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Chlorophytum comosum: A Bio-Indicator for Assessing the Accumulation of Heavy Metals Present in The Aerosol Particulate Matter (PM)

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Abstract: The present research focuses on the use of *Chlorophytum comosum* as a bio-indicator able to accumulate, through its leaves, heavy metals present in the aerosol particulate matter (PM) in the city of Milan (Italy). For this purpose, some specimens were exposed in selected sites at the Milan University Campus for increasing periods (7, 30, 60, 128 and 165 days). The collected leaves were then analyzed to quantify Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn concentrations by inductively coupled plasma optical emission spectroscopy (ICP–OES). The leaves' surfaces were also examined by scanning electron microscopy coupled with energy dispersion spectroscopy (SEM-EDS). *Chlorophytum comosum* has proved to be a good system for studying the accumulation of heavy metals. The metals present with the higher concentration were Zn and Mn followed by Cd and Cr while Co, Ni and Pb were present in lower concentration. Although the sites investigated are not very far from each other, differences in the concentration of the heavy metals analyzed were found. Furthermore, in the monitoring period considered (July 2018–December 2018) the plant was a good proxy for tracking the concentration of zinc in Milan's PM.

Keywords: bio-indicators; *Chlorophytum comosum*; heavy metals; ICP-OES; aerosol particulate matter

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1. Introduction

The problem of monitoring air pollution, and in particular aerosol particulate matter (PM), is now a priority, and pollutants concentrations are regulated at both international and national level (Directive 2008/50/EC).

In Europe, air pollutants emissions have been recently reduced, leading to an improvement of the air quality. However, air quality problems persist and many people in Europe live in large cities, where air quality standards are exceeded. Among air pollutants, PM represents a threat to human health because of its particle size and ability to penetrate into the respiratory and circulatory systems, and also because of its chemical composition. Among the chemical constituents, many heavy metals play a key role because of their high toxicity.

Air pollutants monitoring (NO_2, O_3, SO_2, PM, etc.) is generally carried out through the use of analytical instrumentation, established by the regulations in force. The instruments are located in the monitoring stations placed in different areas of interest in order to investigate both sites characterized by high pollution and representative of the urban background. At these stations, PM is collected on filters subsequently analyzed to assess the main chemical constituents to acquire information on both toxic substances, including heavy metals and emission sources [1–5].

The use of bio-indicators could represent a complementary method to trace environmental pollution in different matrix such as air, soil, water, etc. [6–10]. It is worth noting that biomonitoring is efficient, highly specific and low cost with respect to conventional methodologies. Biomonitoring uses biological organisms (such as plants, animals, fungi, etc.) to assess concentrations of contaminants over wide spatial-temporal scales [10].

In recent decades, many plant species, lichens, mosses, ferns, higher plants, have been used as bio-indicators and/or as bio-accumulators to assess trace element contamination [10–20].

In the case of plants, air quality biomonitoring studies mainly use the leaves, are more exposed to the effects of pollutants and are also the site of their accumulation.

Metals are absorbed from the soil, through the root system, and from the air through the plant's aerial organs.

The bioaccumulation efficiency of trace elements is due to the considerable cation exchange capacity, which is attributable both to the fact that cell wall constituents (mainly carboxylic acids) are negatively charged and can form ionic bonds with cations in soluble form [21], and to the biochemical activities of plasma membranes or cytoplasm [22]. The efficiency of metal retention depends on many factors, for example, tissue age and growth conditions [23].

Heavy metals are present in aerosol PM in low and trace concentrations. They are of natural or anthropogenic origin and different kinds of sources contribute to their emissions including traffic and industrial activities. Milan, located in the center of the Po Valley (Northern Italy), represents a hot spot regarding atmospheric pollution and the limits set for PM10 (particles with aerodynamic diameters lower than 10 μm) and PM 2.5 (particles with aerodynamic diameters lower than 10 μm) by the current regulation are often exceeded [24–26].

In this study, *Chlorophytum comosum* (also known as spider plant) was tested as a bio-indicator to monitor atmospheric pollution in Milan. In particular the presence of airborne heavy metals through their uptake and accumulation in the plant leaves was studied. The choice fell on *Chlorophytum comosum* because it reproduces vegetatively and is adapted to the climatic conditions of Milan.

Cd, Co, Cu, Cr, Mn, Ni, Pb and Zn were chosen to be investigated in this study because of their toxicity and adverse effects on human health. It is worth noting that among these As, Cd, Ni and Pb should be determined on the basis of the legislation in force in Italy (D. Lgs. 155/2010). These elements represent an environmental risk and are also classified by the IARC (International Agency for Research on Cancer) as carcinogenic to humans.

The use of *Chlorophytum comosum* as a pollutants accumulator is already attested in the literature. This plant is a soil remediator being able to absorb Pb [27], Cd [28–30], Se and As [31] while its leaves accumulate Hg [32]. It is also able to absorb toxic organic pollutants such as formaldehyde [33,34] and benzene [35] and is also able to retain CO_2 [36,37]. In spite of the numerous studies dealing with the spider plant capacity in reducing atmospheric pollutants, to our knowledge, specific studies aimed at the assessment of metals absorption on its leaves in order to monitor atmospheric pollution, are not present in the literature.

It is known that the surface morphology of the leaves influences the ability of a specific plant to retain PM [38,39]. Furthermore, depending on the chemical species, PM could be retained on the leaves' surfaces or in the epicuticular waxes [40,41]. The mechanism by which heavy metals are absorbed by leaves is not yet fully understood but it probably occurs through absorption into the cuticle and subsequent penetration into the stomatal pores [41,42]. *Chlorophytum comosum* is among the 120 plant species assayed for phytoremediation of pollutants from indoor air [43] accumulating PM into the leaves and contributing in this way to improve air quality. Parameters such as the physiological features of the plant and leaf size greatly influences the potential of the plant to adsorb the deposited PM and heavy metals.

Taking into account all this variability, the aim of this study was to assess if *Chlorophytum comosum* was able to retain the typical heavy metals present in the aerosol PM. Due to the specific characteristics of this plant (all individuals of the species are genetically equal), it was selected as a potential bio-indicator and as a proxy of urban atmospheric pollution due to heavy metals. For this purpose, a few individuals of this species were exposed in a restricted area of Milan and collected at selected interval times reaching 165 days of exposure.

Heavy metals were quantified, after the leaves samples digestion, by inductively coupled plasma optical emission spectroscopy (ICP–OES). Scanning electron microscopy coupled with energy dispersion spectroscopy (SEM–EDS) was applied to study the leaves' morphology and the chemical composition of the particles present on their surfaces. The quantitative results obtained were then compared with the metals concentrations trends determined in the aerosol particulate matter collected in Milan by the Regional Agency for the Environmental Protection (ARPA Lombardia).

2. Materials and Methods

Sixteen plants of *Chlorophytum comosum* were placed in four sites in Milan city in the area known as "Città Study" where the Milan University Campus is located (Figures 1 and 2). In particular, the four selected sites were: ARPA Lombardia (Regional Agency for the Environmental Protection of the Lombardy Region) monitoring station (Via Pascal), the Department of Biosciences, the Department of Chemistry and the University Botanical Garden (Via Golgi) (see Figure 2 for the precise locations). It is worth noting that, as this a pilot and preliminary study, it was decided, both for logistical and economic issues, to select only four sites. These sites presented some differences even if located within the same city area.

In all the four sites the plants were protected from direct water and strong air currents. In the case of the Chemistry Department and Bioscience Department, the plants were placed on a protected balcony; in the case of the Botanical Garden, a suitable plastic cover was created to protect the plants from direct runoff; at the ARPA monitoring station, the plants were placed, as indicated by the red arrow in Figure 1c, below the two gravimetric PM samplers inside the enclosure of the station. Moreover, the plants were placed at different heights in order to assess possible differences due to pollutants impact. In particular, the samples located near ARPA station and Botanical Garden were at ground level while the samples placed at Chemistry Department and at Biosciences Department were at 6 m of altitude.

In each site, four plants were exposed, two in July 2018 and two in October 2018, for each site, as reported in Table 1. The collections of the leaves' samples took place after 7, 30, 60, 128 and 165 days of exposure. It is worth noting that the samples corresponding to an exposure period of 30 days came from the plants exposed in October. In fact, due to logistical and organizational reasons, it was not possible to collect the 30-day samples corresponding to the specimens exposed in July. Furthermore, for simplicity, the collections performed at 7 days from the lants exposed in July, are not indicated.

When the plants specimens were exposed, they were 30 days old, grown in the greenhouse of the Botanical Garden and provided by the Department of Biosciences. *Chlorophytum comosum* plants were grown on Vigorplant C14 which is a commercial land for planting. The plants (Figure 1) showed bright green leaves with a white stripe along the central axis with an average length of 21 cm and an average width of 0.5 cm.

Samples were collected and processed as described by Gawrońska and Bakera (2014) [43] Leaves with no obvious damages were chosen and picked up without using metallic scissors and stored at 4 °C [19,43,44]. Before their manipulation, leaves were washed several times with distilled water, frozen in liquid nitrogen and grinded. The powders were dried in an oven at 75 °C until constant weight was achieved [45].

In order to assess metals concentration, the powder samples were submitted to a digestion procedure. In particular 5 mL of HNO_3 and 1 mL of H_2O_2 were added to 0.25 g of powder and mineralized using the CEM device model MARS 1 (CEM Srl, Cologno al Serio (BG), Italy). The following program was set: 1 min at 250 W; 1 min a 0 W; 5 min at 250 W; 4 min at 400 W; 4 min at 600 W. Once finished, MQ (MilliQ) water was added till 50 mL and the samples were filtered (filters with pores of 0.45 μm).

Together with the plants specimens, as a comparison, a not-exposed plant was analyzed. The plant was kept in an indoor environment (in particular, in a room inside the university not exposed to any internal pollution source) and analyzed at the end of the experiment.

The metals monitored were Cd, Co, Cu, Cr, Mg, Ni, Pb and Zn. Their quantification was carried out by inductively coupled plasma optical emission spectroscopy (ICP–OES) using a Perkin Elmer instrument model Optima 8000 (Perkin Elmer, Milano, Italy). A QA/QC procedure was performed as described in Fermo et al. 2020 [46]. The multi-elemental solutions used as working standards cover a range from 20 ppb to 20 ppb.

Table 1. Sampling sites where *Chlorophytum comosum* plants were exposed in Milan together with exposure date, collection date and exposure duration; 4 plants were exposed in each site, 2 in July and 2 in October; for the plants exposed in July a collection at 7 days, not indicated in the table, was also performed; samples collected at 30 days come from plants exposed in October.

Sampling Site	Site ID	Exposure Date	Collection Date and Exposure Duration		
ARPA Regional Agency for the Environmental Protection	ARPA	July 2018	September 2018—60 days	November 2018—128 days	December 2018—165 days
		July 2018	September 2018—60 days	November 2018—128 days	December 2018—165 days
		October 2018	-	November 2018—30 days	-
		October 2018	-	November 2018—30 days	-
Biosciences Department University of Milan	Bio Dept	July 2018	September 2018—60 days	November 2018—128 days	December 2018—165 days
		July 2018	September 2018—60 days	November 2018—128 days	December 2018—165 days
		October 2018	-	November 2018—30 days	-
		October 2018	-	November 2018—30 days	-
Chemistry Department University of Milan	Chem Dept	July 2018	September 2018—60 days	November 2018—128 days	December 2018—165 days
		July 2018	September 2018—60 days	November 2018—128 days	December 2018—165 days
		October 2018	-	November 2018—30 days	-
		October 2018	-	November 2018—30 days	-
Botanical Garden University of Milan	Botanical Garden	July 2018	September 2018—60 days	November 2018—128 days	December 2018—165 days
		July 2018	September 2018—60 days	November 2018—128 days	December 2018—165 days
		October 2018	-	November 2018—30 days	-
		October 2018	-	November 2018—30 days	-

SEM–EDS analysis were performed by a Hitachi model TM4000 and a Hitachi model TM1000 instrument (Nanovision Srl, Brugherio (MB), Italy) equipped with an EDS microprobe used for the semi-quantitative analyses following a procedure already applied in other cases [47]. For sample preparation some small fragments of leaves plant, obtained from the specimens after 165 days of exposure, were cut by means of pliers and a surgical scalpel; then, the sample was directly placed on a double-sided graphite adhesive disc placed on the stub and inserted into the instrument chamber. Microanalysis was performed by TM400 instrument using an energy dispersive spectrometry EDS Oxsford -AztecOne. Analyses were carried out with an acceleration voltage of 5 kV, 10 kV, 15 kV and 20 kV and under high vacuum conditions.

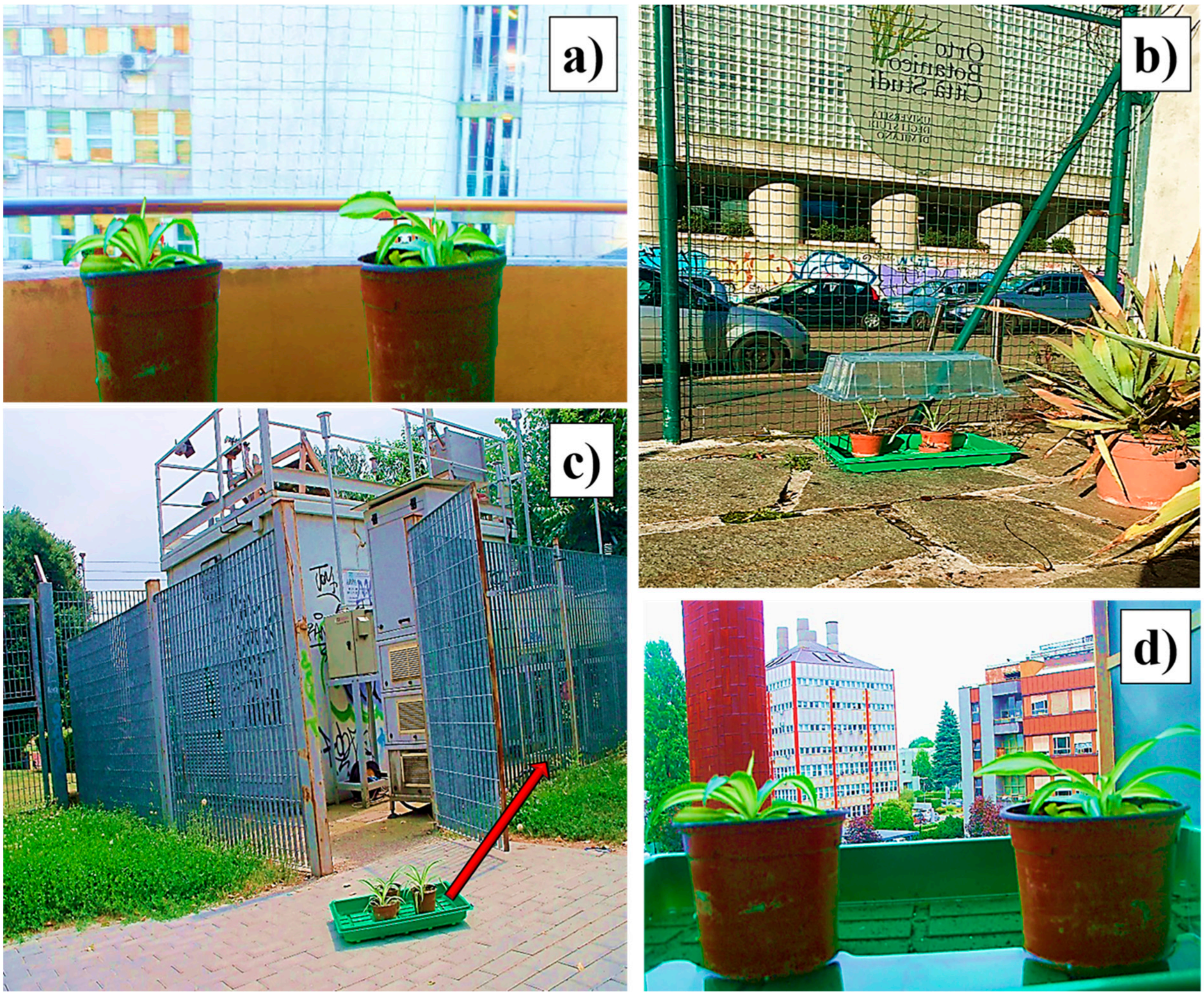

Figure 1. Some of the investigated locations; (**a**) Bioscience Department; (**b**) Botanical Garden; (**c**) ARPA Lombardia monitoring station; (**d**) Chemistry Department. In all the sites plants were located sheltered from water: in case of site (**a**,**d**) they were placed on a protected balcony; in case of (**b**) a suitable plastic cover has been created to protect the plants from direct runoff; in case of (**c**) the plants were placed, as indicated by the red arrow, below the two gravimetric PM samplers inside the enclosure of the ARPA monitoring station.

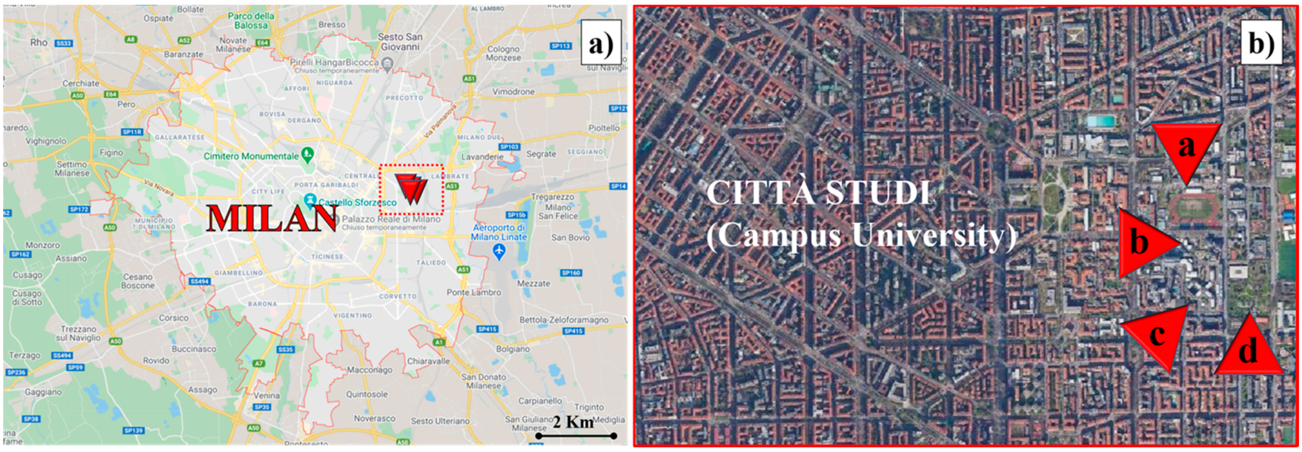

Figure 2. The investigated area in Milan (**a**) with the indications of the sampling sites (**b**); in this case a represents ARPA station; b the Bioscience Department; c the Chemistry Department and d the Botanical Garden.

3. Results

To monitor the presence of the selected heavy metals (Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn) in the air of Milan, 16 plants were exposed in 4 different areas of the city and the leaves collected, as described in Table 1. For the samples collected at 7, 30, 60 and 128 day only Cr, Pb and Zn were measured while for the samples collected at 165 days all the 8 elements were quantified. In Figure 3a,b the trends observed for Cr and Zn for the four examined sites are shown. Zn is present in some cases in concentrations higher than 150 ppm while Cr is at maximum about 5 ppm. Pb concentrations (not shown in this case) reached a maximum at about 20 ppb. In some cases (missing data in Figure 3a,b) it was not possible to get a sample suitable for the analysis.

Together with the values determined on the exposed samples, the concentrations detected for the not-exposed plant (see paragraph Methods and Materials), used as comparison, are shown. It is worth noting that this plant was analyzed after 165 days (corresponding to the maximum exposure period). As mentioned in the introduction, even if all the specimens should be similar, there is certain variability among the plants and the comparison with the reference is not easy to make. In the case of Cr, only the samples at 165 for ARPA and Bioscience Department are clearly higher, while the other cases are similar even if it cannot be excluded that the initial concentration in the not-exposed plant was slightly lower. As for Zn, the concentrations determined for the exposed plants are higher with only very few exceptions.

In Figure 4a,b, the trends observed for all the elements for the four examined sites at 165 days are shown. Together with the heavy metals concentration determined for the exposed species, the values determined for the not-exposed plant are reported as well. With the only exception of copper, for which the concentration in the not-exposed plant is comparable with those determined for the exposed plants, for all the other elements *Chlorophytum comosum* can be considered as a good bioindicator for heavy metals accumulation (in case of Cr surely at 165 days). The metals present with the higher concentration are Zn and Mn followed by Cd and Cr while Co, Ni and Pb are present in lower concentration (at maximum about 30 ppb for Ni and about 20 for Pb).

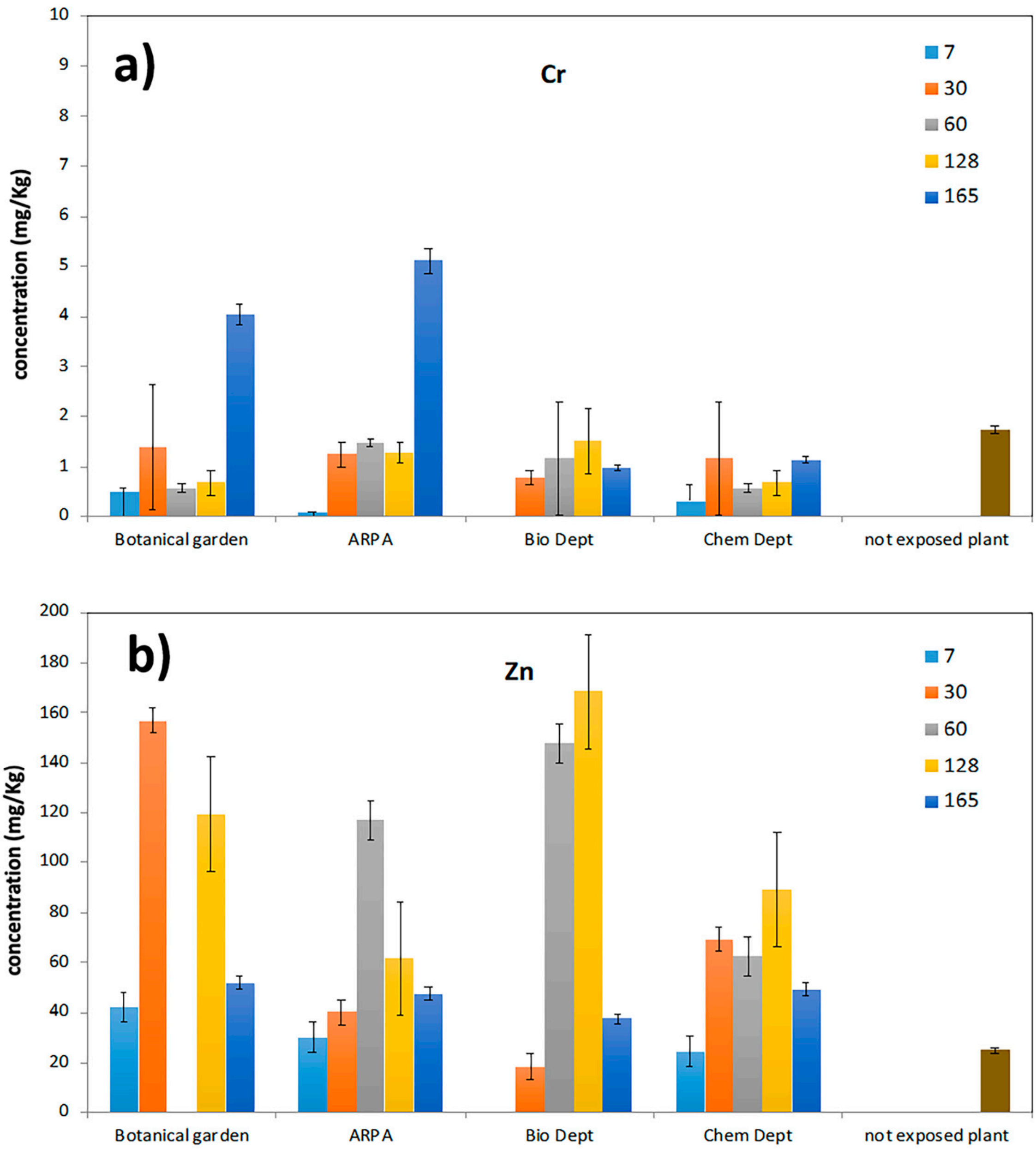

Figure 3. Concentrations trends for Cr (**a**) and Zn (**b**) in the *Chlorophytum comosum* analyzed samples in the different sites in Milan and for different exposure times (7, 30, 60, 128 and 165 days); the concentrations determined for the not-exposed plant have been added for both metals (reported in brown colour).

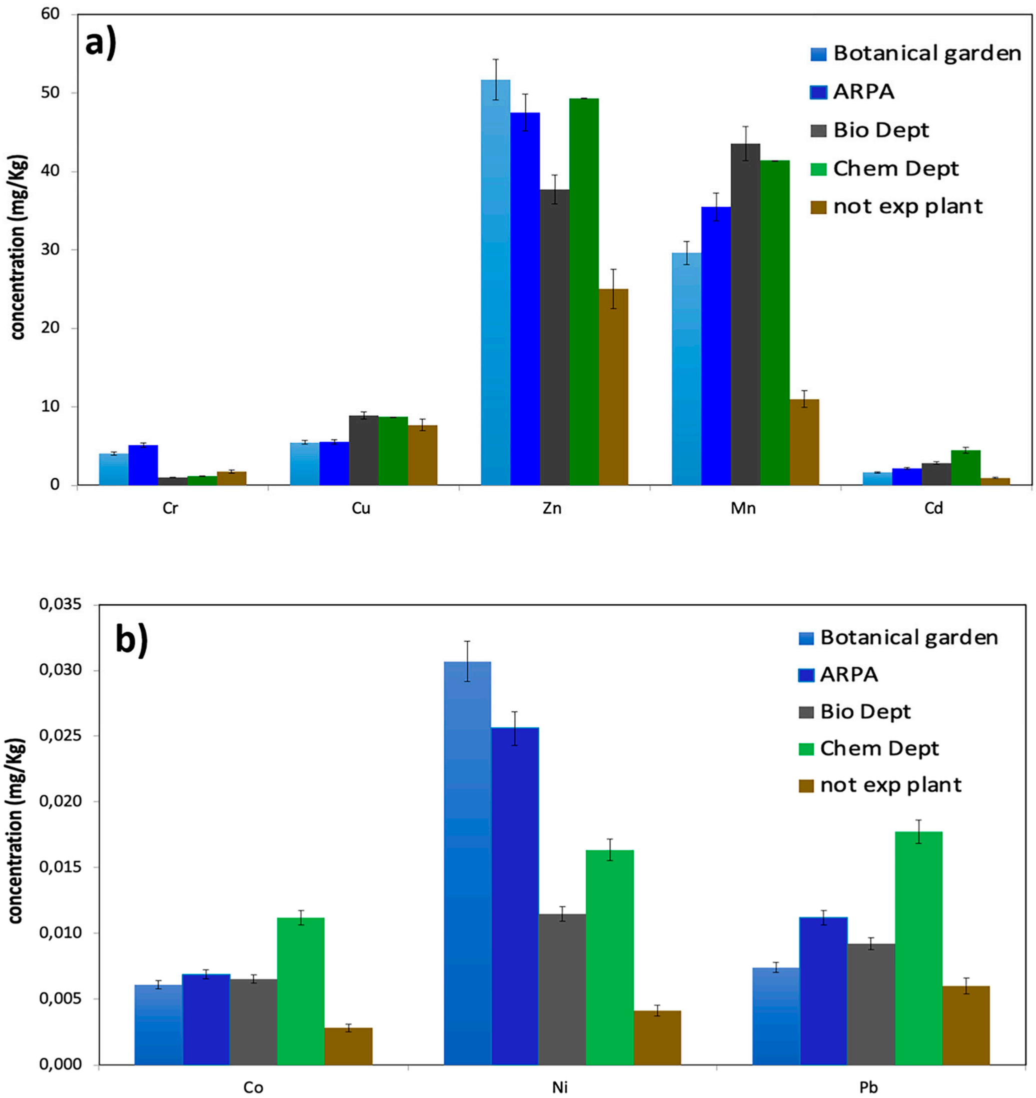

Figure 4. Concentrations trends for Cr, Cu, Zn, Mn, Cd (**a**) and Co, Ni, Pb (**b**) in the *Chlorophytum comosum* analyzed samples in the different sites in Milan and for an exposure time of 165 days; the metals concentrations for the not-exposed plant used as reference are also reported.

In order to assess the presence of particles on the leaves' surfaces some measurements were carried out by SEM-EDS technique. As it is evident from Figure 5, the particles dimensions are quite variable ranging from some µm to more than 100 µm. Thanks to the comparison between BSE (back scattered electrons) and mix (BSE + secondary electrons) images, it is possible to better evidence the three-dimensionality of the surface. In fact, from mix images, it appears clearer if a particle is present on the surface (for example the larger particles in Figure 5a,b) or are embedded (as for the smaller spherical particles in Figure 5c,d). In Figure 5e,f a large particle present on the leave surface is shown. EDS analysis evidenced, on the leaves' surface, the presence of macro elements such as Ca, K and Na in accordance with what already reported in Aberoumand et al. [44]. Mg and Cl were also present. Most of the particles on the surface were silicates. Heavy metals were not highlighted probably because they are contained in the particles more embedded into the leave structure.

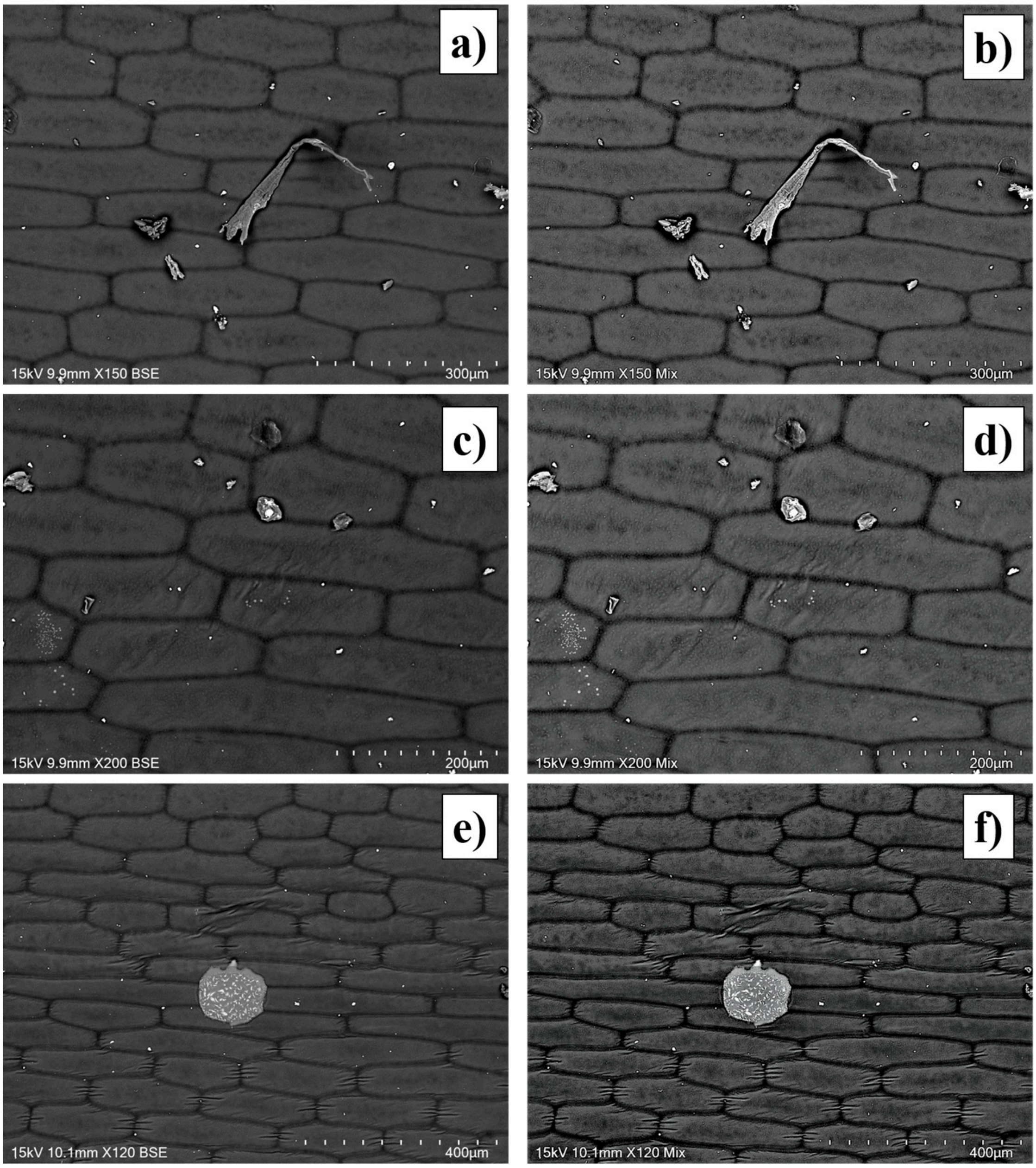

Figure 5. SEM images acquired in BSE (back scattered electrons) mode (**a**,**c**,**e**) or mix (BSE + secondary electrons) mode (**b**,**d**,**f**) evidencing the presence of particles of micrometric dimensions on *Chlorophytum comosum* leaves.

In Figure 6, some punctual analyses performed on single particles are reported. While the particle analyzed in Figure 6a is probably a chloride, in Figure 6b,c, some aluminum silicates were highlighted.

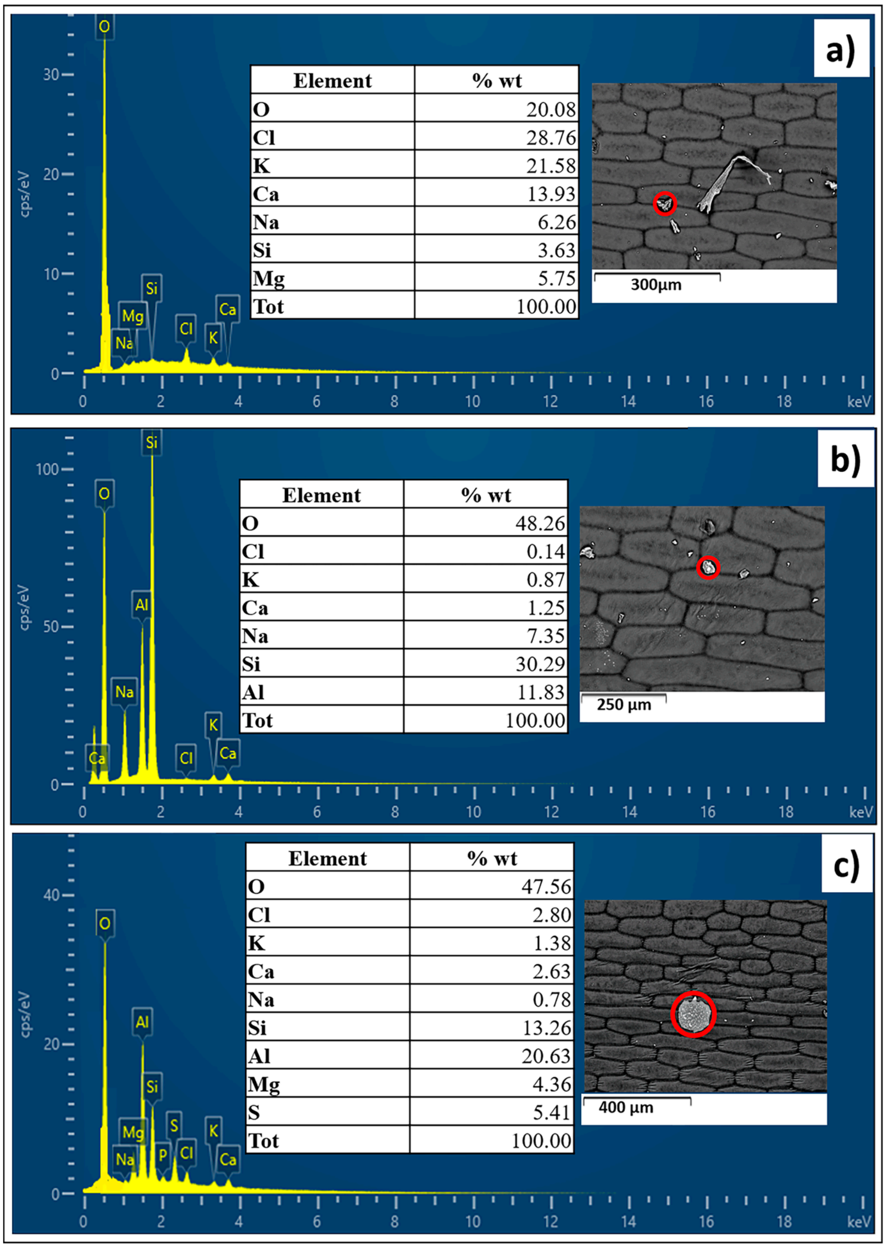

Figure 6. EDS analyses (**a**–**c**) acquired on single particles present on the leaves' surfaces and evidenced with a red circles in (**a**–**c**).

4. Discussion

It is important to point out that this represents a pilot study and, for this reason, the investigated area in Milan was not so large and the four investigated locations not so distant from each other. Different highs from the ground level were chosen in order to study the effect of the distance from sources such as traffic. In fact, at the Botanical garden and ARPA station, the plants were placed at ground levels while at the Chem Dept and Bio Dept they were at an altitude of 6 meters (see Figure 1). A different behaviour was observed for Cr (Figure 3a) whose concentrations at 165 was higher at Botanical Garden and ARPA where the specimens were at ground level. Hence, it can be hypothesized that Cr is associated to some source linked to road dust where this element was identified at low level [48].

On the base of the results obtained and reported in Figure 4, it can be stated that the heavy metals considered in this study, with the exception of copper, come from atmospheric pollution. This is demonstrated thanks to the comparison with the not-exposed plant.

It is worth noting that the metals penetrated inside the leaves [41,42] since heavy metals were not detected on the surface by SEM-EDS analysis.

Among heavy metals Zn, Mn and Cu are those present in the higher concentration in the aerosol particulate matter [24,25]. Zn, Cu and Pb are associated with traffic emissions [25] while Mn together with Zn are due to industrial emissions [24,25]. With respect to what is reported in Marcazzan et al. [25], a lower contribution of Pb should be expected since lead concentration in the atmosphere started to decrease since the introduction of the green gasoline. This justifies the low concentrations detected in *Chlorophytum comosum* for this element.

It is also worthwhile to note that Fe and Zn are micro elements naturally present in *Chlorophytum comosum*, as evidenced by Aberoumand et al. 2009 [44]. Indeed, Zn was also detected in the not-exposed plant confirming the presence of a natural background value, as shown in Figures 3b and 4a.

This blank value determined in the not-exposed plant is about of the same order of Zn concentration detected in *Chlorophytum comosum* for the different sites at 7 days (Figure 3b). Then, starting from 30 days, Zn increases reaching a maximum at 60 or at 128 days depending on the site. Indeed, the concentration at 165 is lower for all the sites and this can be explained taking into account that dilution of metals with plant growth can decreases the total metal concentration in older plants [41].

In the same period, during which *Chlorophytum comosum* was exposed (i. e for 165 days from July to December 2018) data of atmospheric concentrations of heavy metals measured on the filters collected by ARPA Lombardia by means of gravimetric systems in the monitoring station of Milano Via Pascal, were considered (data were both downloaded from the ARPA Lombardia website [49] and also made available by the office responsible for the monitoring). All the other elements of interest for this study, i.e., referred to the same period, were in many cases below the detection limit or not available with the exception of Zn. As a consequence, a comparison between Zn concentrations detected in *Chlorophytum comosum* leaves exposed at ARPA site were compared with the metal concentration detected in the aerosol PM (in particular PM10) for the same period. At this purpose Zn values detected on each filter (24 h of sampling) were added up in order to obtain the total concentrations corresponding to the different sampling periods considered for the plants.

The results obtained are reported in Figure 7. It is worth noting how there is a good correlation up to 60 days. After this, Zn in PM10 continue to increase (as obviously expected being the concentrations detected on the filters added up) while for the plant, as previously mentioned, a decrease due to metal dilution with plant growth is observable. In any case, it can be stated that *Chlorophytum comosum* represents a good proxy to trace Zn trend in the aerosol particulate matter of Milan.

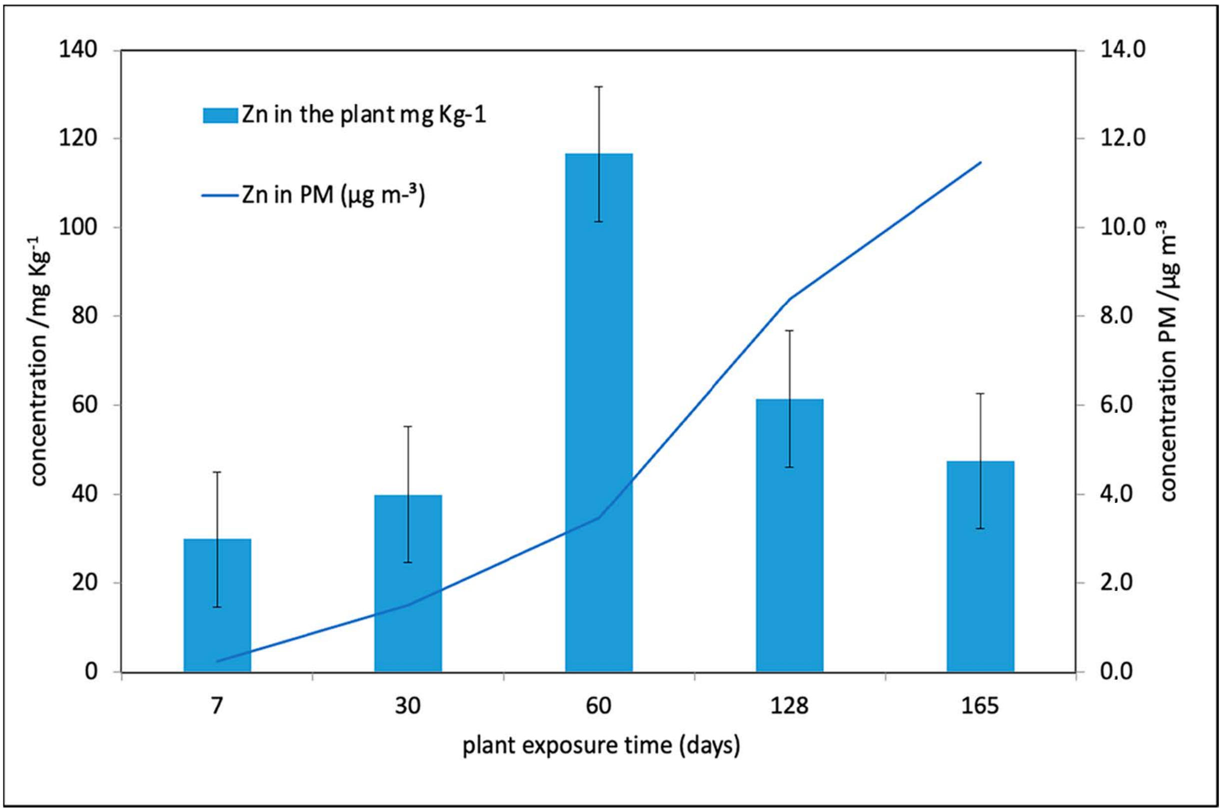

Figure 7. Concentrations trends for Zn in *Chlorophytum comosum* specimens exposed at the ARPA monitoring station in Milano Via Pascal compared with Zn concentrations determined in the aerosol particulate matter (PM10) for the same periods.

A relation between airborne heavy metals in the Milan area and another bio-indicator such as honeybees, has been recently evidenced [50] considering in this specific case Cd, Ni and Pb. To our knowledge, this is the first time that *Chlorophytum comosum,* and, more in general, a plant species, has been used as a bio-indicator for tracing heavy metals concentrations in the aerosol particulate matter of Milan over time. This pilot study may be continued in the future considering, for example, other monitoring sites more directly exposed to pollution sources such as traffic. Monitoring air pollution through low-cost bio-indicator such as *Chlorophytum comosum* could be very useful in tracing the variability of heavy metals concentration in different sites across the city providing a more detailed indication of pollution levels. This information is of priority importance because of the adverse effects of heavy metals on human health [51] but also on the constructed building materials since they are involved in the surface degradation process acting as catalysts in the formation of black crusts [52,53]. Moreover, this bio-indicator also has an ornamental function and blends perfectly into the landscape and this represents in our opinion a further benefit.

5. Conclusions

In the present research *Chlorophytum comosum* (spider plant) was used as a bio-indicator to trace heavy metals concentration present in the aerosol particulate matter in the city Milan. At this purpose exposure periods ranging from 7 days up to 165 days were investigated. The metals present with the higher concentration were Zn and Mn followed by Cd and Cr while Co, Ni and Pb were present in lower concentration. The accumulations trends are different and depends on many parameters, as already attested in the literature. By SEM–EDS analysis, it was observed that heavy metals were not on the leaves' surface, but they have penetrated.

It has been demonstrated that *Chlorophytum comosum* represents a good proxy to trace Zn trend in the aerosol particulate matter of Milan. Maximum Zn concentration at ARPA station was assessed in the specimens exposed for 60 days (even if in other two sites the maximum was at 128) while the samples collected at 165 showed a lower Zn content due to metal dilution that takes place with the growth of the plant. Further investigation would be required to investigate the metals accumulation process in *Chlorophytum comosum* in more depth. This project represents a first pilot study, which will deserve further deepening in the future.

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