,17]. In fact, these characteristics can be directly influenced by the type of emission process and source [18,19]. PM is an extremely heterogeneous mixture of airborne solid particles and liquid droplets, varying in size, shape, chemical composition, solubility, toxicity, and origin [20]. It is considered one of the most relevant air pollutants in terms of human health effects [21–23]. In particular, PM₁₀ (particles characterized by aerodynamic diameters $\leq 10 \mu\text{m}$) includes particles that are able to interact at different levels with human respiratory system and to induce negative health effects [24,25]. PM₁₀ mass concentration is used as an air-quality indicator, but to date, exceedances of guideline levels set for PM₁₀ are still frequent in many urban and industrial areas (such as the daily limits of 50 ng m^{-3} for PM₁₀ mass concentrations set by 2008/50/EC).

Dry deposition of PM on leaves is a complex and dynamic process, being influenced both by species-specific characteristics of vegetation and chemical-physical characteristics of airborne particles themselves [26,27]. To date, due to the high complexity of dry deposition processes and the heterogeneity of PM₁₀, the achievement of a complete characterization of leaf-deposited particles is difficult to obtain. Numerous analytical procedures have been applied for the achievement of this task, but it is still uncertain which procedure is the most efficient. One of the main sources of uncertainty is connected to the leaf-washing procedure, being still unsure whether this step should be carried out. In fact, the efficiency of leaf washing together with the chemical and physical characteristics of the particles can influence their encapsulation in leaf structures (waxes layer or stomata pores) [28,29]. These factors can affect the efficiency of any analytical procedure applied in the characterization of leaf-deposited particles.

This study is aimed at evaluating the influence on element concentrations of *A. donax* leaves of two types of environmental contaminations to which plants are exposed: atmospheric PM₁₀ and river water pollution. To this aim, *A. donax* leaves, PM₁₀ sampled filters, and river water samples were collected in parallel at sites impacted by different pollution sources. Element concentrations determined in the three matrices were compared. Washed and unwashed leaves were analyzed and compared to differentiate between superficial deposition and uptake into leaf tissues of PM₁₀ elements. Furthermore, due to the hyper-accumulation ability of this riparian species, element concentrations detected in *A. donax* leaves were compared with those measured in river water samples. This was aimed at evaluating to what extent river-water contamination can affect leaves elemental composition.

2. Materials and Methods

2.1. Study Area and Sampling Sites

The study was carried out in Terni city, an urban and industrial hot spot of Central Italy. The choice of Terni was mainly driven by the presence of intense local emission sources. This study area is characterized by typical urban sources such as vehicular traffic and domestic heating and by a power plant for waste treatment and an extensive steel plant, occupying about 158 ha (Figure 1). Due to its peculiar geomorphological and meteorological conditions, Terni basin is characterized by high PM₁₀ mass and element concentrations, which make this area one of the most critical for human health in Central Italy [30–35]. In addition, these emission sources determine very relevant spatial variations of element concentrations in both PM₁₀ and river water, making this area particularly suitable for studying correlations among biomonitors and environmental conditions. Six sampling sites (TE1, TE2, TE3, TE4, TE5, and TE6) were individuated along the river Nera and chosen for the collection of *A. donax* leaves and river-water samples. TE1 is located near the power plant in the western part of the city; TE2 and TE3 are near the main trafficked streets of the city center; and TE4, TE5, and TE6 are

sited around the steel plant, in the eastern part of the city (Figure 1, Table 1). In particular, TE6 is located upstream from the wastewater systems for the treatment of the steel plant effluents.

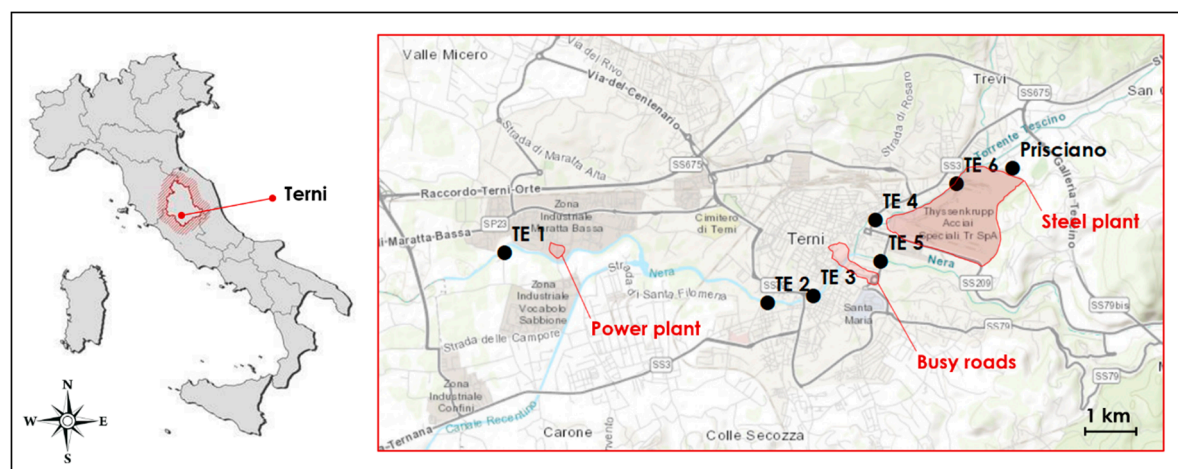


Figure 1. Sampling sites of *A. donax* leaves and river-water samples along the river Nera in Terni (Central Italy) and air-quality station “Prisciano” controlled by ARPA Umbria (regional agency for environmental protection): Highlighted are the main PM₁₀ anthropogenic emission sources present in the study area.

Table 1. Latitude and longitude of the six sampling sites in Terni.

SAMPLING SITES	LATITUDE	LONGITUDE
TE1	42°33'43.84" N	12°35'47.18" E
TE2	42°33'22.27" N	12°38'21.02" E
TE3	42°33'25.29" N	12°38'47.81" E
TE4	42°33'58.02" N	12°39'24.08" E
TE5	42°33'40.12" N	12°39'27.33" E
TE6	42°34'13.53" N	12°40'11.41" E

2.2. *Arundo donax* Leaves and River Water Samples Collection and Preparation

A. donax leaves and river-water samples were collected monthly at the six sampling sites (Figure 1) from March to July 2017. For each site, 3 plants were selected and 6 leaves were collected from each plant for a total of 18 leaves collected each month. Leaves were detached at least a week after the last rainfall event from the same internode (second-last from the top of the stems) in order to avoid the youngest leaves and to ensure longer exposition time to both river water and PM₁₀ atmospheric pollution. Furthermore, leaves were collected at a height comparable to that of PM₁₀ active samplers (about 2 m from the ground). Leaves samples were then stored at −18 °C in paper bags to avoid external contamination. *A. donax* leaves collected northeast of the Terni basin (42°38'25.95" N, 12°48'34.98" E), far from the direct impact of anthropogenic emission sources, were used as background samples. Half of the collected leaves were washed thoroughly three times with 250 mL of deionized water (produced by Arioso UP 900 Integrate Water Purification System) for 5 min by using a rotating mixer (Rotator, Glas-Col, USA). The dry weight calculation (30 replicates) was carried out by oven drying 1 g of fresh leaves at 60 ± 2 °C until constant weight. Washed and unwashed leaves collected monthly at each site were then pulverized by grinding in a mill with Teflon balls, and the obtained powders were homogenized and weighed (analytical balance Gibertini Europe 60; Gibertini Elettronica Srl, Milan, Italy). Subsequently, three replicates of about 30 mg of each sample (homogenized powders of washed or unwashed leaves collected monthly at each site) was subjected to a microwave-assisted acid digestion (Ethos Touch Control with Q20 rotor, Milestone, Bergamo, Italy). The acid digestion was carried out for 30 min at 180 °C by using a HNO₃/H₂O₂ mixture (2:1, v/v; 2 mL of ultrapure concentrated HNO₃ 67%, Promochem, LGC Standards GmbH, Wesel,

Germany; 1 mL of H₂O₂ 30%, Promochem, LGC Standards GmbH, Wesel, Germany). The digested solutions were then diluted to 100 mL of deionized water. Since all the sampled plants were in close proximity to the river and the root system was often in direct contact with the river water (frequent overflowing of the river), each month, about 50 mL of river water was collected at each sampling site for a total of 30 water samples. River water samples were taken from 10 to 15 cm below the water surface, according to American Public Health Association (APHA), 1998 [36].

2.3. PM₁₀ Samples Collection and Preparation

PM₁₀ was sampled monthly on Teflon membrane filters (PTFE membranes, 37 mm diameter, 2 µm pore size, PALL Corporation, Port Washington, New York, NY, USA) from March to July 2017 at 23 monitoring sites spread over the Terni basin by using innovative and very-low volume (0.5 l min⁻¹) PM₁₀ active samplers (High spatial resolution sampler—HSRS, Fai Instruments, Fonte Nuova, Italy). The localization and the geographical coordinates of the 23 PM₁₀ sampling sites as well as the characteristics of the used HSRS are deeply described in Massimi et al. 2017 and Massimi et al. 2019 [11,31]. The collected monthly PM₁₀ membrane filters were subjected to a chemical fractionation procedure, previously optimized and validated [37,38], useful for separating the water-soluble and insoluble fraction of each PM₁₀ elemental component, thus increasing its selectivity as a source tracer [11,39,40]. Firstly, after removing the supporting polymethylpentene ring from each membrane filter, PM₁₀ filters were extracted in 10 mL of deionized water for 30 min at 25 °C by using an ultrasonic bath (Proclean 10.0 ultrasonic cleaner, Ulsonix, Germany) and were then filtered on cellulose nitrate filters (0.45 µm pore size, Merck Millipore Ltd., Billerica, MA, USA). Secondly, both the membrane and cellulose nitrate filters were acid digested for 30 min at 180 °C in the microwave oven by using the HNO₃/H₂O₂ mixture (2:1, v/v) previously described. The digested solutions were then diluted to 50 mL with deionized water.

2.4. ICP-MS Analysis

The collected river water samples and all the acid-digested solutions were filtered with syringe filters (25 mm diameter, 0.45 µm pore size, GVS Filter Technology, Morecambe, England, UK) before instrumental analysis. The concentrations of 16 elements (Ba, Cd, Cr, Cs, Cu, Fe, Li, Mn, Mo, Ni, Pb, Rb, Sb, Sn, Sr, and Ti) were determined in all the samples (river-water samples, water-extracted and acid-digested PM₁₀, and washed and unwashed *A. donax* leaves) by a quadrupole inductively coupled plasma mass spectrometer (ICP-MS, model 820-MS; Bruker, Bremen, Germany) equipped with a glass nebulizer (0.4 mL min⁻¹; Analytik Jena AG, Jena, Germany). External matrix-matched standard calibration curves were performed for all the analyzed elements in the 1–500 µg L⁻¹ range by serially diluting standard stock solutions (1000 ± 2 mg L⁻¹; Exaxol Italia Chemical Manufacturers Srl, Genoa, Italy). To control the nebulizer efficiency, yttrium and rhodium were set at 5 µg L⁻¹ as internal standards for all measurements and were prepared from standard stock solutions (1000 ± 2 mg L⁻¹; Panreac Química, Barcelona, Spain; Ultra Scientific, North Kingstown, RI, USA; Merck Millipore Ltd., Billerica, MA, USA). The values of blanks, subjected to similar sample preparation and analytical procedures, were deducted from all measurements, and the limits of detection (LODs; Supplementary Material S1; Tables S1.1–3) were set at 3 times the standard deviation (Std Dev) of 10 replicate blank determinations. Standard deviations of the replicates were all below 20%. The used instrumental conditions and the performance of the method are detailed in Astolfi et al. 2018 [41].

2.5. Data Elaboration

Concentrations of the 16 elements derived from the three replicate analyses of washed and unwashed leaves, collected monthly at each site, were averaged in order to obtain a single monthly value. This was aimed at properly comparing leaves element concentrations with results from the chemical analysis of PM₁₀ samples (one filter sampled monthly for each site). The concentrations determined in the washed and unwashed *A. donax* leaves were divided by the dry weight of each sample (ng mg⁻¹). Then, monthly element concentrations were averaged for each monitoring site

(Supplementary Material S2; Tables S2.1,2). The averaged element concentrations detected in washed leaves were subtracted to the unwashed ones to evaluate the elemental amount superficially deposited on leaves (SD in ng mg^{-1}). Element concentrations ($\mu\text{g l}^{-1}$) were determined in river water samples collected at each site for each of the 5 collection months (three replicates of 10 mL). Also, for river water samples, results obtained from the three replicates analyses were averaged to obtain one monthly result relative to each site. Then, monthly element concentrations were averaged for each monitoring site, and these are reported in Supplementary Material S2 (Table S2.3). The element concentrations of the water-soluble and -insoluble PM_{10} were divided by the air volume sampled on each PM_{10} membrane filter (ng m^{-3}). Total concentrations were calculated as the sum of the two solubility fractions. Since the *A. donax* leaves were collected at different sites with respect to the PM_{10} samples, ordinary kriging (OK, spherical semivariogram model) interpolation [42,43] was applied to the PM_{10} soluble, insoluble, and total element concentrations monthly determined at the 23 PM_{10} sampling sites. Then, these concentrations were averaged over the 5 months collection period in order to estimate their concentrations (Supplementary Material S2; Tables S2.4,5) at the leaves collection sites (TE1, TE2, TE3, TE4, TE5, and TE6).

2.6. Statistical Analysis

Normal distribution of data was tested by using the Kolmogorov–Smirnov test. Then, paired t-tests were used to assess the statistical significance of the differences between mean values of each element detected in unwashed and washed leaves. Pearson correlation was used to assess the correlations between SD results and element concentrations in the water soluble and insoluble fraction of PM_{10} ; washed leaves element concentrations and the element concentrations in the two fractions of PM_{10} ; and washed leaves and river water element concentrations. Statistical analyses were carried out using IBM SPSS Statistics 25 software (IBM Corp., Armonk, NY, USA).

2.7. Scanning Electron Microscopy (SEM) Analysis of PM_{10} Samples

PM_{10} sampling on polycarbonate membranes (PCTE membranes, 37 mm diameter, 0.8 μm pore size, Sterlitech Corporation, Kent, Washington, USA) was carried out for three days, from 2 to 4 March, by using two HSRs working in parallel at the air-quality station “Prisciano”. The station is located at the eastern side of the city ($42^{\circ}34'20.30''\text{N}$ $12^{\circ}40'44.23''\text{E}$) in proximity to the steel plant, and it is controlled by the regional agency for environmental protection (ARPA Umbria) (Figure 1). Small portions of each polycarbonate membrane were cut, fixed to aluminum stubs by self-adhesive carbon disks (TAAB, 12mm diameter), and coated with an ultrathin carbon layer in a vacuum evaporator (108 Carbon A; Scientific Instruments Ltd., Cressington, England, UK). Micrographs of each sample were acquired by a high-resolution field emission scanning electron microscopy (HR-FESEM; model AURIGA; Carl Zeiss Microscopy GmbH, Jena, Germany) equipped with an energy dispersive spectrometer for X-ray microanalysis (XEDS; model QUANTAX; Bruker Italia S.r.l., MI, Italy). Micrographs were acquired through the use of backscatter electron detector (BSD) at magnification ranging from 25,000 \times to 600,000 \times and at working distance (WD) ranging from 9.6 mm to 12.4 mm.

3. Results and Discussion

3.1. Element Concentrations in *Arundo donax* Leaves

Figure 2 reports the concentrations of elements associated to the steel plant emission (Cr, Fe, Mo, Ni, and Ti) in unwashed and washed leaves. All these elements showed a marked concentration gradient in both washed and unwashed leaves, indicating that the measured concentrations are sensitive to environmental concentrations. A similar trend was found for all the considered elements, with higher concentrations at sites surrounding the steel plant.

Cr, Ni, and Ti showed higher concentrations (ng mg^{-1}) in leaves collected at TE5 and TE6 (Figure 2a,d,e), which are the sites closest to the steel plant. Furthermore, for these elements, concentrations in unwashed leaves were significantly higher than those in washed leaves. This means that a major

part of the measured concentrations in unwashed leaves is probably due to superficial deposition of atmospheric particles. PM_{10} particles containing these elements are known to be emitted at high concentrations by the steel plant [31]. Chromium is usually used to increase the steel resistance to chemical oxidation, and nickel is used to increase the steel strength, ductility, and toughness. Titanium is used in steelmaking for deoxidation, grain-size control, carbon and nitrogen control, and stabilization [44]. The variation among the selected sites, observed for the leaf deposition of these elements, underlined the impact of the steel plant and proved the reliability of *A. donax* leaf deposition results for the individuation of the steel plant tracers.

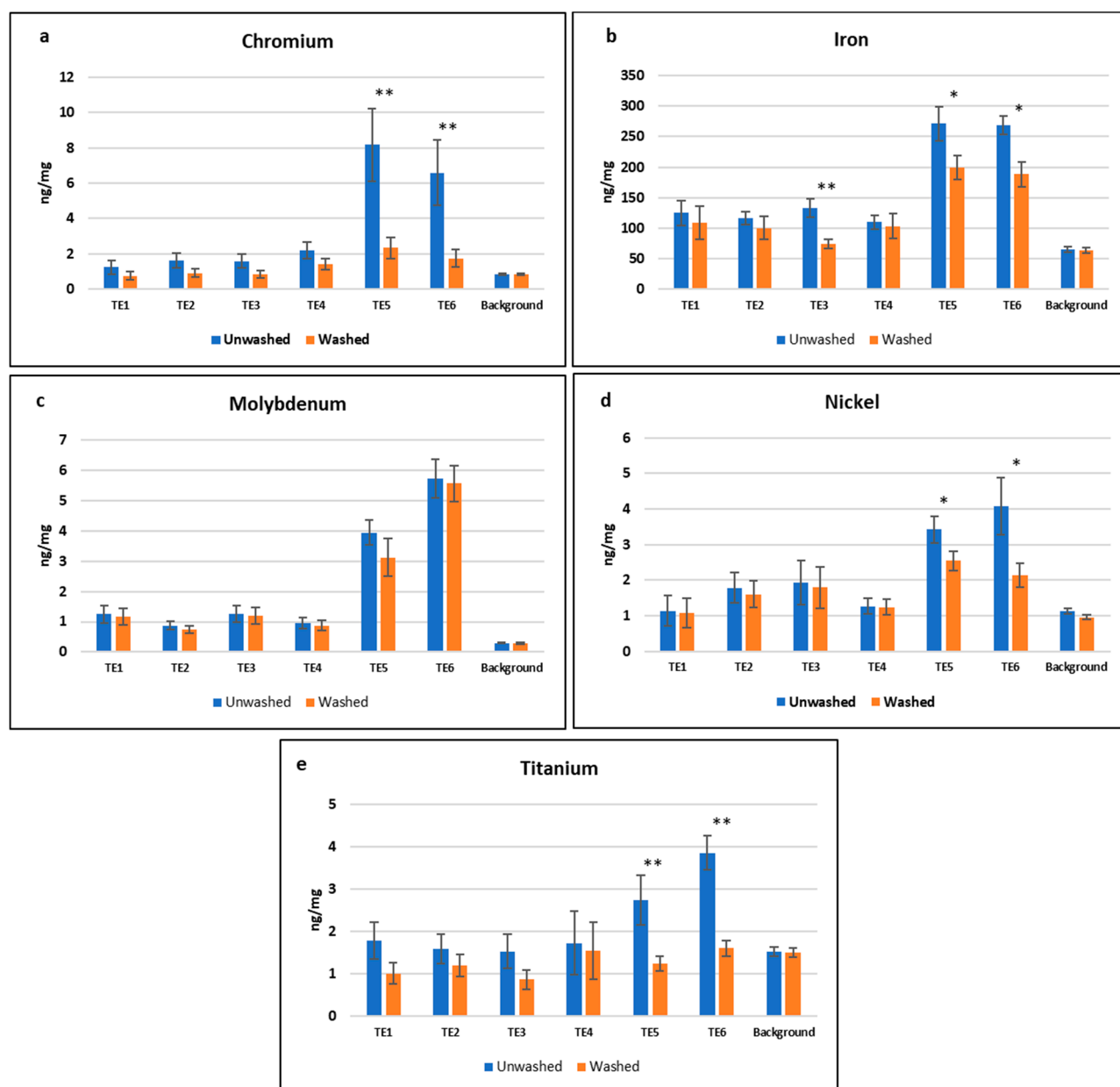


Figure 2. Comparison between averaged concentrations ($ng\ mg^{-1}$) of (a) Cr, (b) Fe, (c) Mo, (d) Ni, and (e) Ti detected in unwashed and washed leaves at the six sites: *p*-values obtained by applying paired sample *t*-test (* $p < 0.05$; ** $p < 0.001$) and standard deviations calculated between monthly concentrations are reported.

In Figure 2b, we can observe that Fe concentrations ($ng\ mg^{-1}$) detected in unwashed leaves were higher at the sampling sites TE3, TE5, and TE6. Also, in this case, concentrations were significantly higher in unwashed leaves. Iron is the principal component of stainless steel, and higher deposition values in *A. donax* leaves collected at TE5 and TE6, which are the closest sites to the steel plant,

confirmed its attribution to emissions from the steel plant. However, Fe is also a well-known tracer for vehicular traffic, being related to the mechanical abrasion of brakes and vehicle components [30,45,46]. The increase of Fe concentration at TE3, located near the city center, is mainly related to its emission from the close busy roads. Therefore, the trend of Fe leaf deposition underlined the impact of two different emission sources: steel plant (at TE5 and TE6) and vehicular traffic (at TE3).

Higher concentrations of molybdenum (Mo) were found at the same sites (TE5 and TE6) as for Cr, Ni, and Ti, highlighting the impact of the steel plant. In fact, Mo is typically used as secondary components to improve the resistance of stainless steel [44]. However, Mo concentrations in washed and unwashed leaves were very similar, indicating that this element is deeply bound to the leaves (Figure 2c). This difference may be due to a different uptake process (i.e., root absorption from water or soil) or to the different chemical and/or physical characteristics of atmospheric particles deposited on leaves. Further details on these issues can be obtained by comparing the element concentrations in leaves with those found in atmospheric PM₁₀ and river-water samples.

3.2. Comparison between Leaf Deposition and PM₁₀ Element Concentrations

To evaluate the potential of this biological approach, based on the evaluation of PM₁₀ deposition on *A. donax* leaves for the assessment of the impact of the PM₁₀ emission sources, we compared the elements superficial deposition on leaves (SD) with the spatially resolved atmospheric element concentrations detected in the PM₁₀.

From Figure 3, we can observe that, for most of the identified steel plant tracers (Cr, Fe, Ni, and Ti), the SD showed a similar trend to total concentrations in PM₁₀ (Figure 3). For these elements, the difference between unwashed and washed concentrations in *A. donax* leaves seems then to be reliably representative of their atmospheric concentrations. In the case of Mo, much poorer correlations between SD and PM₁₀ concentrations were found (Figure 3c). For this element, we also reported the comparison between PM₁₀ and washed leaves concentrations (Figure 3d), which showed a much higher correlation. In order to investigate the different behavior of Mo with respect to the other steel plant tracers, we considered the solubility and the morphological characteristics of particles emitted by the steel plant.

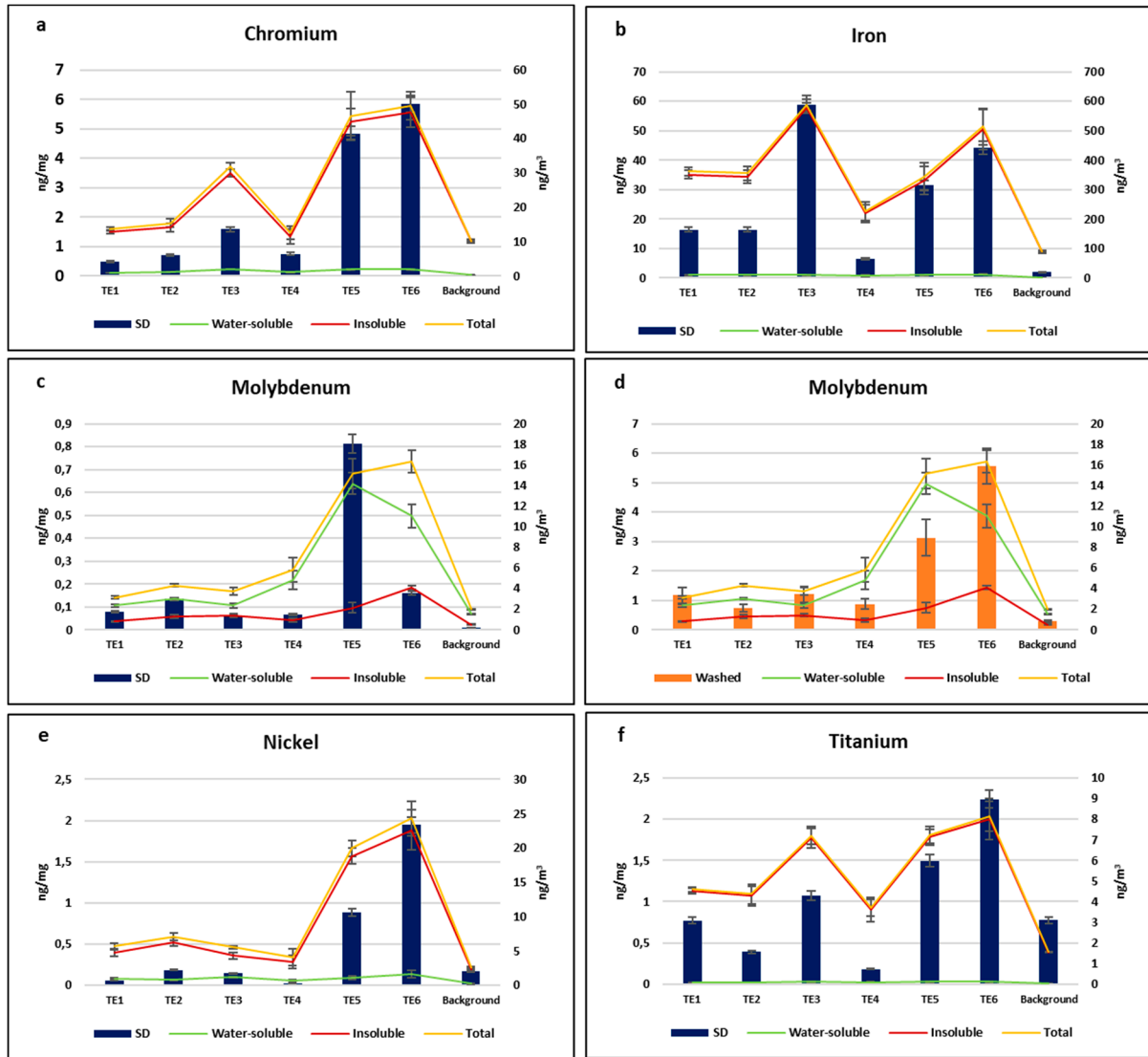


Figure 3. Comparison between averaged superficial deposition (SD) results (ng mg⁻¹) and concentrations in the water-soluble, insoluble, and total fraction of PM₁₀ (ng m⁻³) of (a) Cr, (b) Fe, (c) Mo, (e) Ni, and (f) Ti: comparison between averaged Mo concentrations in washed leaves (ng mg⁻¹) and in the water-soluble, insoluble, and total fraction of PM₁₀ (ng m⁻³) (d). Standard deviations calculated between monthly SD values, washed leaves, and PM₁₀ interpolated concentrations are reported.

Indeed, dimensions and morphological characteristics of airborne particles have proven to be able to influence the deposition of PM₁₀ on leaves and its interaction with leaf tissues [26,47,48]. For this reason, we carried out SEM analyses on PM₁₀ sampled on polycarbonate membranes through HSRS working near the steel plant (Figure 4).

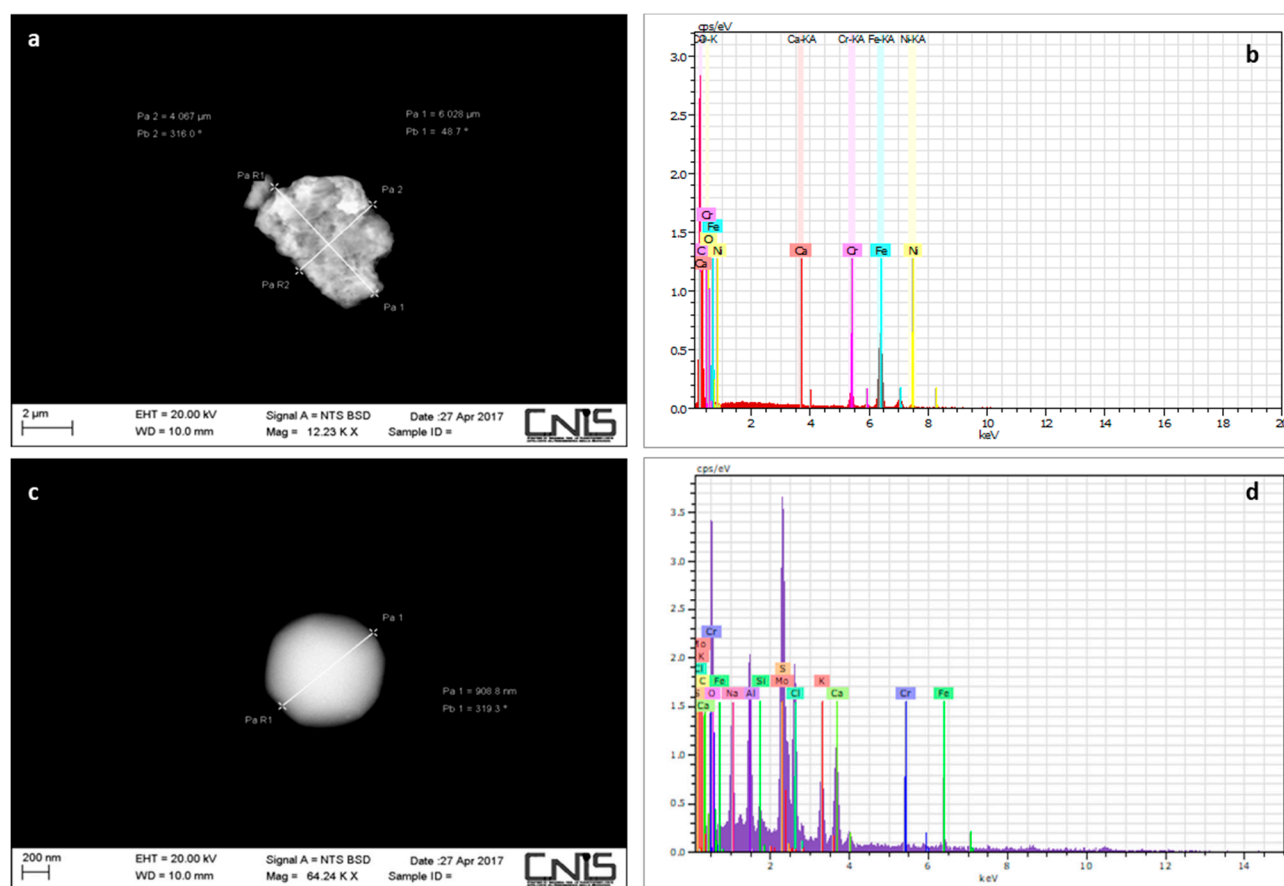


Figure 4. SEM micrograph (a) and respective EDX spectrum (b) of a steel particle (Cr, Fe, and Ni) sampled near the steel plant. SEM micrograph (c) and respective EDX spectrum (d) of a Mo particle sampled near the steel plant.

From Figure 4, we can observe the micrograph (Figure 4a) with the respective EDX spectrum (Figure 4b) of a particle containing the basic stainless-steel components: Cr, Ni, and Fe. This steel particle is coarse (up to 5 μm in diameter) and is characterized by an irregular, angular, and sharp morphology. The peculiar dimension and morphology of this and other analyzed coarse particles with the same chemical composition seems to be related to mechanical-abrasive emission processes. On the other hand, in Figure 4c, we can observe a fine particle (with diameter smaller than 1 μm) containing Mo and being spherical in shape, which is the typical morphology of airborne particles formed by high temperature processes [49,50]. Even though these two types of particles are emitted by the same emission source (steel plant), they appeared to be characterized by different dimension and morphology, revealing the presence of two different emission processes (high temperature and mechanical-abrasive processes). The different physical characteristics of these particles may be considered responsible for the different behavior observed in Figures 2 and 3. In particular, coarse particles containing Cr, Fe, and Ni seem to have been deposited on the leaf surfaces, making it easy to wash them off and to detect significant differences between washed and unwashed leaves. On the other hand, fine particles containing Mo could be more likely encapsulated into the wax layer or stomata pores situated on the leaf surface, making it more difficult to wash them out from the leaves [28,29]. This can result in the lowest difference between unwashed and washed leaves, detected for molybdenum concentrations. In Figure 3 we also reported water-soluble and -insoluble fractions of each element in PM₁₀. As it can be noted, Cr, Fe, Ni, and Ti are almost exclusively present as insoluble species, while Mo is mainly present in the water-soluble fraction. Besides the small dimensions of particles containing Mo, the different behavior observed for this element may be due to the higher solubility of species containing Mo that might be then directly absorbed by the leaf surface.

Table 2 reports Pearson's correlation coefficients (ρ) calculated between elements superficially deposited on leaves or bounded to leaf tissues (washed leaves) and their concentrations in the water-

soluble and -insoluble fractions of PM₁₀. In general, the highest positive correlations were found between concentrations in the insoluble fraction of PM₁₀ and SD of Cr, Fe, Ni, Mn, Ti, and Zn. Most of these elements (Cr, Ni, Fe, and Ti) are tracers of the steel plant; as already shown, particles containing these elements are mainly characterized by coarse dimensions. Mn is also well correlated to SD; this element is also known as a source tracer for steel-producing processes [51,52], but it is also used as tracer of non-combustive emissions from vehicular traffic [18,53]. This source produces particles scarcely soluble and belonging to the coarse dimensional fraction of PM as well [54]. It is then reasonable to hypothesize that coarse and insoluble particles are deposited on leaf surface and easily washed out during the leaf washing step. For this kind of PM contribution, the determination of SD may constitute a reliable biomonitoring procedure. In the case of Mo, as already pointed out, a good correlation was found between washed leaves and the soluble fraction of PM₁₀. Mo is present in PM₁₀ mainly as soluble species belonging to the fine fraction; these characteristics promote a stronger interaction with leaf structure, and washing procedure is not able to detach Mo-containing particles. A positive correlation was found also between washed leaves and insoluble Ni. In this regard, it is worth noting that fine particles containing Ni were also individuated through SEM analysis (Supplementary Material, Figure S1). These particles are probably released by the same high-temperature process but contain Ni as insoluble species. The correlation between washed leaves and Ni may indicate that the uptake into leaf tissues is mainly driven by physical interaction of small particles with wax layer and stomata pores. In particular, dimensions of *A. donax* stomata pores are reported to be $23.2 \pm 1.7 \mu\text{m}$ for length and $9.7 \pm 1.2 \mu\text{m}$ for width [55]. Even if particles encapsulation in leaf structures is reported to be a relevant mechanism for particles $\leq 10.6 \mu\text{m}$, this process results in being dominant especially for fine particles $\leq 2.6 \mu\text{m}$ [28,29]. Correlations between SD results and PM₁₀ element concentrations were much lower for all the other analyzed elements and tracers of other PM sources with emissions lower than that of the steel plant. For example, correlations were poor for water-soluble Cd, Cs, Rb, and Tl, which have been identified as reliable tracers for biomass burning in the Terni basin [56,57] and as weak for insoluble Cu and Sn, which are well known as rail network and vehicular traffic tracers [11,31,58,59]. SD of atmospheric elements can be then considered reliable only for the evaluation of the impact of strong PM sources (steel plant and vehicular traffic).

3.3. Comparison between River Water Samples and *A. donax* Leaves Elemental Content

To evaluate the potential influence of river-water pollutants on the elemental composition of leaves, where heavy metals adsorbed by roots can be stored and transferred [60,61], we analyzed the element concentrations of water samples (Figure 1). Since metals adsorbed by roots are expected to be included in leaf tissues, element concentrations in river water were compared with the element concentrations in washed leaves (Figure 5). It is worth underlining that some of the analyzed elements are known to be micronutrients for this riparian species. In this context, low concentrations of Cu are known to be relevant for plant growth and development, while Mn and Zn are connected to enzymatic processes, playing essential metabolic roles [8,62,63].

The steel plant tracers (Cr, Fe, Mo, Ni, and Ti), previously individuated for PM₁₀, showed their maximum concentrations in the river water samples collected at TE5 (Figure 5). On the contrary, high concentrations were not found at TE6, where high concentrations in *A. donax* washed leaves were found instead. Indeed, wastewater systems for the treatment of the effluents from cold and hot rolling sections of the steel plant are located in the southern part of the steel industry plant, at close proximity to TE5 [64]. We can thus hypothesize that the higher concentrations of Cr, Fe, Mo, Ni, and Ti at TE5 water samples are related to local disposal of steel plant wastewater in the Nera river. Due to the heavy metal hyper-accumulation ability of this riparian species [65,66], high concentrations of these steel plant tracers in washed leaves may be then due to the influence of river-water contamination. The very relevant differences at TE6 (still strongly affected by emissions from the steel plant) underlined the lower reliability of leaves for the evaluation of the river heavy-metal contamination.

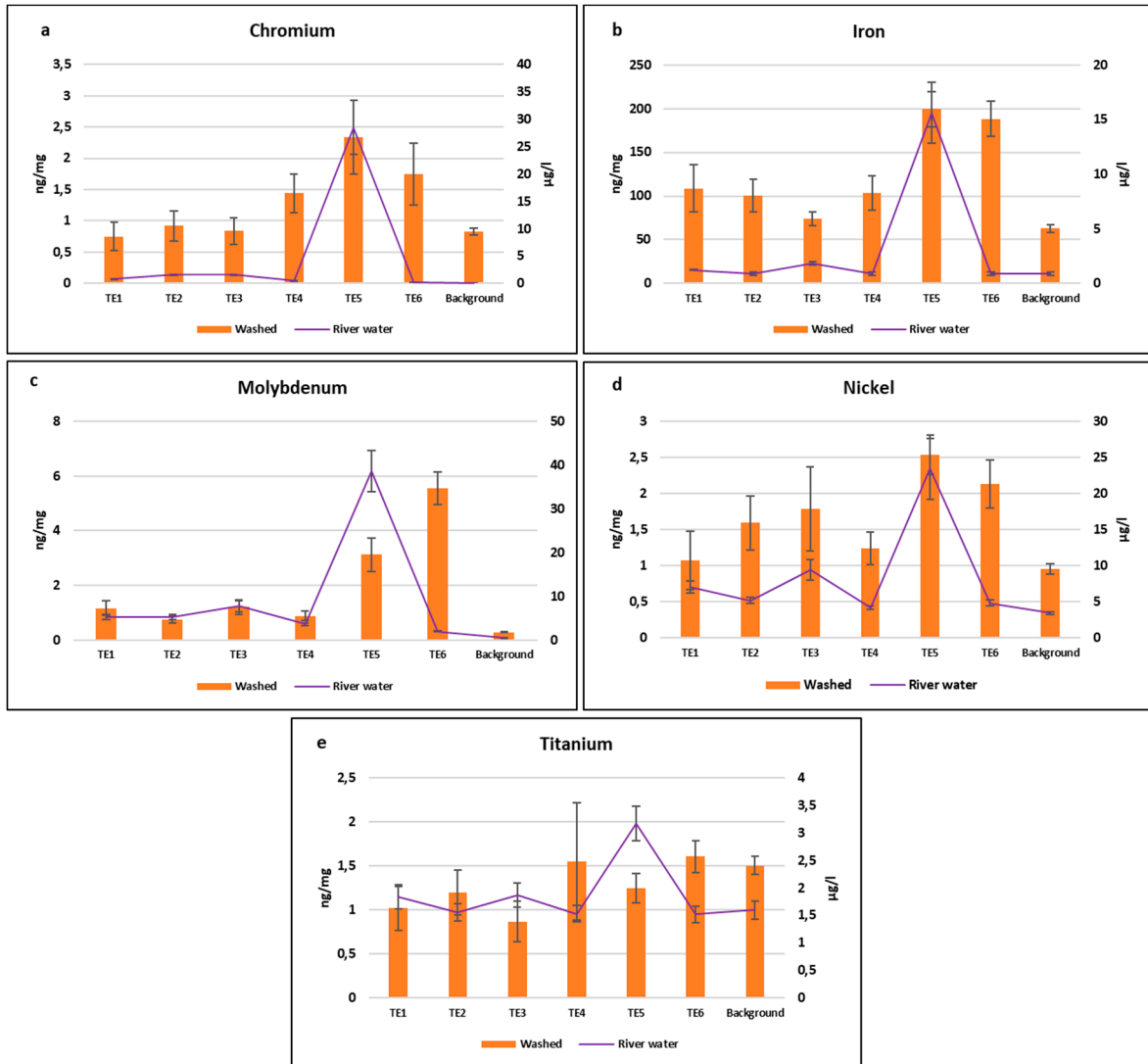


Figure 5. Comparison between averaged concentrations of Cr, Mo, and Ni detected in river water samples ($\mu\text{g L}^{-1}$) and *A. donax* washed leaves (ng mg^{-1}): Standard deviations calculated between monthly concentrations are reported.

We also calculated Pearson’s correlation coefficients between element concentrations detected in river-water samples and washed leaves (Table 3). Correlations were in general much lower than those related to PM_{10} concentrations. The highest correlation between these two datasets was found for Cd; this result could be explained by considering the hyper-accumulation and translocation abilities of *A. donax* toward Cd [67]. However, in this set of measurements, Cd showed a low variability in both river water and washed leaves (Supplementary Material S2; Table S2.2,3), and this is reasonably the main reason for the significant correlation found. Then, the use of this riparian species seems to have a low reliability for the evaluation of the concentration in the river water.

Table 2. Pearson's correlation coefficients calculated between SD and washed leaves element concentrations and their concentrations in the water-soluble and -insoluble fractions of PM₁₀: Mean monthly concentrations at each site were included in the elaboration (N=30). Positive linear correlations (Pearson's coefficient>0.8) between the two variables are reported in red.

Pearson's	Ba	Cd	Cr	Cs	Cu	Fe	Li	Mn	Mo	Ni	Pb	Rb	Sb	Sn	Sr	Ti
SD/Water soluble PM₁₀	-0,06	0,31	0,74	0,31	-0,39	0,49	0,62	0,77	0,78	0,77	0,21	0,00	-0,65	0,34	-0,56	0,79
SD/Insoluble PM₁₀	-0,12	0,22	0,87	0,38	-0,08	0,93	0,25	0,92	0,16	0,95	-0,79	0,12	-0,74	0,53	-0,62	0,93
Washed leaves/Water soluble PM₁₀	0,01	0,18	0,49	0,10	0,08	0,31	0,67	0,73	0,90	0,63	0,02	0,51	0,45	-0,43	0,19	0,17
Washed leaves/Insoluble PM₁₀	-0,59	0,24	0,59	-0,14	0,18	0,02	-0,03	0,75	0,35	0,82	0,55	-0,08	0,43	-0,66	0,21	0,01

Table 3. Pearson's correlation coefficients calculated between river water and washed leaves element concentrations: Mean monthly concentrations at each site were included in the elaboration (N=30). Positive linear correlations (Pearson's coefficient>0.8) between the two variables are reported in red.

Pearson's	Ba	Cd	Cr	Cs	Cu	Fe	Li	Mn	Mo	Ni	Pb	Rb	Sb	Sn	Sr	Ti
Washed leaves/ River Water	0,38	0,81	0,76	0,18	0,34	0,53	-0,20	-0,55	0,17	0,71	-0,10	-0,35	0,06	-0,20	-0,44	-0,23

4. Conclusions

For the first time, in this study, we were able to compare the different influence of PM₁₀ atmospheric pollution and river contamination acting in parallel in the study area of Terni on the elemental content of *A. donax* leaves.

Thanks to the availability of newly developed PM₁₀ samplers (HSRS), spatially resolved element concentrations were detected in PM₁₀ samples and compared to SD results. This was helpful to evaluate the reliability of this biomonitoring approach, based on the utilization of leaves and the chemical characterization of leaf deposited PM, for the evaluation of atmospheric element concentrations. The good correlations between SD results and atmospheric PM₁₀ concentrations of Cr, Fe, Ni, Mn, Zn, and Ti confirmed the reliability of these results for the evaluation of the impact related to intense local emission sources.

On the other hand, in our study, washed leaves and river-water element concentrations were poorly correlated, underlying a lower efficiency of this biological approach for the evaluation of the river contamination.

These preliminary results encourage further investigations on the utilization of this riparian species, largely distributed in urban areas of Italy, for future studies on PM leaf deposition. It also encourages its application as a low-cost alternative for the monitoring of atmospheric PM and its elemental components.

Supplementary Materials: The following are available online at www.mdpi.com/2073-4433/11/3/226/s1, Table S1.1: limits of detection (LODs) of the concentrations (µg/L) detected in river water samples of the analyzed elements, set at 3 times the standard deviation (SD) of 10 replicate blank determinations, Table S1.2: limits of detection (LODs) of the concentrations (µg/L) detected in PM₁₀ samples, of the water-soluble and insoluble fraction of the analyzed elements, set at 3 times the standard deviation (SD) of 10 replicate blank determinations, Table S1.3: limits of detection (LODs) of the concentrations (µg/L) detected in washed and unwashed *A. donax* leaves of the analyzed elements, set at 3 times the standard deviation (SD) of 10 replicate blank determinations, Table S2.1: mean values and standard deviations calculated between monthly values of element concentrations detected in unwashed *A. donax* leaves at the six monitoring sites, Table S2.2: mean values and standard deviations calculated between monthly values of element concentrations detected in washed *A. donax* leaves at the 6 monitoring sites, Table S2.3: mean values and standard deviations calculated between monthly values of element concentrations detected in river water samples at the six monitoring sites, Table S2.4: mean values and standard deviations calculated between monthly values of interpolated concentrations of water-soluble fraction of PM₁₀ elements at the six monitoring sites, Table S2.5: mean values and standard deviations calculated between monthly values of interpolated concentrations of insoluble fraction of PM₁₀ elements at the six monitoring sites, Table S2.6: mean values and standard deviations calculated between monthly values of interpolated concentrations of the total fraction of PM₁₀ elements at the six monitoring sites, Table S3: Certified values for the SRM 1515 (apple leaves) used and accuracy obtained by SRM (ng mg⁻¹). Figure S1: SEM micrograph (a) and respective EDX spectrum (b) of a steel particle (Fe, Ni and Cu) sampled near the steel plant.

Author Contributions: All authors have read and agree to the published version of the manuscript. Conceptualization, M.R. and L.M.; data curation, M.R. and L.M.; formal analysis, M.R., M.L. A., M.A. F. and L.M.; funding acquisition, S.C. and L.M.; investigation, M.R. and L.M.; methodology, M.R. and L.M.; project administration, S.C. and L.M.; resources, S.C. and L.M.; software, M.R. and L.M.; supervision, S.C. and L.M.; validation, M.R. and L.M.; visualization, M.R., S.C. and L.M.; writing – original draft, M.R. and L.M.; writing – review & editing, S.C. and L.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Sapienza University of Rome; grant 2017 RG11715C7C8801CF, Principal Investigator Dr. S. Canepari; grant 2018 AR1181641E22B570, Principal Investigator Dr. L. Massimi. The APC was funded by Sapienza University of Rome.

Acknowledgments: The authors gratefully thank FAI Instruments (Fonte Nuova, Rome, Italy), the citizens of Terni, and the Terni district of ARPA Umbria (regional agency for environmental protection), with special regard to Giancarlo Caiello, Caterina Austeri, and Marco Pompei for the support in the installation and management of the sampling equipment as well as for the help in the choice of the sampling sites and to Iqra Javed for providing language help.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Perdue, R.E. Arundo donax—Source of musical reeds and industrial cellulose. *Econ. Bot.* **1958**, *12*, 368, doi:10.1007/BF02860024.
2. Bell, G.P. Ecology and management of Arundo donax, and approaches to riparian habitat restoration in Southern California. In *Plant Invasions: Studies from North America and Europe*; Backhuys Publishers: Leiden, The Netherlands, 1997; pp. 103–113.
3. Papazoglou, E.G.; Karantounias, G.A.; Vemmos, S.N.; Bouranis, D.L. Photosynthesis and growth responses of giant reed (Arundo donax L.) to the heavy metals Cd and Ni. *Environ. Int.* **2005**, *31*, 243–249, doi:10.1016/j.envint.2004.09.022.
4. Nsanganwimana, F.; Marchand, L.; Douay, F.; Mench, M. Arundo donax L., a candidate for phytomanaging water and soils contaminated by trace elements and producing plant-based feedstock. A review. *Int. J. Phytoremediation* **2014**, *16*, 982–1017, doi:10.1080/15226514.2013.810580.
5. Bonanno, G. Comparative performance of trace element bioaccumulation and biomonitoring in the plant species Typha domingensis, Phragmites australis and Arundo donax. *Ecotoxicol. Environ. Saf.* **2013**, *97*, 124–130, doi:10.1016/j.ecoenv.2013.07.017.
6. Bonanno, G.; Borg, J.A.; Di Martino, V. Levels of heavy metals in wetland and marine vascular plants and their biomonitoring potential: A comparative assessment. *Sci. Total Environ.* **2017**, *576*, 796–806, doi:10.1016/j.scitotenv.2016.10.171.
7. Fiorentino, N.; Ventrino, V.; Rocco, C.; Cenvinzo, V.; Agrelli, D.; Gioia, L.; Di Mola, L.; Adamo, P.; Pepe, O.; Fagnano, M. Giant reed growth and effects on soil biological fertility in assisted phytoremediation of an industrial polluted soil. *Sci. Total Environ.* **2017**, *575*, 1375–1383, doi:10.1016/j.scitotenv.2016.09.220.
8. Bonanno, G. Arundo donax as a potential biomonitor of trace element contamination in water and sediment. *Ecotoxicol. Environ. Saf.* **2012**, *80*, 20–27, doi:10.1016/j.ecoenv.2012.02.005.
9. Szczepaniak, K.; Biziuk, M. Review: Ecotoxicology, Aspects of the biomonitoring studies using mosses and lichens as indicators of metal pollution. *Environ. Res.* **2003**, *93*, 221–230, doi:10.1016/S0013-9351(03)00141-5.
10. Abril, G.A.; Wannaz, E.D.; Mateos, A.C.; Pignata, M.L. Biomonitoring of airborne particulate matter emitted from a cement plant and comparison with dispersion modelling results. *Atmos. Environ.* **2014**, *8*, 154–163, doi:10.1016/j.atmosenv.2013.10.020.
11. Massimi, L.; Conti, M.E.; Mele, G.; Ristorini, M.; Astolfi, M.L.; Canepari, S. Lichen Transplants as Indicators of Atmospheric Element Concentrations: A High Spatial Resolution Comparison with PM10 Samples in a Polluted Area (Central Italy). *Ecol. Indic.* **2019**, *101*, 759–769, doi:10.1016/j.ecolind.2018.12.051.
12. Ubat, M.; Lehndorff, E.; Schwark, L. Biomonitoring of air quality in the Cologne conurbation using pine needles as a passive sampler—Part I: Magnetic properties. *Atmos. Environ.* **2004**, *38*, 3781–3792, doi:10.1016/j.atmosenv.2004.03.061.
13. Lin, V.S. Research highlights: Natural passive samplers—plants as biomonitors. *Environ. Sci. Process. Impacts* **2015**, *17*, 1137–1140, doi:10.1039/C5EM90016F.
14. Sgrigna, G.; Baldacchini, C.; Esposito, R.; Calandrelli, R.; Tiwary, A.; Calfapietra, C. Characterization of leaf-level particulate matter for an industrial city using electron microscopy and X-ray microanalysis. *Sci. Total Environ.* **2016**, *548–549*, 91–99, doi:10.1016/j.scitotenv.2016.01.057.
15. Janhall, S. Review on urban vegetation and particle air pollution e Deposition and dispersion. *Atmos. Environ.* **2015**, *105*, 130–137, doi:10.1016/j.atmosenv.2015.01.052.
16. Gratani, L.; Crescente, M.F.; Varone, L. Long-term monitoring of metal pollution by urban trees. *Atmos. Environ.* **2008**, *42*, 8273–8277, doi:10.1016/j.atmosenv.2008.07.032.
17. Baldacchini, C.; Sgrigna, G.; Clarke, W.; Tallis, M.; Calfapietra, C. An ultra-spatially resolved method to quali-quantitative monitor particulate matter in urban environment. *Environ. Sci. Pollut. Res. Int.* **2019**, *26*, 18719–18729, doi:10.1007/s11356-019-05160-8.
18. Thorpe, A.; Harrison, R.M. Sources and properties of non-exhaust particulate matter from road traffic: A review. *Sci. Total Environ.* **2008**, *400*, 270–282, doi:10.1016/j.scitotenv.2008.06.007.
19. Slezakova, K.; Pires, J.C.M.; Pereira, M.C.; Martins, F.G.; Alvim-Ferraz, M.C. Influence of traffic emissions on the composition of atmospheric particles of different sizes—Part 2: SEM–EDS characterization. *J. Atmos. Chem.* **2008**, *60*, 221–236, doi:10.1007/s10874-008-9117-y.
20. Pope, C.A., III; Burnett, R.T.; Thun, M.J.; Calle, E.E.; Krewski, D.; Ito, K.; Thurston, G.D. Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution. *Jama* **2002**, *287*, 1132–1141.

21. Ebel, S.T.; Petkau, A.J.; Vedal, S.; Fisher, T.V.; Brauer, M. Exposure of chronic obstructive pulmonary disease patients to particulate matter: Relationships between personal and ambient air concentrations. *J. Air Waste Manag. Assoc.* **2000**, *50*, 1081–1094.
22. Chen, L.C.; Lippmann, M. Effects of Metals within Ambient Air Particulate Matter (PM) on Human Health. *Inhal. Toxicol.* **2009**, *21*, 1–31, doi:10.1080/08958370802105405.
23. Anderson, J.O.; Thundiyil, J.G.; Stolbach, A. Clearing the Air: A Review of the Effects of Particulate Matter Air Pollution on Human Health. *J. Med. Toxicol.* **2012**, *8*, 166–175, doi:10.1007/s13181-011-0203-1.
24. Pope, C.A., III; Dockery, D.W. Acute Health Effects of PM10 Pollution on Symptomatic and Asymptomatic Children. *AJRCCM Issues* **1992**, *145*, doi:10.1164/ajrccm/145.5.1123.
25. Donaldson, K.; MacNee, W. Potential mechanisms of adverse pulmonary and cardiovascular effects of particulate air pollution (PM10). *Int. J. Hyg. Environ. Health* **2010**, *203*, 411–415, doi:10.1078/1438-4639-00059.
26. Sæbø, A.; Popek, R.; Nawrot, B.; Hanslin, H.M.; Gawronska, H.; Gawronski, S.W. Plant species differences in particulate matter accumulation on leaf surfaces. *Sci. Total Environ.* **2012**, *427–428*, 347–354, doi:10.1016/j.scitotenv.2012.03.084.
27. Petroff, A.; Mailliat, A.; Amielh, M.; Anselmet, F. Aerosol dry deposition on vegetative canopies. Part I: Review of present knowledge. *Atmos. Environ.* **2008**, *42*, 3625–3653, doi:10.1016/j.atmosenv.2007.09.043.
28. Terzaghi, E.; Wild, E.; Zacchello, G.; Cerabolini, B.E.L.; Jones, K.C.; Di Guardo, A. Forest Filter Effect: Role of leaves in capturing/releasing air particulate matter and its associated PAHs. *Atmos. Environ.* **2013**, *74*, 378–384, doi:10.1016/j.atmosenv.2013.04.013.
29. Hofman, J.; Wuyts, K.; Van Wittenberghe, S.; Brackx, M.; Samson, R. On the link between biomagnetic monitoring and leaf-deposited dust load of urban trees: Relationships and spatial variability of different particle size fractions. *Environ. Pollut.* **2014**, *189*, 63–72, doi:10.1016/j.envpol.2014.02.020.
30. Sgrigna, G.; Sæbø, A.; Gawronski, S.; Popek, R.; Calfapietra, C. Particulate matter deposition on Quercus ilex leaves in an industrial city of central Italy. *Environ. Pollut.* **2015**, *197*, 187–194, doi:10.1016/j.envpol.2014.11.030.
31. Massimi, L.; Ristorini, M.; Eusebio, M.; Florendo, D.; Adeyemo, A.; Brugnoli, D.; Canepari, S. Monitoring and evaluation of Terni (Central Italy) air quality through spatially resolved analyses. *Atmosphere* **2017**, *8*, 200, doi:10.3390/atmos8100200.
32. Moroni, B.; Ferrero, L.; Crocchianti, S.; Perrone, M.G.; Sangiorgi, G.; Bolzacchini, E.; Cappelletti, D. Aerosol dynamics upon Terni basin (Central Italy): Results of integrated vertical profile measurements and electron microscopy analyses. *Rend. Lincei* **2013**, *24*, 319–328, doi:10.1007/s12210-013-0230-8.
33. Manigrasso, M.; Protano, C.; Astolfi, M.L.; Massimi, L.; Avino, P.; Vitali, M.; Canepari, S. Evidences of copper nanoparticle exposure in indoor environments: Long-term assessment, high-resolution field emission scanning electron microscopy evaluation, in silico respiratory dosimetry study and possible health implications. *Sci. Total Environ.* **2017**, *653*, 1192–1203, doi:10.1016/j.scitotenv.2018.11.044.
34. Zona, A.; Pasetto, R.; Fazzo, L.; Iavarone, I.; Bruno, C.; Pirastu, R.; Comba, P. Fifth report S.E.N.T.I.E.R.I. 2019, Epidemiologia & Prevenzione, Rivista dell'Associazione Italiana di Epidemiologia 2-3, 43, Supplement 1. Available online: http://www.epiprev.it/materiali/2019/EP2-3_Suppl1/SENTIERI_FullText.pdf (accessed on 07 January 2020).
35. Available online: <https://www.arpa.umbria.it/monitoraggi/aria/Default.aspx> (accessed on 07 January 2020).
36. APHA. *Standard Methods for Examination of Water and Waste Water*, 20th ed.; American Public Health Association: Washington, DC, USA, 1998.
37. Canepari, S.; Cardarelli, E.; Giuliano, A.; Pietrodangelo, A. Determination of metals, metalloids and non-volatile ions in airborne particulate matter by a new two-step sequential leaching procedure Part A: Experimental design and optimization. *Talanta* **2006**, *69*, 581–587, doi:10.1016/j.talanta.2005.10.023.
38. Canepari, S.; Cardarelli, E.; Pietrodangelo, A.; Strincone, M. Determination of metals, metalloids and non-volatile ions in airborne particulate matter by a new two-step sequential leaching procedure Part B: Validation on equivalent real samples. *Talanta* **2006**, *69*, 588–595, doi:10.1016/j.talanta.2005.10.024.
39. Canepari, S.; Pietrodangelo, A.; Perrino, C.; Astolfi, M.L.; Marzo, M.L. Enhancement of source traceability of atmospheric PM by elemental chemical fractionation. *Atmos. Environ.* **2009**, *43*, 4754–4765, doi:10.1016/j.atmosenv.2008.09.059.

40. Piacentini, D.; Falasca, G.; Canepari, S.; Massimi, L. Potential of PM-selected components to induce oxidative stress and root system alteration in a plant model organism. *Environ. Int.* **2019**, *132*, 105094, doi:10.1016/j.envint.2019.105094.
41. Astolfi, M.L.; Marconi, E.; Protano, C.; Vitali, M.; Schiavi, E.; Mastromarino, P.; Canepari, S. Optimization and validation of a fast digestion method for the determination of major and trace elements in breast milk by ICP-MS. *Anal. Chim. Acta* **2018**, *1040*, 49–62, doi:10.1016/j.aca.2018.07.037.
42. Cressie, N. Spatial Prediction and Ordinary Kriging. *Math. Geol.* **1988**, *20*, 405–421, doi:10.1007/BF00892986.
43. Cressie, N. The origins of kriging. *Math. Geol.* **1990**, *22*, 239–252, doi:10.1007/BF00889887.
44. Blair, M.; Stevens, T.L. *Steel Castings Handbook*, 6th ed.; Steel Founders' Society and ASM International: Novelty, OH, USA, 1995; pp. 2–34.
45. Adachi, K.; Tainosho, Y. Characterization of heavy metal particles embedded in tire dust. *Environ. Int.* **2004**, *30*, 1009–1017, doi:10.1016/j.envint.2004.04.004.
46. Birmili, W.; Allen, A.G.; Bary, F.; Harrison, R.M. Trace Metal Concentrations and Water Solubility in Size-Fractionated Atmospheric Particles and Influence of Road Traffic. *Environ. Sci. Technol.* **2006**, *40*, 1144–1153, doi:10.1021/es0486925.
47. Litschke, T.; Kuttler, W. On the reduction of urban particle concentration by vegetation—A review. *Meteorol. Z.* **2008**, *17*, 229–240, doi:10.1127/0941-2948/2008/0284.
48. Morakinyo, T.E.; Lam, Y.F. Simulation study of dispersion and removal of particulate matter from traffic by road-side vegetation barrier. *Environ. Sci. Pollut. Res.* **2016**, *23*, 6709–6722, doi:10.1007/s11356-015-5839-y.
49. Umbria, A.; Galan, M.; Munoz, M.J.; Martin, R. Characterization of atmospheric particles: Analysis of particles in the Campo de Gibraltar. *Atmosfera* **2004**, *17*, 191–206.
50. Bouhsina, S.; Cazier, F.; Noual, H.; Dewaele, D.; Delbende, A.; Courcot, D.; Aboukais, A. Characteristics of suspended particulate matter emitted from an iron and steel company—A multi technique approach for search of tracers. *Chem. Eng. Trans.* **2008**, *16*, 79.
51. Tunno, B.J.; Dalton, R.; Michanowicz, D.R.; Shmool, J.L.C.; Kinnee, E.; Tripathy, S.; Cambal, L.; Clougherty, J.E. Spatial patterning in PM_{2.5} constituents under an inversion-focused sampling design across an urban area of complex terrain. *J. Expo. Sci. Environ. Epidemiol.* **2016**, *26*, 385–396, doi:10.1038/jes.2015.59.
52. Thurston, G.D.; Ito, K.; Lall, R. A source apportionment of U.S. fine particulate matter air pollution. *Atmos. Environ.* **2011**, *45*, 3924–3936, doi:10.1016/j.atmosenv.2011.04.070.
53. Song, F.; Gao, Y. Size distributions of trace elements associated with ambient particular matter in the affinity of a major highway in the New Jersey–New York metropolitan area. *Atmos. Environ.* **2011**, *45*, 6714–6723, doi:10.1016/j.atmosenv.2011.08.031.
54. Canepari, S.; Perrino, C.; Olivieri, F.; Astolfi, M.L. Characterisation of the traffic sources of PM through size-segregated sampling, sequential leaching and ICP analysis. *Atmos. Environ.* **2008**, *42*, 8161–8175, doi:10.1016/j.atmosenv.2008.07.052.
55. Shakoor, S.A.; Soodan, A.M.; Kumar, K. Morphological Diversity and Frequency of Phytolith Types in Gaint Reed *Arundo donax* (L.). *World Appl. Sci. J.* **2014**, *29*, 926–932, doi:10.5829/idosi.wasj.2014.29.07.14.
56. Simonetti, G.; Buiarelli, F.; Di Filippo, P.; Pomata, D.; Riccardi, C.; Ristorini, M.; Astolfi, M.L.; Canepari, S. Spatial Distribution of Levoglucosan and Alternative Biomass Burning Tracers in an Urban and Industrial Hot-spot of Central Italy. *Atmos. Res.* **2020**, *239*, 104904.
57. Minguillón, M.C.; Querol, X.; Baltensperger, U.; Prévôt, A.S.H. Fine and coarse PM composition and sources in rural and urban sites in Switzerland: Local or regional pollution? *Sci. Total Environ.* **2012**, *427–428*, 191–202, doi:10.1016/j.scitotenv.2012.04.030.
58. Gietl, J.K.; Lawrence, L.; Thorpe, A.J.; Harrison, R.M. Identification of brake wear particles and derivation of a quantitative tracer for brake dust at a major road. *Atmos. Environ.* **2010**, *44*, 141–146, doi:10.1016/j.atmosenv.2009.10.016.
59. Dongarrà, G.; Manno, E.; Varrica, D. Possible markers of traffic-related emissions. *Environ. Monit. Assess.* **2008**, *154*, 117, doi:10.1007/s10661-008-0382-7.
60. Mirza, N.; Pervez, A.; Mahmood, Q.; Shah, M.M.; Shafqat, M.N. Ecological restoration of arsenic contaminated soil by *Arundo donax* L. *Ecol. Eng.* **2011**, *37*, 1949–1956, doi:10.1016/j.ecoleng.2011.07.006.
61. Barbosa, B.; Boléo, S.; Sidella, S.; Costa, J.; Duarte, M.; Mendes, B.; Cosentino, S.L.; Fernando, A.L. Phytoremediation of Heavy Metal-Contaminated Soils Using the Perennial Energy Crops *Miscanthus* spp. and *Arundo donax* L. *Bioenerg. Res.* **2015**, *8*, 1500–1511, doi:10.1007/s12155-015-9688-9.

62. Carranza-Álvarez, C.; Alonso-Castro, A.J.; Alfaro-De La Torre, M.C.; García-De La Cruz, R.F. Accumulation and Distribution of Heavy Metals in *Scirpus americanus* and *Typha latifolia* from an Artificial Lagoon in San Luis Potosí, México. *Water Air Soil Pollut.* **2007**, *188*, 297–309, doi:10.1007/s11270-007-9545-3.
63. Kabata-Pendias, A.; Mukherjee, A.B. *Trace Elements from Soil to Human*; Springer: Cham, Switzerland, 2007; ISBN 978-3-540-32714-1.
64. Capelli, L.; Sironi, S.; Del Rosso, R.; Céntola, P.; Rossi, A.; Austeri, C. Olfactometric approach for the evaluation of citizens' exposure to industrial emissions in the city of Terni, Italy. *Sci. Total Environ.* **2011**, *409*, 595–603, doi:10.1016/j.scitotenv.2010.10.054.
65. Sabeen, M.; Mahmood, Q.; Irshad, M.; Fareed, I.; Khan, A.; Ullah, F.; Hussain, J.; Hayat, Y.; Tabassum, S. Cadmium Phytoremediation by *Arundo donax* L. from Contaminated Soil and Water. *BioMed. Res. Int.* **2013**, doi:10.1155/2013/324830.
66. Atma, W.; Larouci, M.; Meddah, B.; Benabdeli, K.; Sonnet, P. Evaluation of the phytoremediation potential of *Arundo donax* L. for nickel-contaminated soil. *Int. J. Phytoremediat.* **2017**, *19*, 377–386, doi:10.1080/15226514.2016.1225291.
67. Fiorentino, N.; Fagnano, M.; Adamo, P.; Impagliazzo, A.; Mori, M.; Pepe, O.; Ventorino, V.; Zoina, A. Assisted phytoextraction of heavy metals: Compost and *Trichoderma* effects on giant reed (*Arundo donax* L.) uptake and soil N-cycle microflora. *Italian J. Agron.* **2013**, *8*, 244–254, doi:10.4081/ija.2013.e29.



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).