

Article

Atmospheric Deposition around the Industrial Areas of Milazzo and Priolo Gargallo (Sicily–Italy)—Part B: Trace Elements

Filippo Brugnone ^{1,*}, Walter D'Alessandro ², Francesco Parello ¹, Lorenzo Brusca ², Filippo Saiano ³, Lorenza Li Vigni ¹, Mario Sprovieri ⁴ and Sergio Calabrese ^{1,2,*}

¹ Dipartimento di Scienze della Terra e del Mare, Università degli Studi di Palermo, Via Archirafi, 36, 90123 Palermo, Italy

² Istituto Nazionale di Geofisica e Vulcanologia, Section of Palermo Via Ugo la Malfa, 153, 90146 Palermo, Italy

³ Dipartimento di Scienze Agrarie, Alimentari e Forestali, Università degli Studi di Palermo, Viale delle Scienze ed.4, 90128 Palermo, Italy

⁴ Istituto per lo Studio degli Impatti Antropici e Sostenibilità in Ambiente Marino, Consiglio Nazionale delle Ricerche (IAS—CNR), Capo Granitola, Via del Mare, 3, 91021 Campobello di Mazara, Italy

* Correspondence: filippo.brugnone@unipa.it (F.B.); sergio.calabrese@unipa.it (S.C.)

Abstract: The concentrations of trace elements in atmospheric bulk depositions (wet plus dry) were investigated from two highly industrialised areas of Sicily (southern Italy) from June 2018 to July 2019, in order to recognise the main natural and anthropogenic sources. A side objective of this study was to improve the common sampling procedures and analytical methods used for monitoring trace elements in atmospheric deposition. The trace element VWM (Volume-Weighted Mean) concentrations ranged from less than 0.01 $\mu\text{g L}^{-1}$ for trace elements such as Cs, Tl, and U, up to 24 $\mu\text{g L}^{-1}$ for minor elements (Al, Zn, Sr), in the filtered aliquot, while they reached concentrations up to 144 $\mu\text{g L}^{-1}$ for the same elements, in the unfiltered aliquot. Therefore, significant differences in concentrations between these two aliquots were found, particularly for Al, Fe, Ti, Zn, Cr, Pb, Se, Cs, and U. This implies that filtering operations may produce a consistent underestimation of concentrations of certain ‘constituents’ of the atmospheric deposition. Natural (marine spray, local and regional geogenic input, volcanic emanations) and anthropogenic sources (industrial emissions, auto vehicular traffic, and diffuse background pollution) which influence rainwater chemistry were identified. Enrichment factors (EFs), with respect to the upper crust composition, provided clear evidence of the different sources above mentioned: Ti, Fe, Al, Cs, Cr, Rb, and Co have low EFs (<1), and are referable to the (local and/or regional) geogenic input, while Se, Sb, Zn, B, Cd, Cu, Mo, Sr, As, with high EFs (>10), highlight the influence of marine and/or industrial sources. The study produced a novel dataset on the atmospheric deposition rate of several trace elements, which had never been studied in the investigated areas. Finally, a comparison of trace element deposition rates in the studied areas with the atmospheric deposition reported for 53 different sites, belonging to 20 different European nations, was made. The comparison showed that some elements, such as Al, V, Zn, and Mo had higher median deposition fluxes in the Sicilian sites than in European monitoring sites.

Keywords: atmospheric deposition; rainwater; industrial pollution; trace elements; anthropogenic contribution



Citation: Brugnone, F.; D'Alessandro, W.; Parello, F.; Brusca, L.; Saiano, F.; Li Vigni, L.; Sprovieri, M.; Calabrese, S. Atmospheric Deposition around the Industrial Areas of Milazzo and Priolo Gargallo (Sicily–Italy)—Part B: Trace Elements. *Atmosphere* **2023**, *14*, 737. <https://doi.org/10.3390/atmos14040737>

Academic Editors: Xuejun Liu and Giacomo Alessandro Gerosa

Received: 21 February 2023

Revised: 17 March 2023

Accepted: 17 April 2023

Published: 19 April 2023



Copyright: © 2023 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 (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Studies on trace elements composition of atmospheric precipitation are an important tool for the environmental monitoring of pollution—not only of the atmosphere but also of soils and water resources. Considering the widespread and persistent sources of anthropogenic pollution on a planetary scale, their impact on air quality, and, consequently, on human health, studies on atmospheric deposition have fundamental importance. Indeed, an increasing number of studies have been made in this field regarding areas with a high rate of urbanisation and industrialisation, such as India, China, Japan, the USA,

Europe, and West Asia [1–7]. For more than two decades, several international agencies monitored environmental pollution levels through the study of concentrations and deposition fluxes of certain pollutants, assessing their long-range transboundary transport, and providing guidelines and protocols for proper monitoring; these include, for example, the Co-operative Program for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants (EMEP) for European countries, the Ministry of Environmental Protection (MEP) in China, the Japan Center for a Sustainable Environment and Society (JACSSES) in Japan, and the National Atmospheric Deposition Program (NADP), which is the organization overseeing the long-term sampling and analysis of precipitation across the United States.

Atmospheric deposition occurs through three main mechanisms: wet, dry, and occult deposition [8,9]. The ensemble of the three forms of deposition is defined as bulk deposition. Rainfall plays an important role in removing particles and soluble gaseous pollutants from the atmosphere through scavenging mechanisms [1,2]: rainout is the in-cloud scavenging process which mainly absorbs or dissolves gases and fine particles within cloud droplets and washout is the below-cloud scavenging, which is an efficient process to remove coarse particles [3,10]. The scavenging process in the cloud removes more than 70% of aerosol particles in number and more than 99% in mass [11] and is related to the activation of cloud condensation nuclei (CCN). The washout process occurs during the fall of raindrops from the base of the clouds to the ground. Weak precipitations, having less than 0.1 mm h^{-1} intensity, can remove 50–80% of the below-cloud aerosol, in both number and mass, within a few hours [4,11,12]. This process can change the chemical composition of the rainwaters due to the interaction between the raindrops and the suspended atmospheric particles. Dry deposition occurs through various mechanisms, such as turbulent diffusion, sedimentation, Brownian diffusion, interception, inertial forces, electrical migration, thermophoresis, and diffusionphoresis [11,13]. Finally, a sort of ‘occult deposition’ manifests through the water droplets deposited by fog, mist, or cloud interception.

The contribution of each form of atmospheric deposition is strongly conditioned by the characteristics of the investigation areas and, especially, by local weather conditions. In rainy areas, the contribution of dry deposition is almost negligible compared to the contribution of wet deposition [14]. On the contrary, in arid or semi-arid areas, where processes such as erosion and geogenic dust transport are very pronounced, dry deposition prevails over wet deposition contributing to the chemical composition of the total deposition. The wet deposition also shows a seasonal variability, representing the main contribution of bulk deposition during the rainy season (usually from September to March for the southern Mediterranean area), while it contributes little to the chemical composition of bulk deposition during the dry season (from April to August in the southern Mediterranean area) [5,15]. Instead, occult deposition plays a significant role only in the case of the frequently cloud-covered zone or by adjective fog but is negligible in urban areas [11].

Concentrations of trace elements in rainwater have been widely investigated, mainly for elements or metalloids that represent a risk to human health and ecosystems due to their toxicity, such as mercury (Hg), lead (Pb), cadmium (Cd), chromium (Cr), copper (Cu), among others [16,17]. Due to industrialization and urban growth, the abundance of these potentially toxic elements has increased in recent decades [18]. Some elements, such as Cu and Zn, are essential nutrients but they can cause harmful effects depending on their concentration levels [11]. For example, cadmium is considered very toxic because of its high solubility and is classified as potential carcinogenic [19,20]. It is also ecologically hazardous because of its easy uptake by plants, its tendency to accumulate in crops, and its persistent nature once it is in the environment [20]. Lead is the most widespread toxic metal on Earth due to anthropogenic activities [20], and it is also recognized by the World Health Organization as one of the most dangerous chemical elements for human health [21,22]. Copper, chromium, cadmium, lead, and zinc are trace elements of mainly anthropogenic origin, and they are emitted into the atmosphere from various industrial processes, motor vehicle traffic, and agricultural activities [23,24]. Indeed, copper, chromium, and lead are

derived from diesel exhaust from vehicles and lubricant oil combustion [25,26]. Chromium can also be a waste product of coal combustion and is also used in the textile industry [20]. Lead is also widely used in the ceramics industry [27]. Cadmium comes mainly from vehicular emissions and partly from industrial emissions [28]. Aucélio et al., 2007 [29], and Hjortenkrans et al., 2007 [30], verified that cadmium comes from lubricating oil and tire wear from vehicles. Finally, zinc is widely used in agriculture, in the form of zinc salt (e.g., $ZnSO_4$) and/or ZnO aqueous solutions [20]. The current Italian legislation on environmental protection [31], implemented by European legislation (2008/50/CE), provides for the monitoring of atmospheric deposition of only a few trace metals (As, Cd, Ni, Pb); considering the development in recent years of new technological and energy-related applications (e.g., solar panels, high-efficiency batteries, electronic equipment, catalytic converters) and the consequent exponential increase in the use and demand of a specific group of less-studied trace elements, the current legislation is affected by significant gaps. Indeed, recent studies draw attention to a group of trace elements known as Technology-Critical Elements (TCEs), including tellurium (Te), germanium (Ge), gallium (Ga), indium (In), niobium (Nb), tantalum (Ta), the platinum group elements (PGEs: Pt, Pd, Rh, Os, Ir, Ru), and the rare earth elements (YREEs: La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) [32].

Another important question concerns which in which form (dissolved or particulate) trace elements are found in rainwater. Most of the studies found in the literature were focused on the soluble fraction of the atmospheric trace element deposition [33–37], but recently researchers have paid more attention to the insoluble fraction [20,38–40]. Lead, aluminium, iron, and silicon, for example, exist mainly in poorly soluble forms [20,40], while trace elements such as zinc, cadmium, and chromium are very soluble and for this reason represent a high risk for human health and, in general, for many environmental matrices. Cadmium and lead have low solubility at high mass particles concentration [40]. In the dry deposition, the contribution of the soluble fraction is usually less than that of the insoluble fraction for all trace elements [20]. Evaluation of the trace element soluble and particulate fractions is essential since the soluble and particulate forms have different fates in the environment, especially concerning bioavailability [41].

The long-range transport of air pollutants emitted by industrial activities in Central Europe affects the chemical composition of the bulk deposition throughout the Mediterranean basin. Saharan dust has been demonstrated to have, seasonally, a strong impact on the wet deposition of trace elements in the Mediterranean area and even in the north of Europe. The chemical signatures of the two sources, especially for the concentration of trace elements in bulk deposition, are very different [40].

For trace elements existing entirely in coarse particulate form, their wet deposition depends on the below-cloud scavenging of local emissions rather than regional emissions. However, for trace elements existing in fine particulate form, which can act as CCN for the formation of precipitation, most of the wet deposition might arise from in-cloud scavenging and regional emissions become prevalent. Trace elements contained in dry deposition are usually of more local origin than those contained in wet deposition, which may also originate from regional-scale sources [42]. Air mass trajectories combined with the chemical composition of rainwater provide information on the origin of atmospheric pollutants [43,44]. Beyond the differences in emission sources, different land uses and size distributions of trace elements in atmospheric aerosols are considered to influence the trace element wet/dry ratios of different sites [20]. Long-term variations in the chemical characteristics of bulk deposition provide important tools for the temporal evolution of atmospheric pollution and can be used as an indicator to evaluate natural processes versus anthropogenic influences [45].

The main aim of this paper is to analyse the chemical concentrations of a vast number of hitherto little-studied trace elements in atmospheric depositions and to calculate the relative deposition fluxes at two industrial polluted areas of Sicily, Milazzo, and Priolo

Gargallo, which were classified by the Italian Ministry of the Environment as areas at high risk of environmental crisis (hereafter AERCA—*Area ad Elevato Rischio di Crisi Ambientale*).

A side objective of this study is to review and evaluate the common sampling procedures and analytical methods used for monitoring trace elements in atmospheric deposition. Therefore, the concentrations of trace elements were measured on two different aliquots of rainwater samples, by using two complementary methodologies, to evaluate the potential underestimation of atmospheric deposition when the insoluble fraction is not considered. The main natural and anthropogenic sources of trace elements, the temporal variation of the chemical composition of the bulk deposition, and a comparison with the composition of atmospheric deposition in other European countries will be also presented and discussed.

2. Study Area

The study areas are in the north-eastern and south-eastern sectors of Sicily, Italy (Figure 1). They are heavily urbanized areas, and they are affected by heavy industrial-type anthropogenic pressure. Both Milazzo and the areas between Augusta, Priolo Gargallo, and Melilli have been defined as contaminated sites of national priority for remediation because of diffuse environmental contamination caused by large industrial settlements. Several epidemiological studies have shown a possible association between exposure to environmental contaminants at these sites and the altered health status of resident populations [46]. To monitor the footprint of anthropogenic (urban and industrial) emissions, five sites were selected for both the Milazzo AERCA and the Priolo Gargallo AERCA. Three monitoring sites in the Milazzo area were chosen at sensitive sites, including schools (two kindergartens and one high school). The remaining two sites were chosen in urban areas progressively further away from the industrial area to quantify the spatial distribution of trace element concentrations. A study site in the Priolo Gargallo area was chosen at a kindergarten. Two samplers (SIR and ARP) were placed in a densely populated urban area, at the ARPA (Regional Environmental Protection Agency) environmental monitoring stations. The Priolo and Augusta sites were selected to intercept industrial emissions, taking into account the prevailing wind directions from the south-east and east.

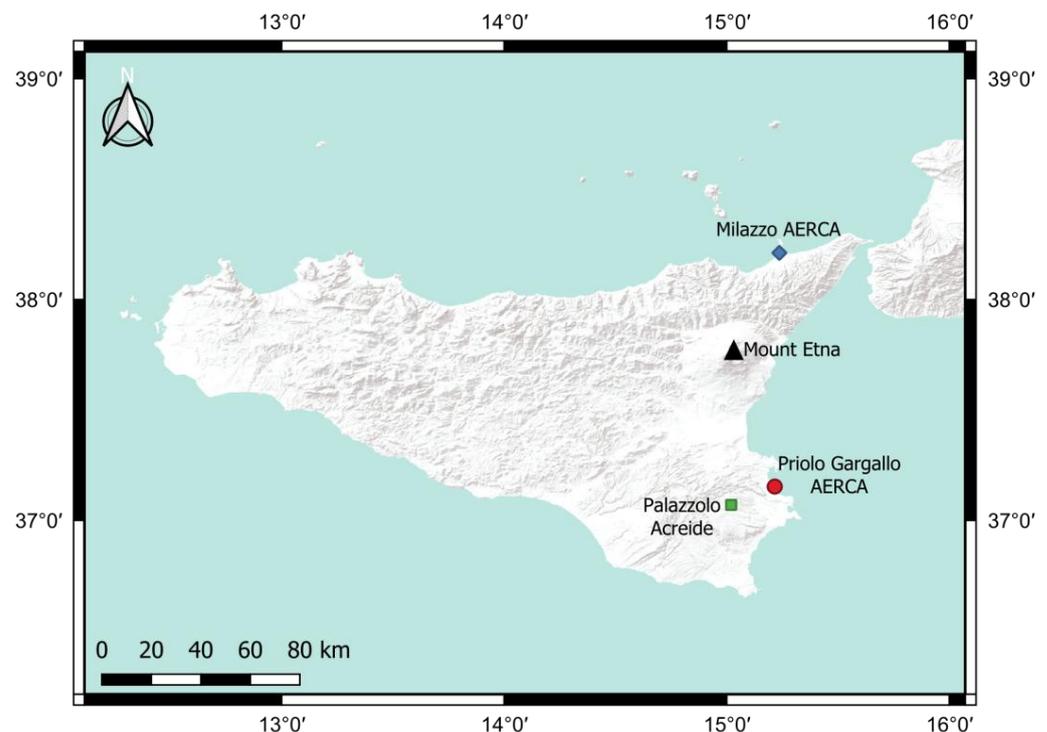


Figure 1. Localization of study areas. Base map: ESRI Terrain. Coordinates in degrees and minutes (reference system: EPSG 4326).

One additional study site, Palazzolo Acreide (Siracusa), is in a sparsely urbanised area far from industrial areas and was monitored as a representative of the local background. For more details of the studied areas and climatic settings, refer to the companion paper by Brugnone et al., 2023a [47–52].

3. Material and Methods

A total of 131 samples of rainwater were monthly collected from June 2018 to July 2019, using a network of 11 bulk collectors; 60 samples were collected from the Milazzo AERCA and 71 from Priolo Gargallo AERCA (Figure 1 and Table 1).

Table 1. The monitoring network and information of sampling sites.

Locality	ID	AERCA	Type of Site	Position UTM WGS84	Altitude (m a.s.l.)	Distance from Sea (km)
Contrada Gabbia	GAB	Milazzo	Industrial	33S 527148 4228670	15	0.43
Archi	ARC	Milazzo	Industrial	33S 524760 4227710	34	1.05
Pace del Mela	PAV	Milazzo	Urban	33S 527271 4226464	107	2.55
S. Lucia del Mela	LUC	Milazzo	Urban	33S 524222 4222617	150	6.11
Milazzo	MIL	Milazzo	Urban	33S 520799 4230495	20	0.36
Siracusa	SIR	Priolo Gargallo	Urban	33S 523613 4106275	63	0.44
Siracusa	ARP	Priolo Gargallo	Urban	33S 524666 4104347	76	1.95
Melilli	MEL	Priolo Gargallo	Urban	33S 511433 4115107	249	5.15
Augusta	AUG	Priolo Gargallo	Industrial	33S 519388 4120387	28	0.10
Priolo Gargallo	PRI	Priolo Gargallo	Industrial	33S 514767 4112657	94	2.97
Palazzolo Acreide	PAL	-	Semi-Urban	33S 491728 4102587	642	28.2

Sampling procedures followed the main published protocols for atmospheric deposition monitoring [53–55]. Bulk collectors consisted of a bottle made of High-Density Polyethylene—HDPE (volume 5 L) and a funnel (Büchner type, diameter 240 mm) made of Polypropylene—PP (for more details see [56]). Sampling bottles were installed inside a Polyvinyl chloride—PVC tube (1.5 m high), to protect water samples from direct sunlight; funnels were open during the entire exposure period, collecting both wet and dry depositions. The bulk collectors were installed on the roof of public and/or private buildings and on two monitoring stations for air quality control, managed by the *Agenzia Regionale per la Protezione dell’Ambiente (ARPA Sicilia)* (see photos in Figure 2).

To investigate the impact of industrial pollutants on rainwaters, five monitoring sites were located near the urban/industrial area of Priolo Gargallo and five in the surrounding of the urban/industrial area of Milazzo, in order to estimate the chemical characteristics of the rainwater in an area not directly influenced by industrial activity (local background), one additional collector was installed at Palazzolo Acreide, a small village about 30 km away from the AERCA of Priolo Gargallo (Figure 1 and Table 1). Funnels and bottles were accurately cleaned before their exposure in the field, using ultrapure water (18.2 MΩ cm resistance Milli-Q water-purification system), and dried under a laminar hood for 24 h. Bulk collectors were assembled and sailed in clean plastic bags until their exposure in the field; bottles and funnels were replaced by clean ones at the end of each monthly sampling period. Collected samples were carried to the laboratory and by gravimetric measurements, the quantity of water was weighted to calculate the amount of rainwater. Collected samples were subdivided in two aliquots for different analytical determinations and to evaluate the difference between soluble (filtered) and less-soluble (unfiltered) fractions:

- i. filtered (0.45 μm membrane filter) and acidified (Ultrapure HNO₃) aliquot was analysed for a large suite of trace elements;
- ii. unfiltered and acidified (Ultrapure HNO₃) aliquot analysed for the determination of the same trace elements.



Figure 2. Examples of bulk collector installations. (a) Siracusa (Scala Greca); (b) Palazzolo Acreide; (c) Melilli; (d) Archi (Milazzo); (e) Augusta; (f) Priolo Gargallo.

During the dry period (no rain in the collectors), dry deposition was recovered following the method described by Menechini [57]: 300 mL of ultrapure water was used to wash both the funnel and the sampling bottle and the obtained solution/suspension of the dry deposition was treated as described above; 8 samples (about 6% of the total samples) consisted of a dry deposition only. Therefore, the collected bulk deposition samples were the sum of the wet and the dry depositions.

All samples were analysed for 27 minor and trace elements (Al, As, B, Ba, Ce, Cd, Co, Cr, Cs, Cu, Fe, Li, Mn, Mo, Ni, Pb, Rb, Sb, Se, Sn, Sr, Te, Ti, Tl, U, V, and Zn). External calibrations were performed with standard solutions obtained by mixing and diluting multi and single-element work solutions (100 mg L^{-1} and 1000 mg L^{-1} , CertiPUR ICP Standards Merck). The calibration routine was done on selected isotopes for each element with 11 calibration points (Supplementary Materials) prepared daily in 10 mL polyethylene tubes by dilution with 2% nitric acid solution, treated as a blank solution. Element contents in the analysed samples were calculated using the spectrometer software (ICP Mass Hunter, version B.01.01). The sensitivity variations were monitored by ^{103}Rh , ^{115}In , and ^{185}Re with $10 \mu\text{g L}^{-1}$ concentration as an internal standard added directly online. The reproducibility of the chemical analysis was verified by 5 replications for each sample and standard and the RSD was always below 20%. The analytical accuracy of trace element determinations was checked by the analysis of four Certified Reference Materials (TM Rain 04, SLR4, SLRS5, SPSSW1), specific to the analysis of trace elements in fresh and rainwater and we calculated an error between 10 to 15% for Al, Ti, V, Cr, Fe, Co, Cu, Zn, Se and Pb, with all other elements having errors of less than 10%. Sample manipulation and analysis were carried out in clean rooms, all plastic ware was washed with ultrapure water, and all the aliquots were stored at $4 \text{ }^\circ\text{C}$ before the analytical determinations. Pre-treatment of the samples and chemical analyses were performed in the laboratories of the *Dipartimento di Scienze della Terra e del Mare (DiStEM)*, the laboratory of the *Istituto Nazionale di Geofisica e Vulcanologia (INGV)*, and the laboratory of *Dipartimento di Scienze Agrarie, Alimentari e Forestali (SAAF)*, all situated in Palermo.

3.1. Analysis of Chemical Data

Descriptive statistics on trace element volume-weighted mean (VWM) concentrations ($\mu\text{g L}^{-1}$) were shown in Table S1 in the Supplementary Materials. The complete dataset of major ions and trace elements concentrations and deposition fluxes is available in [58]. VWM concentration values were calculated by using the following formula:

$$\text{VWM} = \frac{\sum_{i=1}^n C_i P_i}{\sum_{i=1}^n P_i} \quad (1)$$

where C_i is the rainwater concentrations ($\mu\text{g L}^{-1}$) value in the i th sample, P_i is the rainfall depth (L m^{-2}) during the i th sampling period and n is the total number of rainfall events [2]. The annual volume-weighted mean (VWM) was used to reduce the potential effect of different precipitation amounts on the trace element concentrations.

Annual atmospheric deposition fluxes ($\mu\text{g m}^{-2} \text{yr}^{-1}$) for each trace element and each sampling site were calculated from concentrations ($\mu\text{g L}^{-1}$), exposure time (yr^{-1}) of the collectors, and amount of rainfall (L m^{-2}) (2) and were published in Brugnone et al., 2023b [58].

The degree to which trace elements in rainwater were enriched or depleted relative to the crustal source has been evaluated by an enrichment factor (EF_{crust}):

$$\text{EF}_{\text{crust}} = \left[\frac{([X]/[REF])_{\text{rain}}}{([X]/[REF])_{\text{crust}}} \right] \quad (2)$$

where $[X]_{\text{rain}}$ is the total concentration (in $\mu\text{g L}^{-1}$) of an element X in the sample, $[REF]_{\text{rain}}$ is the concentration of a reference element in the sample, and $[X]_{\text{crust}}$ and $[REF]_{\text{crust}}$ are the concentration of the element X and the reference element in the upper continental crustal material [59]. Enrichment factors calculated by Equation (3) for each trace element were reported in Table S2 in the Supplementary Materials.

The non-sea-salt sulfate fractions (see the companion paper Brugnone et al., 2023a [47]) were calculated by the following formula [14,60]:

$$\text{nss-SO}_4^{2-} = [\text{SO}_4^{2-}]_{\text{rain}} - ([\text{Na}^+]_{\text{rain}} \times \left[\frac{\text{SO}_4^{2-}}{\text{Na}^+} \right]_{\text{SW}}) \quad (3)$$

4. Results and Discussion

4.1. Concentration of Trace Elements in Rainwater

The trace element VWM concentrations ranged from about less than $0.01 \mu\text{g L}^{-1}$ for trace elements such as Cs, Tl, and U, up to $24 \mu\text{g L}^{-1}$ for minor elements (Al, Zn, Sr), in the filtered aliquot, while they ranged from about $0.003 \mu\text{g L}^{-1}$ for the same trace elements, up to $144 \mu\text{g L}^{-1}$ for minor elements, in the unfiltered aliquot. Considering the filtered aliquot, and the sum of the concentrations of all trace elements, the sites with the highest annual VWM concentration values were Contrada Gabbia ($66.3 \mu\text{g L}^{-1}$) and Augusta ($55.6 \mu\text{g L}^{-1}$), while the sites with the lowest annual VWM trace element concentration values were Santa Lucia del Mela ($48.8 \mu\text{g L}^{-1}$) and Siracusa—ARPA ($47.0 \mu\text{g L}^{-1}$), for Milazzo and Priolo Gargallo study areas, respectively. A very different trend and very different VWM concentration values were observed by considering the unfiltered samples. The sites with the highest annual VWM concentration values were Archi ($240.3 \mu\text{g L}^{-1}$), and Melilli ($277.3 \mu\text{g L}^{-1}$), while the sites with the lowest annual VWM trace element concentration values were Contrada Gabbia ($177.2 \mu\text{g L}^{-1}$) and Priolo Gargallo ($107.5 \mu\text{g L}^{-1}$), for Milazzo and Priolo Gargallo study areas, respectively.

Indeed, large differences in the VWM concentration values were observed between the two aliquots in which these elements were determined (Figure 3a,b and Table S1 in the Supplementary Materials).

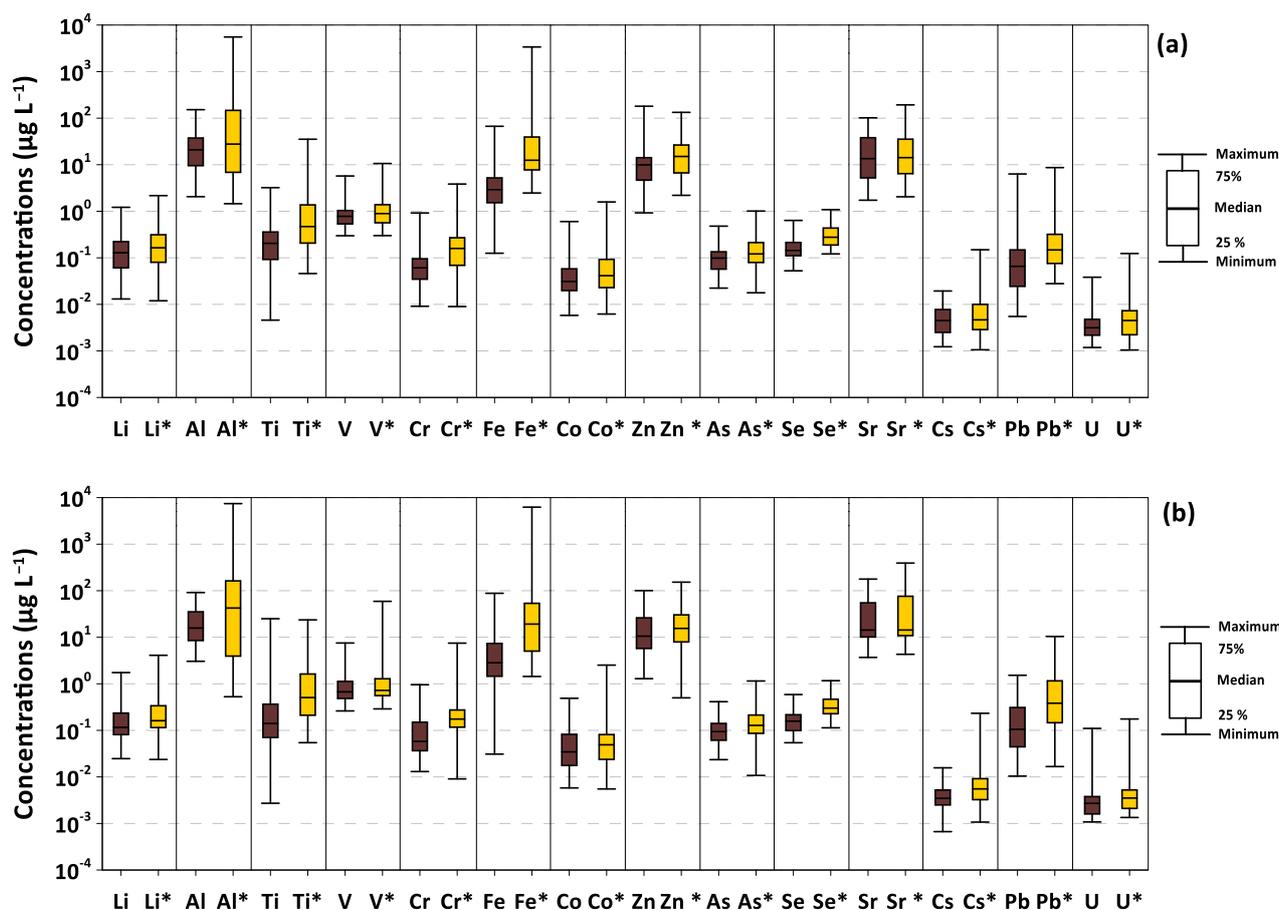


Figure 3. Box whiskers plots of the trace elements VWM concentrations ($\mu\text{g L}^{-1}$) in filtered (brown), and unfiltered (*) (yellow) rainwater samples of Priolo Gargallo (a), and Milazzo study areas (b).

Tellurium VWM concentration values were not listed in Table S1 (Supplementary Materials) because, in 100 out of 131 filtered samples (76.3%), they were below their detection limit while boron and tin were not included because their concentration was not determined in the unfiltered aliquot.

Figure 3 shows the correlation between the concentrations of selected trace elements in the two analysed aliquots (filtered vs. unfiltered). The straight line in each graph indicates the 1:1 ratio between the two concentrations of the specific element. Higher concentrations, even by one order of magnitude, in the unfiltered aliquot were observed for almost all trace elements covered in this study, both in extreme values and in mean and median values (Figure 4).

The most significant differences were measured for iron with a mean ratio between the concentration in the unfiltered and filtered aliquot of 37.3 and aluminium, with a ratio between the concentrations in the two aliquots of 13.7. This was followed by Ti, with a mean ratio of 6.8, Cr (ratio of 4.0), and Cs, with a mean ratio of 3.4. The only elements for which concentrations in the two aliquots were measured to be very similar, with average ratios ranging from 0.95 to 1.17, were Mo, Mn, and Cu. Both in Milazzo and Augusta, the largest differences between filtered and unfiltered aliquots were observed in the second sampling period (from June 2018 to July 2018); this was a rather dry period, characterised by sirocco events with consequent Saharan sand/particles transport in the entire Mediterranean area. Atmospheric deposition during dry periods is characterised by a higher insoluble fraction than during wet periods.

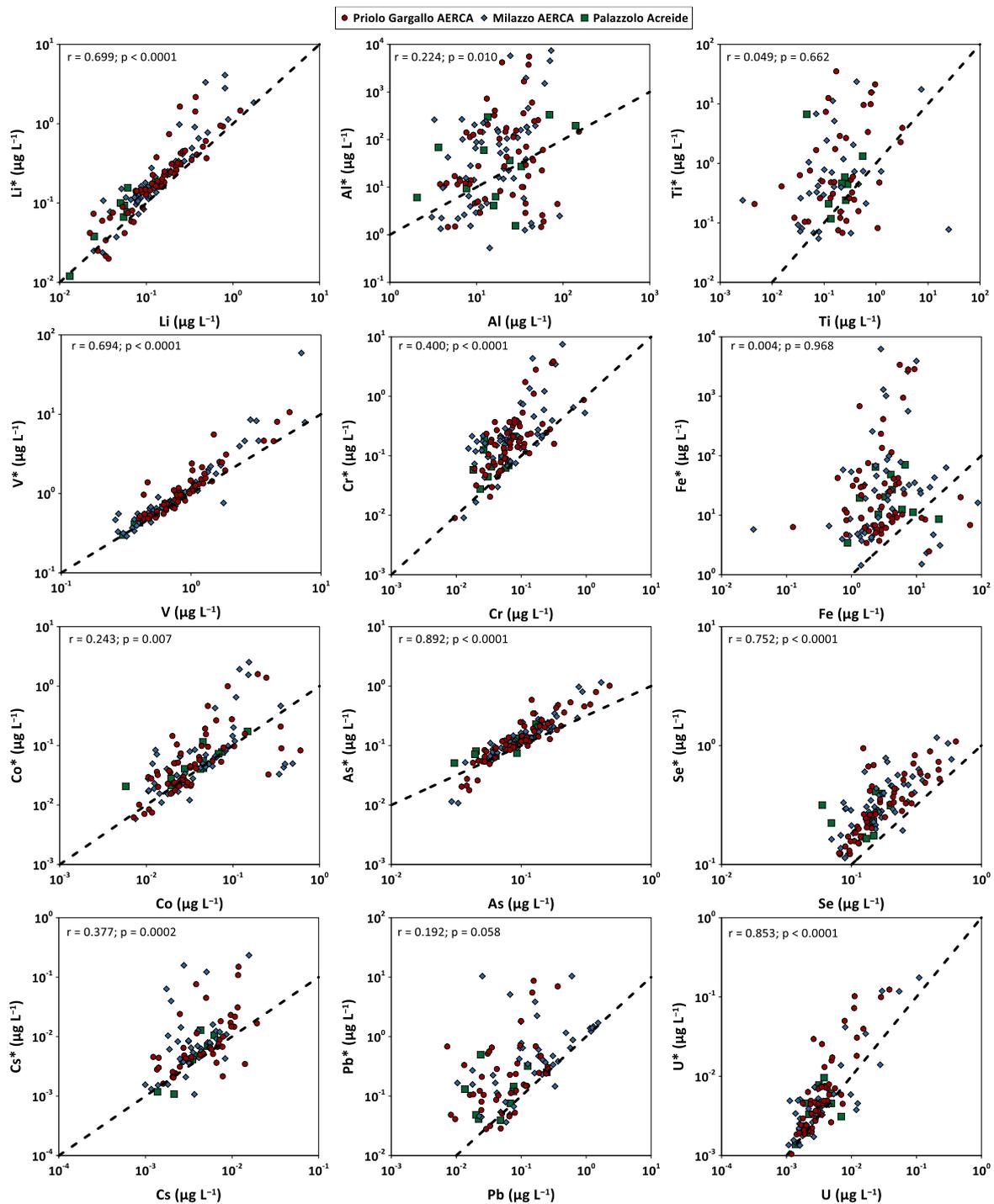


Figure 4. Binary graphs comparing selected trace elements concentrations ($\mu\text{g L}^{-1}$) in the filtered and the unfiltered (*) aliquots. The straight line in each graph indicates the 1:1 ratio between the two concentrations of the specific element.

The obtained results evidence that the filtration classical membrane filters (porosity of $0.45 \mu\text{m}$) do not allow the determination of the contribution of the solid particles ($>0.45 \mu\text{m}$), which is a significant fraction of the bulk deposition. This was especially evident for elements such as Al, Fe, and Ti, which have low solubility under the chemical-physical conditions that normally characterise atmospheric precipitation [60], and they remain undissolved as solid particulate matter and blocked in the filter. On the other hand, when the unfiltered sampled is acidified using ultrapure concentrated HNO_3 (65%), the pH of

the solution becomes acidic ($\text{pH} < 2$) and some elements present in particulate matter (e.g., alumina-iron silicates, carbonates) tend to solubilize. The solubility of Al and Fe is also greatly influenced by the amount of solid material in the solution. As shown by Guerzoni et al., 1999 [40], Al and Fe solubility decrease significantly as the particulate load increases. Aluminium dissolution decreases from more than 20% at aerosol loadings lower than 5 mg L^{-1} , to less than 1% at total aerosol concentrations greater than 100 mg L^{-1} . A similar pattern is also observed for iron, in which dissolution decreases from 6% at aerosol loading lower than 20 mg L^{-1} , to an average of 1% at total aerosol concentrations greater than 200 mg L^{-1} . In this research, solid particulate concentrations were not measured, so it was not possible to determine how particulate concentration may have affected Al and Fe concentrations in the two aliquots analysed.

Other elements, at higher solubility under the chemical-physical conditions typical of rainwater, on the other hand, did not undergo any change because of the filtration process, since they were completely dissolved in the aqueous solution already at the time of raindrop formation or during its path from the base of the cloud to the Earth's surface.

4.2. Main Sources of Trace Elements

The regional environmental protection agency (*Agenzia Regionale per la Protezione dell'Ambiente*—ARPA) that monitors the industrial atmospheric emissions in Sicily reports the fluxes of some trace elements (As, Cd, Ni, Cu, Zn, Se, Pb, and Cr) emitted from the industrial areas of Milazzo AERCA and Priolo Gargallo AERCA [61]. The industrial emissions of Priolo chemical plants in 2015 include As (155 kg yr^{-1}), Cd (111 kg yr^{-1}), Ni (506 kg yr^{-1}), Pb (119 kg yr^{-1}), Cr (581 kg yr^{-1}), Cu (221 kg yr^{-1}), Se (85 kg yr^{-1}), Zn (1342 kg yr^{-1}); Milazzo industrial area emitted in 2015 As (60 kg yr^{-1}), Cd (25 kg yr^{-1}), Ni (1002 kg yr^{-1}), Pb (96 kg yr^{-1}), Cr (101 kg yr^{-1}), Cu (145 kg yr^{-1}), Se (90 kg yr^{-1}), Zn (2560 kg yr^{-1}).

To identify the potential impact of industrial emissions on atmospheric deposition chemistry, the above-mentioned trace elements were plotted against non-sea-salt sulfate (nss-SO_4^{2-}), which was recognised in Brugnone et al., 2023a [47] as a marker of the Priolo Gargallo AERCA and Milazzo AERCA emissions (Figure 5).

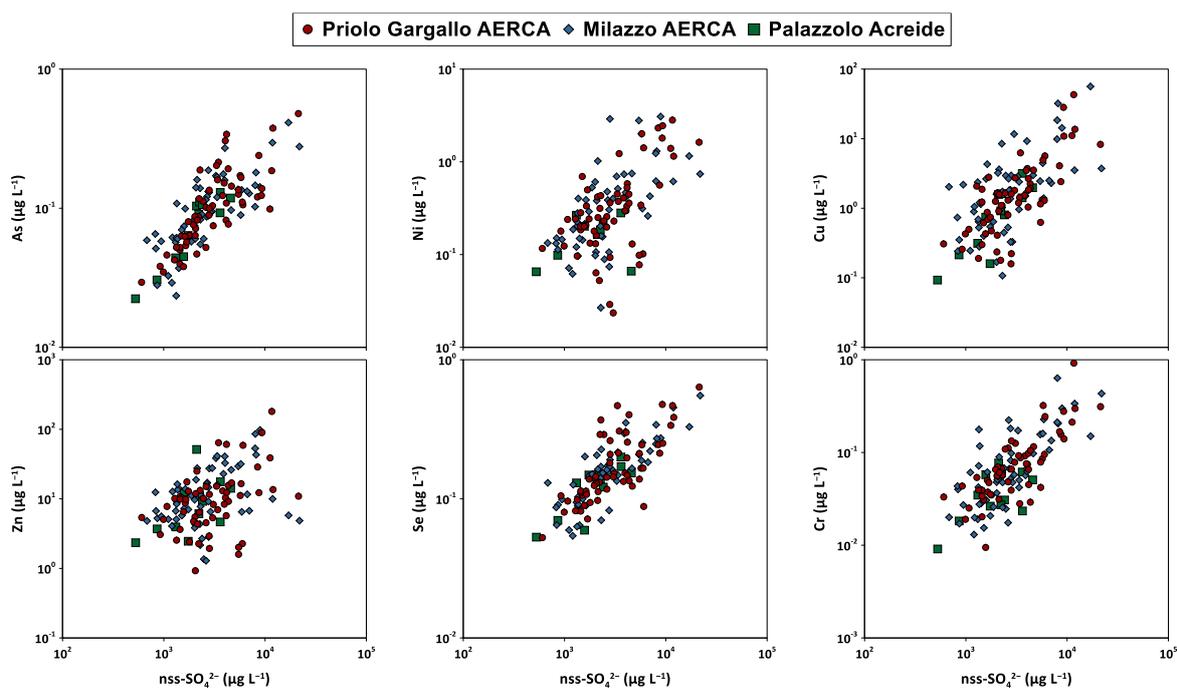


Figure 5. Correlation between some trace elements emitted by industrial plants of the two study areas ($\mu\text{g L}^{-1}$) as reported by ARPA Sicilia [61], and nss-SO_4^{2-} ($\mu\text{g L}^{-1}$).

The highest Pearson's coefficient of correlation was obtained for arsenic in the Palazzolo Acreide area ($r = 0.845$, $p = 0.0005$). A good correlation was also observed for selenium at Milazzo AERCA ($r = 0.838$, $p < 0.0001$), Palazzolo Acreide site ($r = 0.762$, $p = 0.004$), and Priolo Gargallo AERCA ($r = 0.733$, $p < 0.0001$). For copper, the highest coefficient of correlation was obtained for the Palazzolo Acreide site ($r = 0.800$, $p = 0.002$). For nickel, the highest coefficient of correlation was found in the Priolo Gargallo AERCA ($r = 0.703$, $p < 0.0001$). In all three areas, the lowest correlation was found for zinc with r values of 0.445 ($p = 0.004$), 0.272 ($p = 0.037$), and 0.210 ($p = 0.512$) for Priolo Gargallo AERCA, Milazzo AERCA, and Palazzolo Acreide, respectively.

Therefore, these elements in the atmospheric deposition of all the study areas should not be considered exclusively of anthropogenic origin, but other sources, probably geogenic and marine, may contribute to their enrichment in the atmosphere. Similar results were obtained by considering the concentrations of the same elements determined from the analysis of the unfiltered aliquot.

As reported in Brugnone et al., 2023a [47], one of the most important sources of the deposited elements and compounds, especially in the area of Priolo Gargallo AERCA and Milazzo AERCA and to a lesser extent in Palazzolo Acreide, is the marine source. One of the major indicator ions of the marine source is chloride. A positive linear correlation was observed between chloride and boron, with a coefficient of correlation values of 0.796 ($p < 0.0001$), 0.691 ($p < 0.0001$) and 0.652 ($p = 0.022$) for the Milazzo AERCA, Priolo Gargallo AERCA, and the Palazzolo Acreide site, respectively. Furthermore, the B/Cl ratio of the samples takes values close to that of seawater with increasing Cl content (Figure 6). Therefore, the sea is a plausible source for a significant part of the boron present in the analysed samples. Another trace element present in high abundance in seawater was strontium. The best correlation, although not high, was shown for the Milazzo area ($r = 0.467$; $p = 0.0002$). Even for this trace element the contribution from the marine source was not negligible, but other sources must be called in to explain the enrichment in strontium that was observed, relative to chloride, at all monitoring sites. (Figure 6).

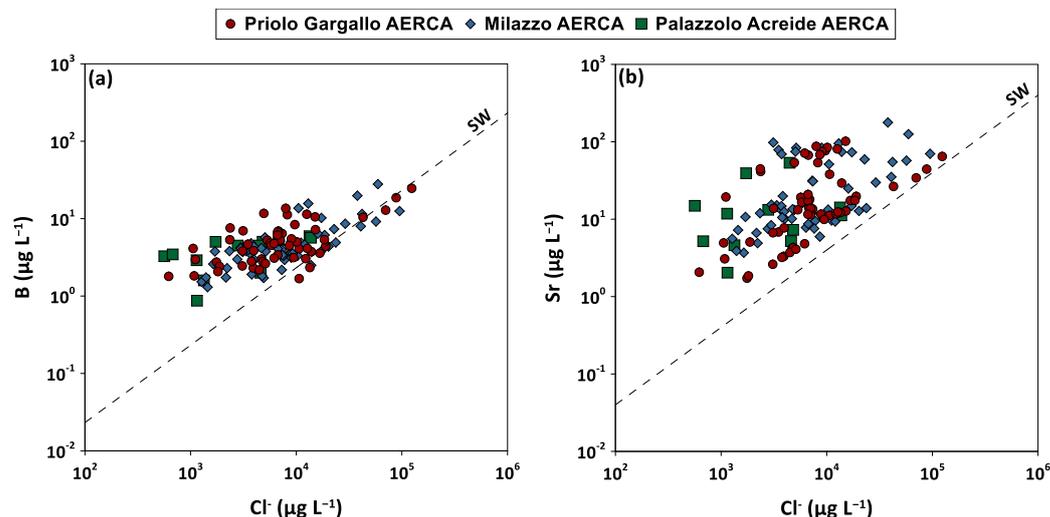


Figure 6. Correlation between boron (a) and strontium (b) against chloride ($\mu\text{g L}^{-1}$). The straight lines (SW) are the seawater ratios.

Special mention may be made to three trace elements, Cd, Te, and Tl, which are highly volatile elements typically enriched in volcanic emissions. Clear evidence of the effect of volcanic eruption on the chemical composition of atmospheric deposition has been found between 24 to 30 December 2018, when a major eruption of Mount Etna occurred. Due to atmospheric conditions and high-altitude wind direction (3000 m a.s.l.) during those days, the volcanic plume headed southward, travelling hundreds of kilometres. As shown

by Brugnone et al., 2020 [62], volcanic emissions associated with the paroxysm, strongly influenced the chemical composition of atmospheric deposition at all the sites in the Priolo Gargallo AERCA, including the Palazzolo Acreide study site, especially concerning F, Al, Cd, Te, and Tl concentrations. In the samples collected a few days after the eruption, concentrations of the above-mentioned elements were up to one order of magnitude higher than the average concentrations of the entire monitoring period. On the contrary, no anomalous concentrations of these elements were observed at the Milazzo AERCA, and it was not reached by the volcanic plume. The unexpected results showed that Etna emissions might have a relevant effect on the atmospheric chemistry and the composition of rainwater up to a distance of at least 80 km from the source.

4.3. Enrichment Factors of Trace Elements

The degree to which a trace element in bulk deposition samples is enriched or depleted relative to the crustal source may be assessed by using an enrichment factor (EF_{crust}). For crustal sources, Li was used as a source indicator element, being that its concentration in rainwater was almost exclusively influenced by crustal sources without any influence from human activities [63]. This element showed comparable values between the two different aliquots analysed, due to its high solubility in the chemical-physical conditions characteristic of rainwater, thus making it easier to compare them. Finally, lithium was chosen as the indicator element because, in all the samples analysed, it was never below the analytical limit of quantification. The EF_{crust} values for some trace elements, both for the filtered aliquot and the unfiltered aliquot, were then calculated according to Equation (3) in Section 3.1; they were listed in Table S2 in Supplementary Materials and shown in Figure 7.

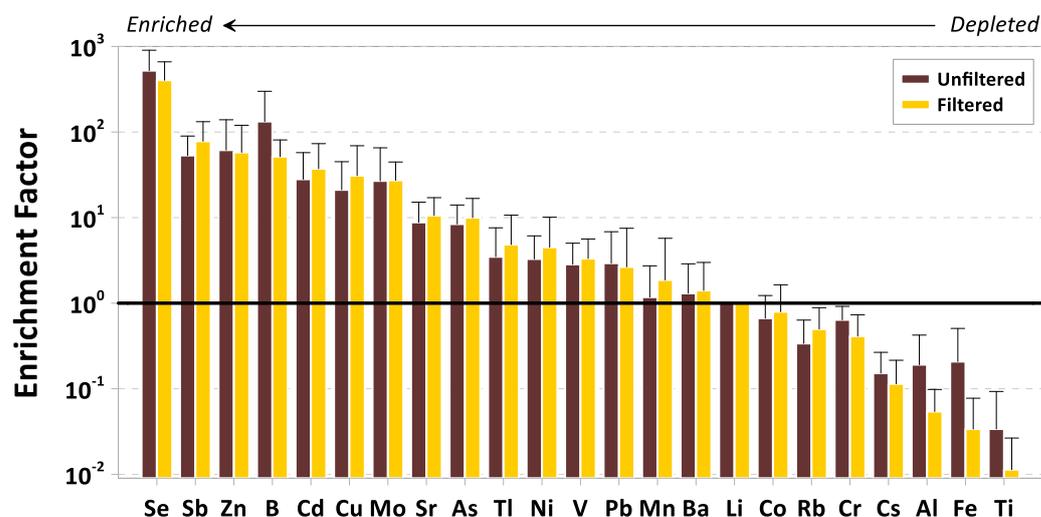


Figure 7. Enrichment factors (EF_{crust}) of trace elements at all the sampling sites and both for the concentrations of the trace elements in the unfiltered aliquot (brown) and in the filtered aliquot (yellow). The standard deviation is shown.

Elements for which the Earth's crust is the only source have an EF_{crust} lower than 10 and close to unity [6]. Elements with EF_{crust} between 10 and 100 might indicate the influence of the chemical composition of local soil [64]. Elements with EF_{crust} greater than 100 could indicate other sources, such as anthropogenic, volcanic, or sea sources, in addition to crustal materials [7,40]. Considering the mean EF_{crust} determined using the concentrations of trace elements in the aliquot subjected to the filtration process, at all the sampling sites, it was observed that Ti, Fe, Al, Cs, Cr, Rb, Co, Ba, Mn, Pb, V, Ni, Tl, and As had a crustal input, while Sr, Mo, Cu, Cd, B, Zn, and Sb belonged to the group of elements with intermediate EFs. Only Se has a mean EF_{crust} value greater than 100 (403) so it may derive from marine, volcanic, or multiple anthropogenic sources. Additionally, taking into consideration the EF_{crust} determined using the concentrations of trace elements in the

aliquot not subjected to the filtration process, it was observed that the same trace elements had a crustal origin and the same elements showed intermediate EF_{crust} values. The only two trace elements with mean EF_{crust} values greater than 100 were B (133) and Se (522).

It was observed that although the concentrations of trace elements determined from the analysis of the unfiltered aliquot were generally greater than those determined in the aliquot subjected to the filtration process, the enrichment factors related to the trace elements contained in the unfiltered aliquot did not differ significantly from the filtered aliquot. The biggest differences in EF_{crust} values may be observed especially for Fe (ratio 6.1), Al (ratio 3.5), B (ratio 2.6), Cr (ratio 1.6), Cs, and Se (ratios 1.3), while the other trace elements were characterized by very similar EF_{crust} values between the two different aliquots (Figure 6). Tl, an element of predominantly volcanic origin, was one of the elements whose EF_{crust} values differed the least between the two aliquots, with EF_{crust} values being higher for the filtered aliquot than the unfiltered one (ratio of 0.72). Lithium, i.e., the element taken as a reference for the calculation of EFs, showed higher concentrations in the unfiltered aliquot (median 0.163 µg L⁻¹) than in the filtered one (median 0.123 µg L⁻¹) and this should explain why, despite the large differences in trace element concentrations observed between the two aliquots, the enrichment factors of the same do not differ much.

4.4. Bulk Deposition Fluxes of Trace Elements

Annual bulk atmospheric deposition fluxes (µg m⁻² yr⁻¹) were calculated by multiplying the VWM concentrations for each trace element (both for filtered and unfiltered aliquot) and the annual rainfall amount (mm) for each sampling site (Table 2 and Brugnone et al., 2023b [58]).

Significantly different levels were found in the atmospheric bulk deposition of the studied territories during the sampling period. Trace element depositions values varied within one or two orders of magnitudes, especially for Al, Ti, Mn, Fe, Cd, Te, and Pb, in all the sampling sites (Figure 8).

The highest average atmospheric deposition values were measured for Al, Fe, B, Zn, Sr, and Ba, while the lowest values were recorded for U, Te, Cs, Cd, and Tl. This trend was observed at all monitoring sites, both in the Milazzo and Priolo Gargallo AERCAs and for both aliquots analysed, the one subjected to the filtration process and the unfiltered one.

The lowest atmospheric deposition values concern the samples collected during June 2019, both for the Milazzo AERCA and the Priolo Gargallo AERCA. During this sampling period, precipitation occurred only at the Palazzolo Acreide monitoring site, so at the other sites, only the contribution of dry deposition was measured. The highest values were recorded, therefore, between October and November 2018. This trend was observed for both the filtered and unfiltered aliquots.

Summing the monthly deposition fluxes of all trace elements determined by the filtered aliquot analysis yielded values ranging from 25.5 µg m⁻² d⁻¹ to 314.1 µg m⁻² d⁻¹ in the Milazzo area and from 18.1 µg m⁻² d⁻¹ to 544.0 µg m⁻² d⁻¹ in the Priolo Gargallo area, with monthly arithmetic mean values of 122.1 µg m⁻² d⁻¹ and 123.4 µg m⁻² d⁻¹, respectively, thus they were very similar in the two areas. The total atmospheric depositions of trace elements thus determined over one year were between 37.2 mg m⁻² yr⁻¹ at Santa Lucia del Mela site and 52.9 mg m⁻² yr⁻¹ in the Contrada Gabbia site, for the Milazzo AERCA and between 37.0 mg m⁻² yr⁻¹ in Priolo Gargallo site and 51.5 mg m⁻² yr⁻¹ in Palazzolo Acreide site, for the Priolo Gargallo AERCA. The high atmospheric deposition value for the Palazzolo Acreide site was explained by the relatively high amount of rainfall accumulated during the sampling year (936.8 mm), which was higher than the rainfall amount measured in the other sites of its study area. Aluminium, strontium, and zinc together constituted 70.4% (Milazzo) and 70.2% (Priolo Gargallo) of the total atmospheric deposition in the two study areas. Strontium had a relative abundance of 27.4% and 21.2%, aluminium alone accounted for the 24.0% and 33.5% of the total trace elements atmospheric deposition, and zinc accounted for the 19.0% and the 15.6%, in the Milazzo and Priolo Gargallo AERCAs, respectively.

Table 2. Annual bulk atmospheric deposition fluxes ($\mu\text{g m}^{-2} \text{yr}^{-1}$) for trace elements in both the study areas. Elements with * are relative to the unfiltered aliquot.

Bulk Deposition Fluxes ($\mu\text{g m}^{-2} \text{yr}^{-1}$)	MEL	SIR	ARP	AUG	PAL	PRI	GAB	LUC	PAV	ARC	MIL
Li	71	119	95	87	60	80	107	70	65	82	129
Li *	106	154	122	107	91	103	143	113	103	103	170
Al	11,452	14,095	14,627	10,854	21,277	10,840	13,637	10,996	10,868	9473	10,088
Al *	115,686	83,106	56,735	45,045	80,124	34,625	65,605	70,569	72,517	77,969	69,712
Ti	80	56	94	83	150	112	57	112	64	69	31
Ti *	1185	907	277	173	485	230	507	356	568	387	312
V	500	557	550	499	514	449	573	360	396	564	430
V *	640	676	596	549	573	497	619	442	491	716	477
Cr	32	43	46	41	32	34	66	25	33	58	35
Cr *	117	177	109	86	80	70	146	102	108	134	110
Mn	1817	1027	946	986	2222	1228	1828	1968	2167	1467	1726
Mn *	2977	1888	1268	1648	3085	1684	2444	2820	3688	1991	2240
Fe	3015	1710	2311	3523	4577	2433	3580	2534	3412	2627	1526
Fe *	69,941	42,264	20,653	17,916	21,935	10,684	32,939	37,497	29,275	54,661	22,420
Co	25	17	17	14	30	24	24	24	32	23	22
Co *	46	31	22	20	40	26	33	37	47	35	30
Ni	243	179	157	203	118	217	396	135	156	355	131
Ni *	291	195	190	178	179	208	347	225	206	379	174
Cu	523	1086	646	759	635	935	1769	2572	1225	780	628
Cu *	763	1642	712	756	754	884	1623	3375	1396	770	685
Zn	8798	6173	3813	5559	8632	9785	11,909	5575	8588	8204	8666
Zn *	17,500	10,774	5294	8099	14,862	17,293	16,359	7818	11,955	10,642	12,791
As	62	61	51	52	59	57	94	53	55	56	56
As *	76	73	56	57	73	63	124	62	72	71	66
Se	105	104	109	87	105	97	99	89	95	84	93
Se *	166	193	188	156	192	202	193	203	225	173	207
Rb	174	185	196	151	152	181	176	134	123	136	164
Rb *	191	182	173	130	158	159	177	154	146	140	175
Sr	8723	12,528	11,076	10,168	10,438	8356	13,463	11,172	9966	12,765	16,761
Sr *	9580	16,144	11,737	10,882	9243	9685	14,655	14,889	11,219	11,709	20,743
Mo	87	158	83	129	116	72	122	77	120	233	120
Mo *	144	180	121	151	164	105	139	117	140	139	142
Cd	13	9.5	8.0	8.0	8.6	12	15	10	15	12	11
Cd *	14	11	7.3	10	8.7	12	16	10	16	12	10
Sb	37	79	47	49	61	47	70	37	43	72	74
Sb *	20	49	30	20	39	38	44	31	32	58	65
Cs	2.3	1.8	1.7	1.7	1.9	2.3	2.3	2.5	1.7	1.6	1.5
Cs *	5.8	3.8	3.1	2.3	4.0	3.3	4.4	5.2	4.3	3.7	3.6
Ba	2800	3581	2685	8072	2204	1882	4695	1214	2320	2816	4508
Ba *	3559	4488	3212	9516	2763	2114	4927	1560	2966	3093	5218
Tl	11	8.1	7.9	6.2	8.7	6.7	15	17	14	12	11
Tl *	10	9.1	8.1	6.5	8.3	7.2	15	17	14	13	12
Pb	130	52	83	60	62	124	240	71	194	101	174
Pb *	215	155	144	122	136	145	381	126	297	180	367
U	1.9	2.3	1.8	1.9	2.7	2.1	1.7	1.5	0.9	1.9	1.6
U *	4.1	5.2	2.5	2.6	3.6	3.2	2.4	2.6	2.7	2.6	2.4

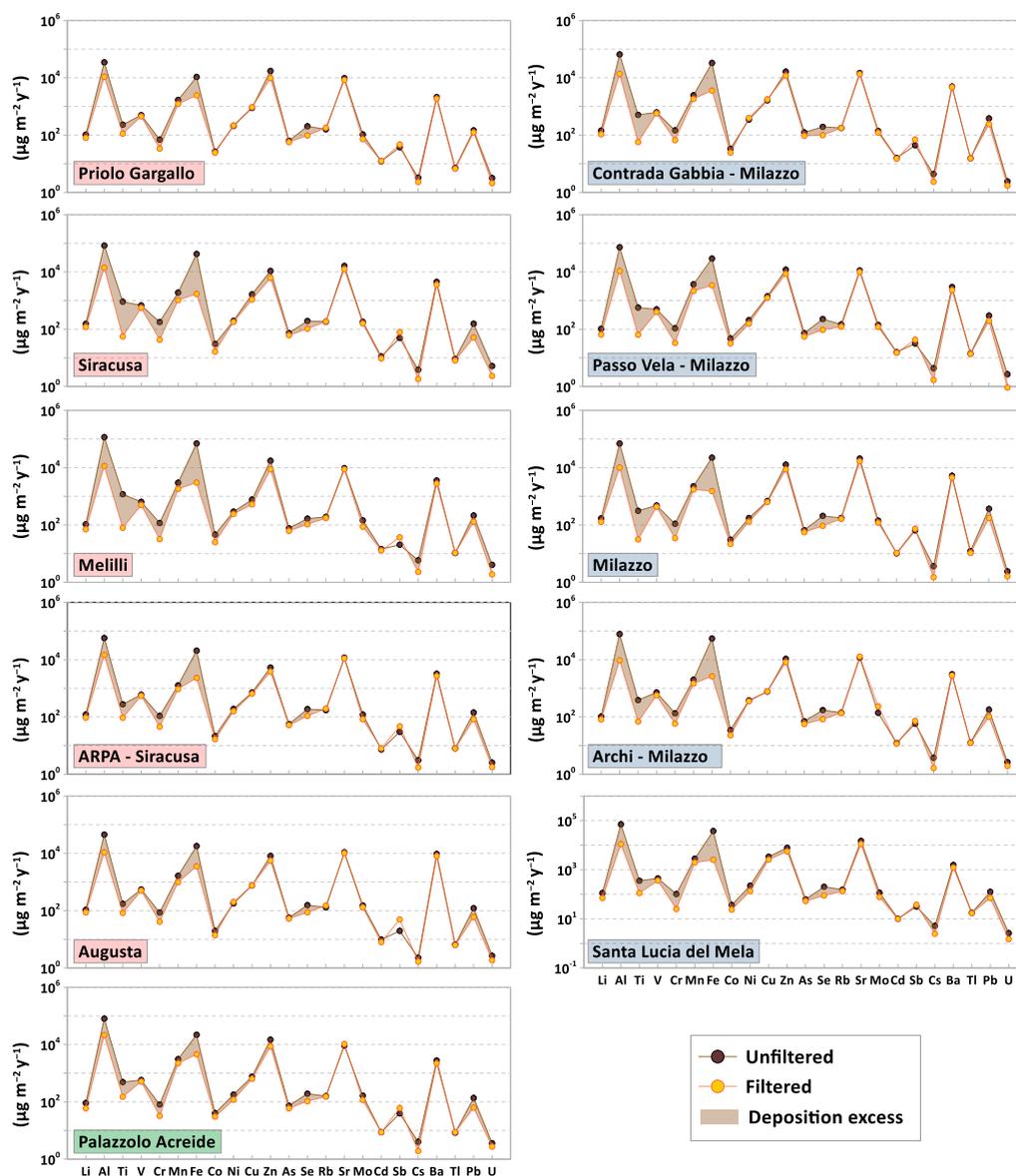


Figure 8. Annual atmospheric bulk depositions for trace elements ($\mu\text{g m}^{-2} \text{yr}^{-1}$), in the filtered and the unfiltered aliquot for all the sampling sites.

Iron represented 6% of the total trace element depositions in both the study area. The relative contributions of the least abundant elements (Li, Ti, Cr, Co, Ni, As, Se, Rb, Mo, Cd, Sb, Te, Cs, Tl, Pb, and U), account for 2.6% and 2.3% for the Milazzo and Priolo Gargallo AERCAs, respectively.

The monthly values of the deposition fluxes of all trace elements determined on the unfiltered aliquot ranged between $8.6 \mu\text{g m}^{-2} \text{d}^{-1}$ and $2509.5 \mu\text{g m}^{-2} \text{d}^{-1}$ in the Milazzo study area and from $10.2 \mu\text{g m}^{-2} \text{d}^{-1}$ to $4653.8 \mu\text{g m}^{-2} \text{d}^{-1}$ in the Priolo Gargallo study area, with arithmetic mean values of $439.9 \mu\text{g m}^{-2} \text{d}^{-1}$ and $422.6 \mu\text{g m}^{-2} \text{d}^{-1}$, respectively, thus they were very similar in the two AERCAs. The total atmospheric depositions of trace elements thus determined over one year were between $140.5 \text{mg m}^{-2} \text{yr}^{-1}$ at Santa Lucia del Mela and $163.4 \text{mg m}^{-2} \text{yr}^{-1}$ at the Archi site, for the Milazzo AERCA and between $78.8 \text{mg m}^{-2} \text{yr}^{-1}$ at the Priolo Gargallo site and $223.2 \text{mg m}^{-2} \text{yr}^{-1}$ at the Melilli site, for the Priolo Gargallo AERCA. Aluminium alone represented 50% of the total trace elements atmospheric deposition in both the study areas. Unlike what has been observed for atmospheric deposition calculated for the filtered samples, in this case iron was the second most abundant element, with relative contributions of 24% and 22% for the Milazzo and

the Priolo Gargallo AERCAs, respectively. Zinc and strontium followed, each contributing on average about 8% to the total trace element deposition, lower than those observed for the filtered aliquot due, as described, to the higher relative contribution of Fe in the atmospheric deposition of the unfiltered samples. Again, the sum of the least abundant elements (Li, Ti, Cr, Co, Ni, As, Se, Rb, Mo, Cd, Sb, Te, Cs, Tl, Pb, and U), account for 1.2% and 1.1% for the Milazzo and Priolo Gargallo AERCAs, respectively.

Atmospheric deposition values of trace elements were calculated using the VWM concentrations of each element for each survey site and the rainfall amounts accumulated during each sampling period. The rainfall amounts used for the calculations were the same for both the depositions calculated for the filtered aliquot and those calculated for the unfiltered ones. The parameter that changed and produced the large differences observed in the depositions calculated for the two aliquots was, therefore, the VWM concentrations of each element. As described before, the trace element concentrations measured in the unfiltered aliquot were on average higher than the concentrations of the same elements measured in the filtered aliquot, especially for elements such as Al and Fe. Not surprisingly, therefore, atmospheric deposition values were also much higher in the unfiltered aliquot than in the filtered aliquot for the same elements for which the largest differences in concentration values were observed.

4.5. Comparison with Other European Monitoring Sites

The Co-operative Program for Monitoring and Evaluation of the Long-range Trans-mission of Air Pollutants (EMEP) in Europe is a 30-years research program that collects chemical datasets from several research centres in twenty European countries, to assess the state of environmental pollution of the European atmosphere in terms of the concentration and transport of trace elements, particularly heavy elements, and POPs [65]. Over the years, the program has established homogeneous quality standards and sampling techniques to which all research institutes participating in it must conform. The last report available online [65] collects data from monitoring campaigns conducted in Europe during 2019, thus partly coinciding with the period in which the research presented in this article was conducted.

The dataset of EMEP includes both wet-only and bulk deposition data. The comparison between our data and the EMEP dataset (total sites = 53) is shown in Figure 9.

The atmospheric deposition fluxes of trace elements relative to different European sites were highly variable (one or more orders of magnitude), as was expected considering the different characteristics of the monitoring sites, especially concerning the sources insisting on the same sites. Comparing the median values of the trace elements deposition flux in the filtered aliquot with the median deposition flux of the European samples, higher values were observed in the Sicilian atmospheric deposition for Mo (+465%), V (+429%), Zn (+361%), Al (+208%), Co (+75%), As (+49%), Se (+48%), and Cu (+38%), while Ti (−69%), Fe (−61%), Pb (−64%), and Cr (−57%) showed lower values than in the European atmospheric deposition. Other elements, i.e., Cr, Mn, Ni, Cd, and Sb, had comparable values in Sicilian and European atmospheric deposition samples (deviations between −16% and +30%). Taking into consideration the atmospheric deposition fluxes of trace elements determined in the unfiltered aliquot, large differences were observed with the values of the same elements in European atmospheric deposition. Positive deviations between deposition fluxes in Sicilian and European atmospheric deposition were observed for Al (+1879%), Mo (+562%), Zn (+542%), V (+506%), Fe (+331%), Se (+196%), Cr (+166%), Co (+147%), As (+87%), Mn (+69%), Ti (+51%), Ni (+49%), Cu (+36%). The only elements that have shown negative deviations were Pb (−35%), Sb (−12%), and Cd (−11%). Among the elements that showed higher deposition values in the two study areas, both in the filtered and unfiltered aliquots, two groups can be distinguished. The first group may be related to the local anthropogenic input and comprises all the elements for which we had evidence of increased emissions in the Milazzo and Priolo AERCAs such as As, Ni, Cu, Zn, Se, and Cr [65]. The second group may be referred to a geogenic source associated with the Saharan

dust input such as Al, Fe, Ti, Mn, Sr, and Mo [40]. Vanadium, which was among the most enriched elements in our samples, probably originated from both sources. Although we have no emission data for the two study areas, petroleum combustion and oil refining are among the major anthropogenic sources of V to the atmosphere, while geogenic dust is its major natural source [66].

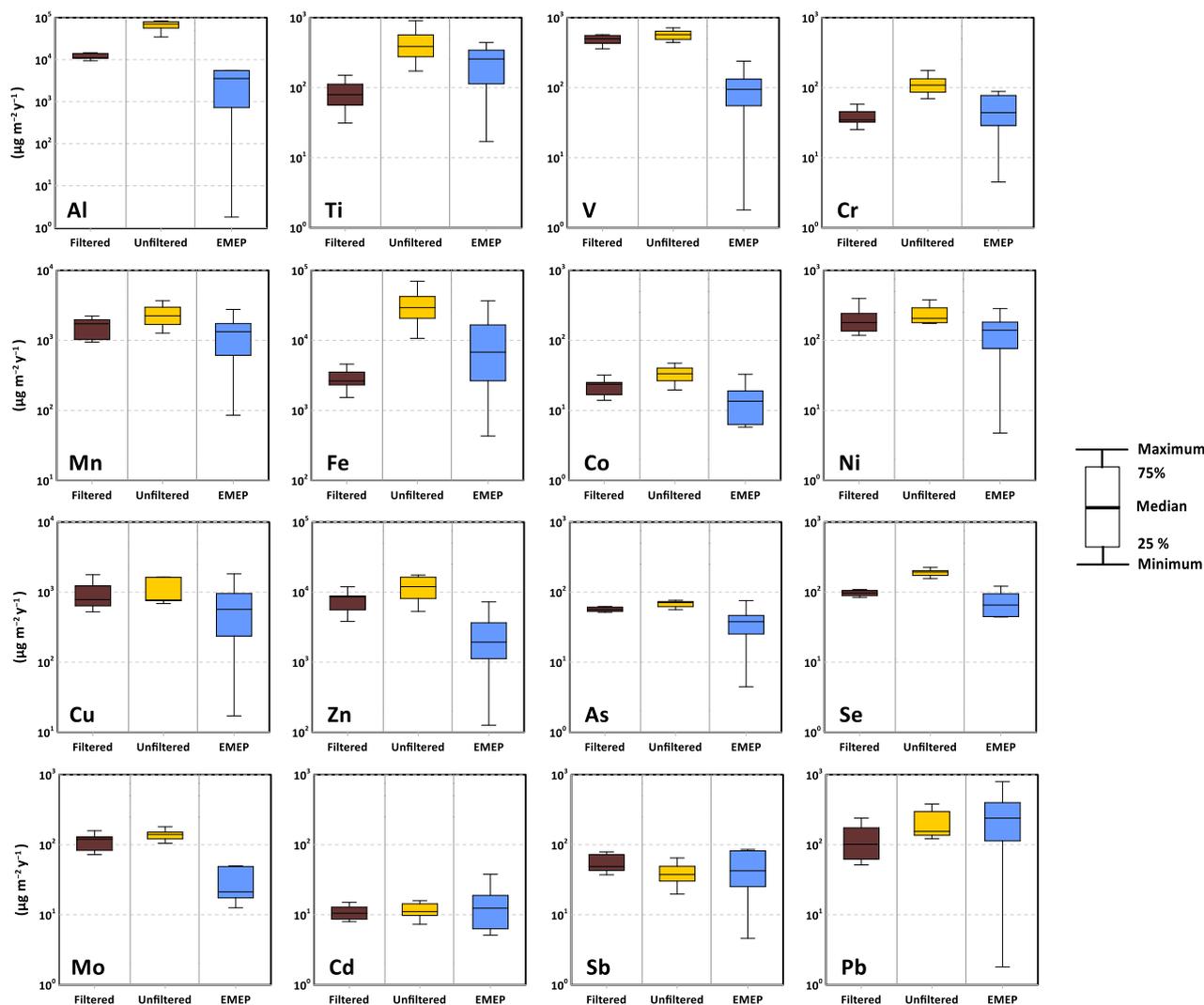


Figure 9. Comparison between some selected trace element deposition fluxes measured in atmospheric deposition samples from Sicily and Europe.

5. Conclusions

This study presented the results obtained after one year of atmospheric deposition monitoring through a network of 11 bulk collectors in two industrialised areas in eastern Sicily (Priolo and Milazzo). The study produced a novel dataset on the chemical composition and annual deposition rate of a large number of trace elements.

Most of the investigated trace elements have multiple origins and estimating how much the different sources contribute to the total deposition is beyond the scope of our study, although it is a topic of great interest. From the obtained results we can distinguish different sources, both natural and of anthropogenic origin, which persist in the atmosphere of eastern Sicily. Among the natural sources, an important geogenic component prevails, both on a local and regional scale (e.g., sirocco events and transport of Saharan dust), and the marine component, especially in the sites closest to the coast. The geogenic source mainly influences the concentrations of Ti, Zn, and Sr, while the marine input contribution

is more evident for B and Sr. Due to the presence of Etna, the volcanic source in Sicily plays an important role. The elements related to this source include Te, Tl, As, and Cd, but also less soluble elements such as Al and Fe, especially after paroxysmal events and ash fallout. Instead, the anthropogenic component is mainly linked to industrial emissions and partly to motor vehicle traffic. The positive correlation between non-marine sulfate concentrations and some trace elements (As, Cu, Se, Zn, Pb, Cr, Ni, Sb) supports an anthropogenic/industrial source for these elements.

This study also highlighted some critical issues regarding common methods of sampling and analysis of atmospheric deposition. The comparison of two different aliquots, filtered and unfiltered, has shown that the filtration method removes from the sample a substantial part of the total deposition (the less-soluble fraction). This may lead to a significant underestimation of the final deposition rate. In particular, the elements that showed the greatest differences between the two aliquots are Al, Fe, Ti, Zn, Cr, Pb, Se, Cs, and U.

Finally, a comparison of trace element deposition fluxes in the studied areas with the atmospheric deposition reported for 53 different European sites (EMEP network), showed that some elements, such as Al, V, Zn, and Mo, had higher deposition rates in the Sicilian sites compared to European ones. Many questions remain open, such as speciation and solubility of trace elements, chemical transformations during their transport, and estimation of soluble versus insoluble fractions. Although further investigations are needed to answer these complex questions, this study provides an initial insight into the atmospheric depositions of many understudied trace elements in two highly industrialised areas of Sicily, and thus it represents a starting point for future studies on environmental protection and ultimately for the wellness of the population. Future studies, currently in progress, will provide additional information regarding the problems highlighted by the present research.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/atmos14040737/s1>, Table S1: VWM concentrations ($\mu\text{g L}^{-1}$) for trace elements in both the study areas. Elements with * are relative to the unfiltered aliquot; Table S2: average crust enrichment factor (EF_{crust}) for 23 trace elements at all the sampling sites. Enrichment values refer to the filtered aliquot; enrichments values refer to the unfiltered aliquot.

Author Contributions: Conceptualization, S.C., F.B., F.P. and W.D.; methodology, S.C., F.B. and W.D.; software, F.B. and L.L.V.; formal analysis, L.B., F.B., F.S. and L.L.V.; writing-original draft preparation, S.C., F.B. and W.D.; writing-review and editing, S.C., F.B., M.S. and W.D.; supervision, M.S.; funding acquisition, M.S. and F.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by the project: Centro Internazionale di Studi Avanzati su Ambiente, ecosistema e Salute umana—CISAS, funded by CIPE-MIUR-CUP B62F15001070005.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are freely available at Interdisciplinary Earth Data Alliance (IEDA), <https://doi.org/10.26022/IEDA/112778> (accessed on 21 February 2023), reference number 2778-1.

Acknowledgments: The authors wish to thank all the people that have logistically supported our sampling and the bibliographic research, including Corrado Regalbuto (ARPA Sicilia), Paolo Trigilio (Provincia Siracusa—X Settore: Ambiente), Gianni Attard (Protezione Civile Priolo), Giuseppe Maimone, Emilio Sofia, Alebrando Fortunato, Palma Rosa Legrottaglie (I.C. Secondo Milazzo—Luigi Rizzo, Milazzo), Don Palmiro Prisutto (Augusta), Sebastiano Gianfriddo, Cosimo Rubino, and Anna Maria Abita (ARPA Sicilia). This work was supported by the project: “Centro Internazionale di Studi Avanzati su Ambiente, ecosistema e Salute umana—CISAS”, funded by CIPE-MIUR-CUP B62F15001070005.

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

References

1. Mishra, A.; Singh, A.K.; Singh, K.A.; Pandey, P.; Yadav, S.; Khan, A.H.; Barman, S.C. Urban Air Pollution and their Effects on Rainwater Characteristics in Lucknow City, India. *J. Environ. Res. Dev.* **2012**, *6*, 1127–1132.
2. Wang, L.; Shen, Z.; Lu, D.; Zhang, Q.; Zhang, T.; Lei, Y.; Xu, H. Water-soluble components in rainwater over Xi'an in northwest China: Source apportionment and pollution controls effectiveness evaluation. *Atmos. Pollut. Res.* **2019**, *10*, 395–403. [[CrossRef](#)]
3. Kajino, M.; Aikawa, M. A model validation study of the washout/rainout contribution of sulphate and nitrate in wet deposition compared with precipitation chemical composition data in Japan. *Atmos. Environ.* **2015**, *117*, 124–134. [[CrossRef](#)]
4. Andronache, C. Estimates of sulphate aerosol wet scavenging coefficient for locations in the Eastern United States. *Atmos. Environ.* **2004**, *38*, 795–804. [[CrossRef](#)]
5. Avila, A.; Alarcón, M. Relationship between precipitation chemistry and meteorological situations at a rural site in NE Spain. *Atmos. Environ.* **1999**, *33*, 1663–1677. [[CrossRef](#)]
6. Al-Momani, I.F.; Ataman, O.Y.; Anwari, A.M.; Tuncel, S.; Köse, C.; Tuncel, G. Chemical composition of precipitation near an industrial area at Izmir, Turkey. *Atmos. Environ.* **1995**, *29*, 1131–1143. [[CrossRef](#)]
7. Al-Momani, I.F.; Momani, K.A.; Jaradat, Q.M.; Massadeh, A.M.; Yousef, Y.A.; Alomary, A.A. Atmospheric deposition of major and trace elements in Amman, Jordan. *Environ. Monit. Assess.* **2008**, *136*, 209–218. [[CrossRef](#)]
8. Dollard, G.J.; Unsworth, M.H.; Harve, M.J. Pollutant transfer in upland regions by occult precipitation. *Nature* **1983**, *302*, 241–243. [[CrossRef](#)]
9. Seinfeld, J.H.; Pandis, S.N. *Atmospheric Chemical Composition and Physics from Air Pollution to Climate Change*; John Wiley and Sons, Incorporated: New York, NY, USA, 1998.
10. Gong, W.; Stroud, C.; Zhang, L. Cloud processing of gases and aerosols in air quality modelling. *Atmosphere* **2011**, *2*, 567–616. [[CrossRef](#)]
11. Amodio, M.; Catino, S.; Dambruoso, P.R.; De Gennaro, G.; Di Gilio, A.; Giungato, P.; Laiola, E.; Marzocca, A.; Mazzone, A.; Sardaro, A.; et al. Atmospheric deposition: Sampling procedures, analytical methods, and main recent findings from the scientific literature. *Adv. Meteorol.* **2014**, *2014*, 161730. [[CrossRef](#)]
12. Zhang, L.; Michelangeli, D.V.; Taylor, P.A. Numerical studies of aerosol scavenging by low-level, warm stratiform clouds and precipitation. *Atmos. Environ.* **2004**, *38*, 4653–4665. [[CrossRef](#)]
13. Zufall, M.J.; Davidson, C.I. Dry deposition of particles. In *Atmospheric Particles*; Harrison, R.M., van Grieken, R., Eds.; John Wiley Sons: Chichester, UK, 1998; Volume 5, pp. 425–473.
14. Loye-Pilot, M.D.; Martin, J.M. *The Impact of Desert Dust Across the Mediterranean*; Guerzoni, S., Chester, S., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1996.
15. Pulido-Villena, E.; Reche, I.; Morales-Baquero, R. Significance of atmospheric inputs of calcium over the southwestern Mediterranean region: High Mountain lakes as tools for detection. *Glob. Biogeochem. Cycles* **2006**, *20*, GB2012. [[CrossRef](#)]
16. Pearson, C.; Howard, D.; Moore, C.; Obrist, D. Mercury and trace metal wet deposition across five stations in Alaska: Controlling factors, spatial patterns, and source regions. *Atmos. Chem. Phys.* **2019**, *19*, 6913–6929. [[CrossRef](#)]
17. Cao, X.; Tan, C.; Wu, L.; Luo, Y.; He, Q.; Liang, Y.; Peng, B.; Christie, P. Atmospheric deposition of cadmium in an urbanized region and the effect of simulated wet precipitation on the uptake performance of rice. *Sci. Total Environ.* **2020**, *700*, 134513. [[CrossRef](#)] [[PubMed](#)]
18. Nicholson, F.A.; Smith, S.R.; Alloway, B.J.; Carlton-Smith, C.; Chambers, B.J. An inventory of trace elements inputs to agricultural soils in England and Wales. *Sci. Total Environ.* **2003**, *311*, 205–219. [[CrossRef](#)]
19. Fraga, C.G. Relevance, essentiality, and toxicity of trace elements in human health. *Mol. Asp. Med.* **2005**, *26*, 235–244. [[CrossRef](#)]
20. Ye, L.; Huang, M.; Zhong, B.; Wang, X.; Tu, Q.; Sun, H.; Wang, C.; Wu, L.; Chang, M. Wet and dry deposition fluxes of trace elements in Pearl River Delta Region (China): Characteristics, ecological risk assessment, and source apportionment. *J. Environ. Sci.* **2018**, *70*, 106–123. [[CrossRef](#)]
21. Silbergeld, E.K.; Waalkes, M.; Rice, J.M. Lead as a carcinogen: Experimental evidence and mechanisms of action. *American J. Ind. Med.* **2000**, *38*, 316–323. [[CrossRef](#)]
22. Fewtrell, L.; Kaufman, R.; Prüss-Üstün, A. *Lead: Assessing the Environmental Burden of Diseases at National and Local Levels*; WHO: Geneva, Switzerland, 2003.
23. Shao, X.; Cheng, H.; Li, Q.; Lin, C. Anthropogenic atmospheric emissions of cadmium in China. *Atmos. Environ.* **2013**, *79*, 155–160. [[CrossRef](#)]
24. Duan, J.; Tan, J. Atmospheric trace elements and Arsenic in China: Situation, sources, and control policies. *Atmos. Environ.* **2013**, *74*, 93–101. [[CrossRef](#)]
25. Adamiec, E.; Jarosz-Krzemińska, E.; Wieszala, R. Trace elements from non-exhaust vehicle emissions in urban and motorway road dusts. *Environ. Monit. Assess.* **2016**, *188*, 369. [[CrossRef](#)] [[PubMed](#)]
26. Pulles, T.; Denier van der Gon, H.; Appelmann, W.; Verheul, M. Emission factors for trace elements from diesel and petrol used in European vehicles. *Atmos. Environ.* **2012**, *61*, 641–651. [[CrossRef](#)]
27. Tan, J.H.; Duan, J.C.; Ma, Y.L.; Yang, F.M.; Cheng, Y.; He, K.B.; Yu, Y.C.; Wang, J.W. Source of atmospheric trace elements in winter in Foshan, China. *Sci. Total Environ.* **2014**, *493*, 262–270. [[CrossRef](#)] [[PubMed](#)]
28. Hu, Y.; Cheng, H. Application of stochastic models in identification and apportionment of trace element pollution sources in the surface soils of a large-scale region. *Environ. Sci. Technol.* **2013**, *47*, 3752–3760. [[CrossRef](#)]

29. Aucélio, R.Q.; de Souza, R.M.; de Campos, R.C.; Miekeley, N.; da Silveira, C.L.P. The determination of trace elements in lubricating oils by atomic spectrometry. *Spectrochim. Acta Part B At. Spectrosc.* **2007**, *62*, 952–961. [[CrossRef](#)]
30. Hjortenkrans, D.S.T.; Bergbäck, B.G.; Häggerud, A.V. Metal emissions from brake linings and tires: Case studies of Stockholm, Sweden 1995/1998 and 2005. *Environ. Sci. Technol.* **2007**, *41*, 5224–5230. [[CrossRef](#)]
31. Decreto Legislativo 13/08/2010, n. Decreto Legislativo 13/08/2010, n.155 Attuazione Della Direttiva 2008/50/CE Relativa Alla Qualità Dell'aria Ambiente e per Un'aria più Pulita in Europa (10G0177) (GU Serie Generale n.216 del 15/09/2010—Suppl. Ordinario n.217. Available online: <https://www.gazzettaufficiale.it/eli/id/2010/09/15/010G0177/sg> (accessed on 10 January 2023).
32. Cobelo-García, A.; Filella, M.; Croot, P.; Frazzoli, C.; du Laing, G.; Ospina-Alvarez, N.; Rauch, S.; Salaun, P.; Schäfer, J.; Zimmermann, S. COST action TD1407: Network on technology-critical elements (NOTICE)—From environmental processes to human health threats. *Environ. Sci. Pollut. Res.* **2015**, *22*, 15188–15194. [[CrossRef](#)]
33. Avila, A.; Rodrigo, A. Trace metal fluxes in bulk deposition, throughfall and stemflow at two evergreen oak stands in NE Spain subject to different exposure to the industrial environment. *Atmos. Environ.* **2004**, *38*, 171–180. [[CrossRef](#)]
34. Azimi, S.; Ludwig, A.; Thévenot, D.R.; Colin, J.L. Trace metal determination in total atmospheric deposition in rural and urban areas. *Sci. Total Environ.* **2003**, *308*, 247–256. [[CrossRef](#)]
35. Hou, H.; Takamatsu, T.; Koshikawa, M.K.; Hosomi, M. Trace elements in bulk precipitation and throughfall in a suburban area of Japan. *Atmos. Environ.* **2005**, *39*, 3583–3595. [[CrossRef](#)]
36. Moaref, S.; Sekhavatjou, M.S.; Alhashemi, A.H. Determination of trace elements concentration in wet and dry atmospheric deposition and surface soil in the largest industrial city, southwest of Iran. *Int. J. Environ. Res.* **2014**, *8*, 335–346. [[CrossRef](#)]
37. Sakata, M.; Marumoto, K.; Narukawa, M.; Asakura, K. Regional variations in wet and dry deposition fluxes of trace elements in Japan. *Atmos. Environ.* **2006**, *40*, 521–531. [[CrossRef](#)]
38. Báez, A.; Belmont, R.; García, R.; Padilla, H.; Torres, M.C. Chemical composition of rainwater collected at a southwest site of Mexico City, Mexico. *Atmos. Res.* **2007**, *86*, 61–75. [[CrossRef](#)]
39. Fernández-Olmo, I.; Puente, M.; Montecalvo, L.; Irabien, A. Source contribution to the bulk atmospheric deposition of minor and trace elements in a Northern Spanish coastal urban area. *Atmos. Res.* **2014**, *145–146*, 80–91. [[CrossRef](#)]
40. Guerzoni, S.; Molinaroli, E.; Rossini, P.; Rampazzo, G.; Quarantotto, G.; De Falco, G.; Cristini, S. Role of desert aerosol in metal fluxes in the Mediterranean area. *Chemosphere* **1999**, *39*, 229–246. [[CrossRef](#)]
41. Theodosi, C.; Markaki, Z.; Tselepidis, A.; Mihalopoulos, N. The significance of atmospheric inputs of soluble and particulate major and trace elements to the eastern Mediterranean seawater. *Mar. Chem.* **2010**, *120*, 154–163. [[CrossRef](#)]
42. Pan, Y.P.; Wang, Y.S. Atmospheric wet and dry deposition of trace elements at 10 sites in Northern China. *Atmos. Chem. Phys.* **2015**, *15*, 951–972. [[CrossRef](#)]
43. Loya-González, D.; López-Serna, D.; Alfaro-Barbosa, J.M.; López-Reyes, A.; González-Rodríguez, H.; Cantú-Silva, I. Chemical composition of bulk precipitation and its toxicity potential index in the metropolitan area of Monterrey, Northeastern Mexico. *Environments* **2020**, *7*, 106. [[CrossRef](#)]
44. Calabrese, S.; Randazzo, L.; Daskalopoulou, K.; Milazzo, S.; Scaglione, S.; Vizzini, S.; Tramati, C.D.; D'Alessandro, W.; Brusca, L.; Bellomo, S.; et al. Mount Etna volcano (Italy) as a major “dust” point source in the Mediterranean area. *Arab. J. Geosci.* **2016**, *9*, 219. [[CrossRef](#)]
45. Tang, A.; Zhuang, G.; Wang, Y.; Yuan, H.; Sun, Y. The chemistry of precipitation and its relation to aerosol in Beijing. *Atmos. Environ.* **2005**, *39*, 3397–3406. [[CrossRef](#)]
46. Fano, V.; Cernigliaro, A.; Scondotto, S.; Pollina Addario, S.; Caruso, S.; Mira, A.; Forastiere, F.; Perucci, C.A. Stato di Salute Della Popolazione Residente Nelle Aree ad Elevato Rischio Ambientale e Nei Siti di Interesse Nazionale Della Sicilia: Analisi Della Mortalità (aa 1995–2000) e dei Ricoveri Ospedalieri (aa 2001–2003). Report: Epidemiologia Sviluppo Ambientale 2019. Assessorato Sanità Dipartimento Osservatorio Epidemiologico (Regione Siciliana); Dipartimento di Epidemiologia ASL RME. Available online: https://www.epicentro.iss.it/ambiente/sicilia_sintesi (accessed on 1 November 2022).
47. Brugnone, F.; D'Alessandro, W.; Parello, F.; Liotta, M.; Bellomo, S.; Prano, V.; Li Vigni, L.; Sprovieri, M.; Calabrese, S. Atmospheric Deposition around the Industrial Areas of Milazzo and Priolo Gargallo (Sicily–Italy)—Part A: Major Ions. *Int. J. Environ. Res. Public Health* **2023**, *20*, 3898. [[CrossRef](#)] [[PubMed](#)]
48. ISPRA Siti di Interesse Nazionale (SIN). 2002. Available online: <https://www.isprambiente.gov.it/it/attivita/suolo-e-territorio/siti-contaminati/siti-di-interesse-nazionale-sin> (accessed on 10 December 2022).
49. Bevilacqua, M.; Braglia, M. Environmental efficiency analysis for ENI oil refineries. *J. Clean. Prod.* **2014**, *10*, 85–92. [[CrossRef](#)]
50. Duplay, J.; Semhi, K.; Mey, M.; Messina, A.; Quaranta, G.; Huber, F.; Aubert, A. Geogenic versus anthropogenic geochemical influence on trace elements contents in soils from the Milazzo Peninsula. *Geochemistry* **2008**, *74*, 691–704. [[CrossRef](#)]
51. Bolle, H.J. Climate, Climate Variability, and Impacts in the Mediterranean Area: An Overview. In *Mediterranean Climate; Regional Climate Studies*; Springer: Berlin/Heidelberg, Germany, 2008. [[CrossRef](#)]
52. Liotta, M.; Bellissimo, S.; Favara, R.; Valenza, M. Isotopic composition of single rain events in the central Mediterranean. *J. Geophys. Res.* **2008**, *113*, D16304. [[CrossRef](#)]
53. WMO. *Guide to Meteorological Instrument and Observing Practice*; WMO No. 8 2018; WMO: Geneva, Switzerland, 2018.
54. EMEP/CCC. *Manual for Sampling and Chemical Analysis*. EMEP Cooperative Program for Monitoring and Heavy Metals and POP Measurements 2009; EMEP/CCC: 2009; NILU: Oslo, Norway, 2009.

55. Harmens, H.; Mills, G.; Hayes, F.; Williams, P. ICP Vegetation Annual Report—2003/2004. ICP Vegetation. 2004. Available online: <https://icpvegetation.ceh.ac.uk/icp-vegetation-annual-report-20032004> (accessed on 13 December 2022).
56. Calabrese, S.; Aiuppa, A.; Allard, P.; Bagnato, E.; Bellomo, S.; Brusca, L.; Parello, F. Atmospheric sources and sinks of volcanogenic elements in a basaltic volcano (Etna, Italy). *Geochim. Cosmochim. Acta* **2011**, *75*, 7401–7425. [[CrossRef](#)]
57. Menichini, E. *Metodi per la Determinazione di Arsenico, Cadmio, Nichel e Idrocarburi Policiclici Aromatici Nelle Deposizioni Atmosferiche*; v, 23, Rapporti ISTISAN 06/38; Ist. Superiore di Sanità: Rome, Italy, 2006.
58. Brugnone, F.; Calabrese, S.; D’Alessandro, W.; Parello, F.; Li Vigni, L.; Saiano, F.; Liotta, M.; Bellomo, S.; Brusca, L.; Sprovieri, M.; et al. Major ions and trace elements composition of rainwater around the two industrial areas of Milazzo and Priolo Gargallo (Sicily-Italy), Version 1.0. *Interdiscip. Earth Data Alliance (IEDA)* **2023**. [[CrossRef](#)]
59. Wedepohl, K.H. The Composition of the Continental Crust. *Geochim. Cosmochim. Acta* **1995**, *59*, 1217–1232. [[CrossRef](#)]
60. Moreda-Piñero, J.; Alonso-Rodríguez, E.; Turnes-Carou, I.; Moscoso-Pérez, C.; Blanco-Heras, G.; Tellado, L.G.; López-Mahía, P.; Muniategui-Lorenzo, S.; Prada-Rodríguez, D. Inorganic ions and trace metals bulk deposition at an Atlantic Coastal European region. *J. Atmos. Chem.* **2016**, *74*, 1–21. [[CrossRef](#)]
61. Abita, A.M.; Basiricò, L.; Pampalone, V. *L’inventario delle Emissioni in Atmosfera della Regione Siciliana. Revisione Dell’aggiornamento All’anno 2015. U.O.C. Qualità Dell’aria; ARPA SICILIA*: Palermo, Italy, 2022.
62. Brugnone, F.; D’Alessandro, W.; Calabrese, S.; Li Vigni, L.; Bellomo, S.; Brusca, L.; Prano, V.; Saiano, F.; Parello, F. A Christmas gift: Signature of the 24th December 2018 eruption of Mt. Etna on the chemical composition of bulk deposition in eastern Sicily. *Ital. J. Geosci.* **2020**, *139*, 341–358. [[CrossRef](#)]
63. Reimann, C.; de Caritat, P. Intrinsic Flaws of Element Enrichment Factors (EFs) in Environmental Geochemistry. *Environ. Sci. Technol.* **2000**, *34*, 5084–5091. [[CrossRef](#)]
64. Xing, J.; Song, J.; Yuan, H.; Li, X.; Li, N.; Duan, L.; Qu, B.; Wang, Q.; Kang, X. Chemical characteristics, deposition fluxes and source apportionment of precipitation components in the Jiaozhou Bay, North China. *Atmos. Res.* **2017**, *190*, 10–20. [[CrossRef](#)]
65. EMEP/CCC-Report 3/2021. Heavy ELEMENTS and POP Measurements 2019. 2021. Available online: https://projects.nilu.no/ccc/reports/EMEP_CCC-Report_3_2021_HM_and_POP_measurements_2019.pdf (accessed on 7 October 2022).
66. Schlesinger, W.H.; Klein, E.M.; Vengosh, A. Global biogeochemical cycle of vanadium. *Proc. Natl. Acad. Sci. USA* **2017**, *114*, E11092–E11100. [[CrossRef](#)] [[PubMed](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.