Toxic metals from atmospheric particulate matter in food species of tomato (*Solanum lycopersicum*) and strawberry (*Fragaria x ananassa*) used in urban gardening. A closed chamber study

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ABSTRACT

In this work, two plant foods, strawberry and tomato, were subjected to exposure to metals from synthetic airborne particles in a closed chamber experiment. The synthetic particles were obtained in the laboratory. Within the closed chamber, particles were added and recirculated for 4 days in a turbulent air stream, causing deposition on the different parts of the plants. They were evaluated because of their increasingly frequent cultivation in urban gardens of cities. The main objectives were to determine whether the species accumulate metals significantly, which species accumulate the most, and in which parts of the plant. Finally, an attempt was made to differentiate the accumulation of pollutants by surface deposition on leaves and fruits from the adsorbed metals into the leaf or the fruit by their stomata or cuticles. The concentration of heavy metals was quantified in fruits, leaves and the soil after exposure. Metals were evaluated as a whole and individually, both in dry and fresh weight basis. The decrease of particulate matter and metals in the air inside the chamber was also studied in order to evaluate the use of both food species as air purifier by vertical gardens. The concentration of metals in plants (mg kg^{-1}) and airborne particles (mg m^{-3}) was measured by microwave plasma optical emission spectroscopy (MP-AES). For the

sake comparison of total amount of metals in the samples concentrations were normalized. Strawberries was the food species that accumulated the largest amount of metals. In a dry weight basis, tomato leaves and strawberry fruits were the parts of the plants with higher accumulation capacity of particles and metals. The potential toxic elements Cd, Ni and Cr in tomato leaves and in strawberry fruits had a higher presence in the interior of the plant system. In a fresh weight basis, the strawberry fruit had the most accumulation capacity for metals.

Keywords: Urban gardens, heavy metals, top-closed chamber, Strawberry, tomato, synthetic airborne particles

1. Introduction

Today, controlling metal content in food and reducing their exposure to humans and animals are major challenges. One of the routes of entry of these contaminants into the food chain is through atmospheric pollution via plants. Air pollutants influence the physiological, biochemical, and morphological condition of plants, and the contributions vary widely between species. According Žalud et al., 2012, particulate matter (PM) can affect plants either by aboveground deposition (deposition on the leaf surface or penetration into leaf tissue) or by soil-root interaction. Metals in plant tissues enter through two main routes, by absorption from soil and deposition from the atmosphere (Salim, 1993), although in general inorganic or organic pollutants can be trapped in the wax of the fruit cuticle (Li & Chen, 2009). All primary aerial surfaces of plants (e.g., fruit and leaf) are covered by cuticle, a non-cellular and hydrophobic surface, to control water loss and gas exchange. The main compositions of plant cuticles include extractable lipids (waxes), insoluble lipids (cutin), non-saponifiable biopolymers (cutan), as well as polysaccharides. Thus, chemical compositions play a key role in the affinity of plant cuticle for hydrophobic pollutants, such as metals or pesticides, since airborne particles, such as $PM_{2.5}$, also carry heavy metals that could penetrate deeper into plant tissues (Farmer et al., 2002; Jouraeva et al., 2002).

Due to their relatively larger size, uptake of coarse particles into the plant tissues through leaves or fruits is not expected. PM > 5 µm is deposited on the leaf surface but can penetrate the plant

cell walls, cellulose-rich, stopping their entry into the plant cell. In contrast, PM < 1 µm (submicron mode) and < 0.1 µm (ultrafine mode) can directly enter the plant cell walls (Hwang et al., 2011). Also, submicrometric particles of Pb (0.05 – 1 µm) were observed inside the stomatal openings (Uzu et al., 2010), obstructing stomatal openings and reducing the CO_2 transfer (Anake et al., 2022). In addition, deposited PM can change the light absorption of leaves and the reflection of photosynthetically active radiation (PAR). As a result, secondary stresses in the plant can be exasperated and physiological processes, such as the photosynthetic rate, are affected, disrupting normal metabolism (Anand et al., 2022; Przybysz et al., 2014). Besides, the presence of heavy metals in plant tissues modifies their molecular structure. The application of heavy metals Cu, Cd and Pb significantly increased the expression of the phytochelatin synthase gene in tomato leaves, meanwhile the proline content was significantly increased (Kisa, 2019). Other authors also report that heavy metals contained in PM which adhere to the PM surface of leaves or fruits can enter the leaf interior and can induce toxicity (Kováts et al., 2021).

The growth of urban agriculture in the developed world is associated with different benefits and risks of this practice (Gaspéri et al., 2018; Taylor et al., 2021). Urban gardens increased in the last 20-30 years in many cities worldwide, and one of their benefits is to allow the self-sufficiency of families, especially at this time of food and economic crisis in the post-pandemic and current war in Ukraine. The transfer of pollutants from urban agriculture to urban ecosystems and in particular from urban ecosystems to agricultural products are the main risks associated with these activities (Mok et al., 2014).

Some authors found high concentrations of heavy metals in soils and vegetables from urban gardens (Clarke et al., 2015; Islam et al., 2014; Säumel et al., 2012), with values above different international standards, such as the EC regulation No. 488/2014 (European Commission, 2014), the EC regulation No. 1881/2006 (European Commission, 2006) or the Codex Alimentarius Commission (FAO/WHO, 2011). Other international organizations have established regulations for limit values for non-essential metals in food to prevent metal toxicity, such as the Food and Drug Administration (FDA), the National Institute for Occupational Safety and Health (NIOSH),

the Occupational Safety and Health Administration (OSHA), and the Canadian Chemical Safety Bureau (Romero et al., 2023). However, in other studies no significant contamination was found in soils and urban vegetables (Konwuruk et al., 2021; Arrobas et al., 2016).

Apart from differences in air pollution between cities, the absence of pollution in plants is probably due to differences in the plant species studied or also to the plant parts analyzed. This is why the aim of this research is to differentiate the accumulation rate of heavy metals between two species of vegetal food species and between different parts of the plant, in the leaves, the fruits, and the soil below the plant. For this purpose, a laboratory experiment in a closed-chamber was designed to contaminate edible plants with heavy metals in atmospheric particles (PMs). The aim was not only to compare the levels of pollutants accumulated by the two plants, but also to find out in which parts of each species the most pollutants are found within their morphological structure. Tomatoes and strawberries are the selected food species for human consumption, and nowadays many of them are cultivated by the same families through urban agriculture, and they will be the two species that were subjected to the experiment of contamination by atmospheric particles with heavy metals. Additionally, it would be interesting to know which of the two food species is most able to clean the indoor air of a space if they are used as components of a vertical garden.

2. Material and methods

2.1. Plant and soil materials

The two vegetal species were considered, cherry tomato (*Solanum lycopersicum cv. Cerasiforme*, Fig. 1-a) and strawberry (*Fragaria x ananassa* cv. *Camarosa*, Fig. 1-b). Four plants of each species were planted in pots. The soil of the pots was homogenized, air dried and sieved for pot assays and ground for analysis according to a previous methodology (Fernández-Espinosa et al., 2022). As the contamination experiments were short-term and did not last more than 4 days, the roots were not studied, only leaves, fruits and the soil. There was no time for the metals deposited on the soil to reach the roots and be translocated into the plant.

106 *The gardening soil*

107 The soil composition was: SiO_2 (2.8%), Fe_2O_3 (18.9%) and Al_2O_3 (1.7%), representing around
108 25% of the soil mineralogical composition, apart of 1.1% Ca and 0.2% Mg. Nutrients content was
109 1.63% N, 0.76% P_2O_5 and 0.12% K_2O. It is neutral (pH 7.2) with high organic carbon content
110 (OC 45.1%), and electrical conductivity (EC) of 19.3 mS m^{-1}, 35% water content at field capacity.

111 Soil ionic content (mg kg^{-1}) determined by ionic chromatography-conductivity detector (Rossini-
112 Oliva et al., 2019) was Na^+ 494 ± 56, K^+ 546 ± 64, Ca^{2+} 10001 ± 1039, Mg^{2+} 2312 ± 65, NO_2^- 1.5
113 ± 0.2, NO_3^- 720 ± 60 and PO_4^{3-} 5084 ± 57. The soil content of some potential hazardous elements
114 (Cd, 1.03±0.14; Cu, 10.1±0.6; Pb, 9.9±1.1, Cr, 2.2±0.3; Ni, 0,088±0.014), all in mg kg^{-1},
115 determined by MP-AES (Rossini-Oliva et al., 2023), is lower than the European guidelines for
116 agricultural soils (Semenkov et al. 2022).

117 Irrigation of pots was performed with municipal water which normal values of pH 7.96 ± 0.02
118 and EC 289 ± 18 μS cm^{-1} and was a good quality municipal water (Ca, 18.8±0.5; Mg, 5.63±0.19;
119 Na, 6.5±0.2; K, 1.8±0.07; Al, 0.034±0.003; Fe, 0.0333±0.0010, all in mg L^{-1}). A nutrient solution
120 was also added, containing in mg L^{-1}, NO_3^-, 540; $H_2PO_4^-$, 95; SO_4^{2-}, 263; K^+, 106; Ca^{2+}, 116; Mg^{2+},
121 67, and in meq L^{-1} NO_3^-, 8.7; $H_2PO_4^-$, 1.0; SO_4^{2-}, 5.5; K^+, 3.5; Ca^{2+}, 5.8; Mg^{2+}, 5.5.

122 *2.2. Experimental design*

123 Many studies have been performed on plants contaminated with gases, but rarely studies with
124 heavy metals and carried out in closed chambers. To develop our comparative plant study under
125 controlled conditions, both species, tomato and strawberry, were subjected to contamination by
126 atmospheric particles and heavy metals in a closed chamber as part of a laboratory experiment.
127 Such chambers are called as closed-top chambers, CTCs, in contrast to other space design such
128 as open-top chambers, OTCs (Tuhkanen et al., 1998; Saxe & Kerstiens, 2005). In this type of
129 study, the controlled conditions simulate as closely as possible field conditions when plant species
130 and food plants may be exposed to multiple contaminants, particulate matter (Yadav et al., 2019;
131 Chiam et al., 2019; Mina et al., 2021) and gases, such as SO_2 (Yadav et al., 2019) or ozone (Thwe

et al., 2015). They have relevant advantages because the studies done field studies may not be accurate due to changes that occur when leaves and fruits are separated from the plant and the subsequent delay in sample analysis after collection and transport (Anand et al., 2022).

Our closed chamber is a 243-liters paralepidid (60 cm x 90 cm x 45 cm, 0.4 m^2 in base) in acrylic transparent windows and a frontal door (Fig. 2). The perpendicular joints between its sides and corners have been made round with fiberglass so that particles do not easily accumulate. All walls, roof, base and door have been covered with a Teflon coating for the same purpose. Over the top panel, on the outside of the chamber, is the fluorescent tube system that will control the photoperiod of the plants (Fig. 2-a). The photoperiod was managed by an electric clock controlling strips of white fluorescent lights giving about 200 lux. The photoperiod treatment was sunrise at 8:30 and sunset at 19:30 as natural photoperiod variation.

Closed-top chamber. Elements

The function of the closed chamber is to simulate an urban garden ecosystem in which airborne particles (PM) are subjected to the process of surface deposition (*s*PM) and internal sorption (*i*PM) or overaccumulation of metals on the different parts of the food plants, leaves, fruits and the soil (FSL plant system). Apart from the photoperiod illumination system, the chamber must incorporate several elements necessary for the simulation of the process.

These elements are (Fig. 2):

- The photoperiod system [a]
- A forced ventilation system [b]
- Two fans for the particle resuspension [c]
- The pollutant (*PM*) introduction hole [d]
- The filter holder as support of filter media [e]
- The pot position platform with irrigation (*IW*) system [f]
- Sensors for indoor ambient variables [g].
- Sampling pump to collect synthetic metallic particles on quartz filters [h].

159 *Ventilation* of the chamber inside was provided by an air mixer (fan) mounted in the center of the
160 chamber (Fig. 2-b). The fan (Box Fan BF 1030) is a simple five-bladed propeller with a power of
161 45 W which induces a horizontal air stream. During the contamination experiments we operated
162 the fan at three mixing modes alternately: 855, 1035, or 1215 rpm (revolution-per-minute), until
163 a maximum 94.6 L min^{-1}, thus generating different airflows, as in a real ecosystem. These mixing
164 modes are referred to as mixing modes 1, 2, and 3, respectively. This ventilation has been operated
165 for periods of 15 minutes with alternating 15- and 30-minute pauses. The ventilation rate was
166 estimated from the formula $\lambda = Q/V$, where Q is the air exchange rate (m^3 s^{-1}) and V is the
167 chamber volume (m^3). So, ventilation rates were 0.018, 0.022 and 0.026 h^{-1} for modes 1, 2 and 3,
168 respectively. Thus, the fan mixed the air and created a homogeneous concentration profile shortly
169 after each injection. Therefore, there were no concentration gradients in these experiments. Also,
170 the behavior of aerosol particles inside the chamber was like that found in real-life conditions
171 with the same ventilation rates (0.018–0.39 h^{-1}) and similar air mixing modes (Hussein et al.,
172 2009). Thus, our findings provide insight into indoor particle behavior.

173 Apart from ventilation, for particles *re-suspension*, injected particles must be sustained in the air
174 for as long as possible without falling to the ground. Therefore, we included 2 powerful (1,500 -
175 3,800 rpm) swing fans in the floor of the chamber (Fig. 2-c). They were oriented vertically and
176 perpendicular to the main airstream, thus preventing pollutant particles from falling on the floor
177 when they are injected into the chamber. Subsequently, the continuous oscillation mechanism was
178 activated. This crossing of air flows causes a turbulent movement of the air inside.

179 The system for the *introduction of pollutant* particles consisted of a hole in the ceiling of the
180 chamber (Fig. 2-d) aligned with the main ventilation system where particles fall down a glass
181 funnel. Thus, to know the indoor air concentrations, we sampled particles into a support/head for
182 quartz filters (Fig. 2-e) placed away from the area where some particles fall directly to the ground
183 after the initial addition.

184 The pots were placed at the right within a *platform* that collects excess irrigation water (*IW*) and
185 residues of dried leaves and soil debris (Fig. 2-f).

186 *Sensors* to monitor the indoor ambient conditions were inside the chamber (Fig. 2-g). They
187 monitored the microclimatic parameters, temperature-ºC, relative humidity-% and CO_2
188 concentration-ppm.

189 *Air sampling, experiments performance*

190 In order to achieve the main objective of food safety, in addition to determining the levels of
191 metals in the contaminated plant samples, their concentration in the indoor air of the closed
192 chamber was also determined. The concentration of particles and metals in the indoor air was
193 determined in all experiments with plants inside the chamber, but the initial air was also sampled
194 before each experiment. These samples were the indoor air quality 'blanks'. Furthermore, in order
195 to determine the rate of reduction of air pollution by the plants, assuming they were used as
196 vertical garden elements (the second objective of the current work), the concentration of particles
197 and metals in the indoor air was determined when the synthetic particles were added into the
198 chamber without the presence of the plants. The averaged value for these samples was designated
199 as the 'reference' of the maximum level of metals in the indoor air.

200 Sampling of metallic particles of the indoor air was performed using an aspirating pump coupled
201 with a head for a filter, the support of airborne particles. Quartz filters (∅ 47 mm, Whatman
202 QM/A) were manually inspected for possible failures and thermally conditioned. The indoor air
203 was aspirated towards an air sampling pump (SKC 224-PCXR8) with the following conditions:
204 air flow 4.0 L min^{-1}, air volume 5.76 m^3 day^{-1} (23 m^3 for 4 days) (Fig. 2-h). After sampling, each
205 filter was immediately stored in the freezer (-22 °C) until spectrometric analysis. The pump was
206 calibrated to within ±2% with a SKC 311 laboratory film flowmeter kit. CO_2 concentration was
207 measured and monitored with an air quality detection and data logging instrument (YesAir IAQ
208 Monitor) designed for continuous indoor air quality monitoring of temperature, relative humidity
209 and gases.

210 *Closed-top chamber. Operation*

The desired contamination of the plant by surface deposition (*s*PM) and subsequent absorption into the plant (*i*PM) must occur gradually throughout the days of exposure and sampling (four days) during which the particles are suspended by air movement. The challenge of the experiment is that contaminant particles entering the chamber do not fly directly to the plant position and deposit on the plant at the start of the experiment.

So, to reach this challenge the optimal position of the interior elements (fans, pots, sensors and the hole) was experimentally assayed by covering all sides of the parallelepiped with white cellulose paper and adding black activated carbon by the hole as colorimetric tracer of the metallic pollutants. When the activated charcoal is injected into the chamber, we observed the black spots on the white cellulose paper. So, the fan is tested at different positions: at the middle of the chamber and in the left wall, and by sending the air directly to the pot and in the opposite direction. The air reaching the opposite wall of the fan bounces back and carries the particles to the rear of the fan. This way, the position of each of the elements inside the chamber was optimized (Fig. 2).

In this way the particles travel to the right wall, impact with it and are bounced back to the left wall and so on for the 4 days. With each collision they lose speed and gradually fall down, while the small fans resuspend the particles that fall to the ground. The particles remain in suspension throughout the experiment because the quartz filter is darker on each day. The stains on the white paper demonstrate that the particles are finally deposited on the pot, but not at the beginning of the addition, so that the desired objective has been achieved. Note that the particles entering the closed chamber and falling down the hole have a diameter of less than 20 microns ($PM_{10\text{-}20}$). Many of these particles falling to the ground, others were deposited in the pot (leaves, fruits and the soil) and the rest remained in suspension ($PM_{5\text{-}10}$). The level of particulate matter within the chamber is the amount of particles suspended in the air, those that did not fall to the ground but also particles resuspended from the ground by the turbulent air flow.

2.3. Preparing the synthetic solid (SS) of metallic particles. Methodology

The plants undergone contamination treatment by suspended atmospheric particles. Particles contain metallic elements as pollutants. These fine particles were prepared in the laboratory

238 according to a method previously reported (Fernández-Espinosa et al., 2002; Smichowski et al.,
239 2008). Synthetic particles were prepared in the laboratory with salts of analytical grade. Salt
240 mixtures, i.e., chlorides, sulphates and mainly nitrates, and soluble carbonates of different metals
241 –B, Al, K, Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb and Cd– were prepared. In order to design a
242 laboratory experiment of accelerated deposition in shorter periods of time (days) than the usual
243 cultivation periods (weeks or months) it was necessary to increase the concentration of metals in
244 the composition of the added particles, much more over the real concentrations.

245 In the following a short description of the preparation of the synthetic particles is included:

246 Drying all salts separately in a desiccator for 48 h (< 7% RH with P_2O_5) to prevent melting (Table
247 2) and weighing for a total of 26 grams of multi-colored mixture, homogenization in a vertical
248 vibrator for 48 h and density determination of the monochrome solid (0.89 g cm^{-3}), milling
249 manually in an agate mortar for particle size/density reduction and sieving (<20 microns),
250 decreasing the density of the synthetic solid (SS) to 0.77 g cm^{-3}, and mixing with mineral talc, an
251 inert solid (without heavy metals) of very low density (0.33 g cm^{-3}) for a final density of 0.56 g
252 cm^{-3} of 98 grams of SS of <20 microns.

253 Besides, care was taken in handling compounds in order to avoid toxicological problems,
254 therefore, handling of this preparation was within a vertical laminar airflow cabinet (IndeLab
255 IDL-48V) provided with HEPA filters and activated charcoal. Once final solid was prepared, its
256 element composition was determined by emission atomic spectrometry.

257 *2.4. Plant pollution experiments*

258 Plants growing was handled from the beginning in a closed room, with a sealed door and no
259 windows. It is in the center of the floor (red room in the map of Fig. 2) and therefore far away
260 from doors and windows, isolated from the outside. In this way, the environmental conditions of
261 temperature, humidity and intake of dust and gases from the street can be kept very constant
262 during the entire time of the experiments. In this enclosed room is the closed-top chamber where
263 the experiments with the pots will be carried out. Temperature and relative humidity inside and

outside the chamber were measured at all times, around 32.5 and 29.0∘C and 49.5% and 55.5% during particle exposure. The CO_2 rate inside the chamber was variable in the range of 189-579 ppm, depending on the photosynthesis of each plant species and day and night, being 341-371 ppm outside.

Plants were transplanted in plastic pots containing 250 g soil. In order to reduce soil compactness, 40 g of glass beads (4 mm in diameter) were mixed in each pot. The plants were irrigated every 2 days from the first moment of transplanting into pots.

Once the synthetic solid was prepared, the pot experiments were performed with the following considerations:

- Blank experiments were carried out without pots inside the chamber and without adding contaminants (-P, -C). To obtain a blank of the indoor air, several quartz filters sampling the indoor air for 4 days were used and analyzed. A representative number of all fruits and leaves of the pot and a portion of its soil were also analyzed, all collected outside the chamber.

- Pollution experiments were carried out with the pots inside the chamber and with the addition of contaminants (+P, +C). Here we analyzed the quartz filter sampling inside the chamber for 4 days, all remaining fruits and leaves of the pot and a representative amount of the soil.

- Blank were performed before the pollution experiments. Those blanks were also made between the pollution experiments to check the correct cleaning of the chamber between assays. Four experiments were run with each plant species and each one took 4 days (96 h).

- Each pot was conditioned inside the closed chamber three days before each pollution experiment. At the end of the experiments, the chamber was cleaned-up for another three days. In this way, each pollution experiment took almost 2 weeks.

The procedure was as follows: it consisted of adding 1.0 g of metallic particles with the ventilation/resuspension system ‘On’ in continuous mode. The particles fall into the chamber in very small doses and slowly. The horizontal airflow transports them to the right-side wall of the chamber, not directly into the pot. Particles were added during a period of hours. In addition, to

keep the particles free of moisture and to avoid agglomeration, the whole is kept at a temperature of about 35°C by means of a heating block all the time. After addition, the forced air system was switched to automatic, operating automatically during the 4 days, both the hourly frequency of the fans and the daily frequency of the photoperiod. The irrigation system was manual, introducing around 50 mL/pot of every two days, as required, to maintain soil humidity.

At the end of each contamination experiment, all leaves and fruits were cut from each plant, taking care not to lose any deposited particles. Several portions of the topsoil under the plant were also collected. Whole leaves were dried in an oven (70°C, 72 h) on large watch glasses. The fruits, with a large amount of water inside, were first cut into smaller pieces with a scalpel and dried in the same way. After drying, the different matrices were ground in a laboratory grinding mill (IKA Works, 20,000 rpm). The moisture content of the plant material was determined for both food plant species and for the four pots and the values obtained were 94.4 ± 0.79 %, 90.8 ± 0.32 % and 81.0 ± 1.82 % for the fruits, leaves and the soil of the Cherry tomato pots, and 93.3 ± 0.87 %, 81.9 ± 0.33 % and 79.7 ± 1.67 % for the fruits, leaves and the soil of the strawberry pots.

2.5. Analytical methodology

Acid digestions were carried out using a *Digi*PREP® MS heating system (SCP Science, Quebec, Canada), with a graphite digestion block and a *Digi*VAC fume hood. Accordingly, entire quartz microfiber filters (~150 mg) and 250 mg portions of pot samples were weighted into 50 mL *Digi*TUBEs and poured with concentrated HNO_3 (65%):H_2O_2 (30%), 7:2 mL Suprapur reagents, heating gradually to 115 ºC with the programmer for 120 min. Then they were cooled and filtered through 0.45 µm Teflon® membrane *Digi*FILTERs in the vacuum *Digi*Manifold and diluted to 20 mL with ultrapure water Type 1, 18.2 MΩ·cm (Milli-Q® Direct system from MerckMillipore, Merck KGaA, Darmstadt, Germany).

2.6. Metals determination. MP-AES

Analytical determinations of the metals B, Al, K, Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb and Cd were performed using a microwave-induced plasma optical emission spectrometer MP-AES

316 Agilent 4210 with the autosampler SPS4 (Agilent Technologies, Santa Clara, USA). Sample
317 introduction was by the inert One-Neb nebulizer with a double-pass glass cyclonic spray chamber,
318 and a quartz torch. The plasma used the online N_2 generator Agilent 4107. Operating conditions
319 were gas flow at 20 L min^{-1} and auxiliary gas at 1.5 L min^{-1} and the following operational settings:
320 uptake time of 82 s, stabilization time of 15 s, read time of 3 s (3 measures of intensities), wash
321 time of 72 s. Before measurements, both viewing position and nebulizer flow were optimized for
322 each element using the Agilent Wavecal solution. Automatic background correction was used.

323 Analytical calibrations were prepared from a 1000 mg L^{-1} Certipur® multi-element standard
324 solution (Merck KGaA, Darmstadt, Germany). Standard concentrations were prepared from 1.0
325 µg L^{-1} to 250 mg L^{-1} in 3% HNO_3. Samples with concentrations above 250 mg L^{-1} were analyzed
326 by shorts dilution. Linear ranges of concentration were selected around the concentrations of the
327 samples depending on the element. A more sensitive wavelength was selected for low
328 concentrations and one less sensitive for higher concentrations (see supplementary Table S1).
329 Good precision and linearity of the calibration curve, low quantification limits and high
330 sensitivities were obtained (Castro et al., 2021).

331 Triplicate analysis of sample solutions were performed and results were calculated for dry base
332 (DW) and also for fresh sample (FW).

333 *Weighted sum method (WSM)*

334 To perform the comparison of blanks, tomato and strawberry fruits, and leaves the weighted sum
335 method was applied to transform the analytical concentrations into weighted sum values (WS, %)
336 (Fernandez-Espinosa et al., 2004). Since the concentrations of each element are very different
337 from each other in orders of magnitude, this method standardizes the different concentration
338 levels of the elements studied to a ratio or percentage scale. The weighted sum method first
339 converts the concentrations of each element into a percentage or ratio with respect to the
340 maximum value of the four pot experiments. The weighted sum in each experiment is the sum of
341 the new ratios for the thirteen elements studied, thus giving a global level of metals and not the
342 absolute sum that would depend on the most abundant metal. Once the analytical concentrations

have been converted into weighted sums, statistical comparison tests can be applied to check whether or not significant differences exist. These global levels of metals were calculated and expressed both on a dry (DW) and fresh (FW) weight basis.

2.7. Quality controls and statistics

For the quality controls and to verify the quality assurance of the analytical methodology, six replicates of the standard reference material *Olea Europaea* leaves, BCR-062 (Griepink et al., 1983) were performed. Table 1 shows the obtained results. The recoveries of the certified elements ranged from 83 to 107%, within AOAC acceptable ranges. F and t-tests ($p = 0.05$) showed no significant differences between obtained and certified concentrations. As a result, the analytical methodology was traceable to the standard reference material, without any significant systematic error.

To compare blanks-samples, tomato-strawberry or fruits-leaves, ANOVA was used when comparing the 4 experiments for the 13 elements, and also Fisher-Snedecor F-tests and Student's t-tests were used when comparing the four mean values. The two-way ANOVA, where differences between and within groups were determined by least-square mean differences and the Fisher-Snedecor's F-test was performed with the significance level set at alpha = 0.05. *F*-tests were done at two-tailed, $F_{calc} < F_{crit}$, $p > 0.05$. *T-tests* were done at one-tailed, $t_{calc} > t_{crit}$, $p > 0.05$ and the probability of significant differences at $p < 0.05$.

Furthermore, multivariate statistical analyses were applied to study the relationships between the content of metal contaminants in the three different parts of the pot (FSL) in relation to the possible entry into the plant system. Single linear regression (SLR, Pearson correlations) and some chemometric techniques, such as Principal component analysis (PCA), a non-supervised pattern recognition, Cluster Analysis (CA) and the supervised techniques Linear Discriminant Analysis (LDA), were employed to find these inter-relations (Jurado et al., 2005). For these analyses the STATISTICA version 8 (2008) software package (StatSoft) was used.

As concerns the SLR, correlation coefficients between all elements were validated for $r > 0.7$. They were checked for the probability (p) (Castro et al., 2021). When the corresponding p values were greater than 0.05, a two-tailed t-test was applied with a 95% confidence level. If the null hypothesis is $r = 0$, then the two-tailed tests assess whether r is significantly different from zero. The PCA was applied to a data matrix formed by the 13 metals and 24 cases = 4 experiments x 2 food species x 3 parts. It was performed with a Varimax rotation of the data matrix, extracting the factors or principal components (PCs) in accordance with a series of quality criteria: the number of eigenvalues higher than 1 (Kaiser criterion), the over 10 % of total variance and the over 70-90% percentage of cumulative variance explained by the corresponding PCs (Montoya et al., 2011). With use of this multivariate technique, it was possible to simplify the interpretation for the present system reducing the thirteen metal accumulated concentrations to a few PCs.

To complete this study, after the PCA, a hierarchical agglomerative Cluster Analysis to the standardized matrix of data set was performed, using Ward's method as the amalgamation rule and Euclidean distances as metric of similarity. Cluster analysis was performed as a supplementary analysis to PCA. This procedure finds natural groupings of the data set. CA classifies the samples as better than the PCA according to similarities between them and provides information regarding those that do not appear significant in the PCA.

Applying linear discriminant analysis (LDA) a classification rule was provided to differentiate between both species and between fruit-soil-leaves with overaccumulation and non-overaccumulation. LDA produces discriminant functions (DFs) that are obtained as linear combinations of the variables that best separate the two species or the over-accumulation process in the different parts of the plant. LDA is a modelling technique in which it is necessary to know previously the affiliation of each sample to a class or group of samples.

3. Results

3.1. Synthetic solid (SS). Final composition

Synthetic solid particles were prepared according to the paragraph included in 2.3. Table 2 shows the results of the analysis of the synthetic particles to obtain their metal composition. The results were compared with the theoretical values and good agreement was obtained. The high value in Mg concentration can be due to the composition of the mineral talc ($Mg_3Si_4O_{10}(OH)_2$) used as the low density inert solid. Also, the high value for boron can be due to the presence of boric acid in the commercial talc used to prepare synthetic particles.

3.2. Quality of plant pollution experiments. Positive contamination of plants, air cleaning and reproducibility of replicates

The main observation of the experiment is that the injection of pollutant particles into the chamber can significantly contaminate the different parts of the plant. If the degree of contamination achieved is similar in all four experiments, then the good quality of these contamination experiments is demonstrated.

Significant positive contamination of plants and air cleaning. Weighted sums of metals

After preparing the synthetic particles, the four contamination experiments can be initiated by injecting them into the chamber, but before this, the initial levels (blanks) of metals in the leaves, fruits and soils of pots were studied. It is thus necessary to study whether the contamination suffered by leaves, fruits and soil was significant and therefore effective. For this, the levels of metals in the four contaminated pots were compared - by means of hypothesis tests - with the same pots before contamination (blanks). This comparison (blanks-samples) required the weighted sum method of the thirteen metals for the four experiments. Similarly, it was necessary to corroborate the cleaning effect on the indoor air of the closed chamber by the presence of the pots of plants during each experiment. This way it can propose what vegetal specie will be more appropriate for employing in a vertical garden.

Table 3 shows values of weighted sums of the four pot experiments and the comparison for the cherry tomato and the strawberry between uncontaminated plants (blanks) and the same contaminated plants (samples) for fruits, leaves and soil, and for the synthetic metallic particles

collected from the indoor air. Blank values were not subtracted from those of the samples. The results of the t-tests showed significant differences (+) between contaminated samples and blanks in all parts of the FSL system and in both species. Thus, the concentrations in leaves, fruits and the soil of the contaminated pots were significantly higher than the initial concentrations of the blanks.

The efficiency of the contamination experiments was also reflected by the ratio *r* 'sample/blank' and the net weighted sums *nWS* 'samples minus blanks' (total accumulated metals), both in brackets in Table 3. As can be seen, a similar rate of metal uptake by strawberry and tomato leaves (*r* ~2), with a slightly higher *WS* in tomatoes, but not significant. However, there was a marked significant difference when comparing tomato and strawberry fruits: For strawberries ratio is 2.0, that is higher than that obtained for tomato, 1.2. WS value for strawberries, 611 is also higher than the corresponding value for tomato. In tomato leaves, metal uptake was much higher than in its fruits, being *r* = 2.1, WS = 612. From the values included in Table 3 it can be concluded that the soil of pots had also similar ratio and accumulation rate in both species. In summary, the weighted sum values showed that the total accumulation capacity followed the order tomato leaves ≅ strawberry fruits > strawberry leaves >> tomato fruits.

In fact, if we sum the amount of metals deposited in the three parts of the FSL system, strawberries accumulated a total *nWS* rate of 1605 and tomatoes 1244. The total *nWS* of metals in the air inside the chamber was 205 for strawberries and 306 for tomatoes. According to these values it can be said that more particles and metals are accumulated on the strawberry plants and that the air inside the closed chamber was therefore better cleaned than in the cherry tomato experiments.

Differences between dry and fresh weight results

It should be noted that these results were based on metal concentrations expressed on a dry weight basis. However, when concentrations were also expressed on a fresh weight basis (Fig. 3), the results show slight differences. This can be due to the differences found in the FW levels of the fruits. FW concentrations showed that the strawberry fruit was the most contaminated part of the plants, with nWS = 113.2, six times more than cherry tomato fruits, nWS = 18.3, and three times

446 more than leaves of tomato, nWS = 34.4 and strawberry, nWS = 41.7. In this case, the weighted
447 sum values showed a different total accumulation capacity following the order strawberry fruits
448 >> strawberry leaves > tomato leaves >> tomato fruits. No significant DW-FW differences were
449 found in the case of soil samples.

450 Furthermore, studying now the comparison among fruits-soil-leaves for the net weighted sums by
451 a n = 4 ANOVA, high significant differences ($p < 0.05$) were found in tomatoes in both dry and
452 fresh weight (DW, $p = 1 \cdot 10^{-9}$ vs. FW, $p = 1 \cdot 10^{-5}$), while in strawberries the significant difference
453 was found in fresh weight (FW, $p = 4 \cdot 10^{-5}$) and were not significant in dry weight (DW, $p = 0.27$).
454 These FSL differences are mainly caused to the tomato fruits, with very low values on DW and
455 FW basis. As consequence, no significant differences were found between tomato and strawberry
456 leaves and strawberry fruits. For both DW and FW results, it seems that the strawberry fruit is
457 much more hazardous about the global metal content than tomato fruit, however to state this
458 conclusion we need to study the individual metal levels.

459 *Reproducibility of replicates. Concentration of metals in DW*

460 The pots of each experiment contain only one plant specimen. The four pots were contaminated
461 separately, one pot and one specimen, so that the study was prolonged for a period of
462 approximately two months for each species. Hren et al., 2009 studied by variabilities in gene
463 expression within groups of plants that each individual plant responds in a different way to stress
464 conditions. In our case, individual pots may respond differently to stimuli of metals, requiring
465 verification of whether each plant respond to the addition of 1 g of particles with heavy metals
466 along the four experiments, giving us the reproducibility rate.

467 In Table 4, RSD (%) in each element indicates the reproducibility of experiments over time (inter-
468 series or intermediate precision). In contrast to Table 3, Table 4 shows the metal concentrations
469 obtained by subtracting blanks from the contaminated samples, which is the net accumulation of
470 metals in the plant. For leaves and fruits, median RSD values of obtained in cherry tomatoes were
471 similar as for strawberries, indicating that metal accumulation is reproducible for both plant foods.

The RSD is slightly higher in leaves than in fruits, but with no significant differences. RSD values in soils were slightly higher than fruits and leaves due to their heterogeneous and amorphous matrix. Furthermore, the two-way ANOVA showed that there were no significant differences ($F_{calc} < F_{crit}$, $p > 0.05$) along the four experiments for both species, confirming the good reproducibility of replicates, and the good quality of the contamination experiments. In addition, Table 3 showed similar precisions between the four experiments ($F_{calc} < F_{crit}$, two-tailed, $p > 0.05$), with no significant differences (–) between analytical determinations of blanks and samples and low RSD values in pollution experiments, suggesting a good reproducibility of the four experiments.

The quality of the experiment can also be measured if the metal composition of the particles deposited in the FSL system is the same as that of the synthetic particles. Some components of particles (Table 2) were magnesium (48%), lead (10%), cadmium and manganese (6%), boron, copper and potassium (5%). Meanwhile, percentages of metals cumulated in plants of tomato and strawberry (Table 4) were 41 – 45% of Mg, 8.6 – 9.8% of Pb, 5.5 – 7.1% of Cd, 5.51 – 5.53% of Mn, 5.9 – 6.4 of B, 5.5 – 6.1% of Cu and 4.5 – 4.9 of K, so in accordance with data of Table 2, which further confirms the quality and optimal performance of the pollution experiments. Based on the percentage differences between particles and plants, we estimated an efficiency of 84.5% in the cherry tomato experiments and 79.3% in the case of strawberries.

Considering the sum of elements, the deposition/absorption rate of particles and heavy metals was much higher in strawberries fruits, 87 mg Kg^{-1} day^{-1}, than in tomatoes, 7.3 mg Kg^{-1} day^{-1}, and similar between leaves of both food species (94 ≅ 129 mg Kg^{-1} day^{-1}) following the same order (*to*L > *st*L ≅ *st*F >> *to*F) as the accumulation capacity found by the weighted sum values listed above, accumulation in leaves being higher than in fruits. Since, fortunately, the leaves of both species are not edible, it is much more interesting to emphasize the accumulation rate in strawberry and tomato fruits, which are both highly appreciated foods [Medina, 2005]. The remarkable difference between the deposition/absorption rates which is twelve times greater in strawberry fruit compared to tomatoes, of only 7 mg kg^{-1} day^{-1}, was due to the perfectly round

and very smooth shape of the small cherry tomato compared to the rough and heterogeneous shape of the strawberry fruit.

The metals deposited in the soil of pots showed similar concentrations for tomatoes and strawberries (around 20 and 38 mg Kg^{-1} day^{-1}, respectively). Strawberries is where more metals accumulated in leaves and fruits, 94 + 87 = 181 mg Kg^{-1} day^{-1}, being less the amount of metals dropped to the soil, 20 mg Kg^{-1} day^{-1}, and vice versa, 136 mg Kg^{-1} day^{-1} in leaves+fruits and 38 mg Kg^{-1} day^{-1} in the soil of tomatoes. The soil of the plant receives less particles because they fall first on leaves and fruits. However, in real crops it is to be expected that during rainfall events many particles deposited on leaves and fruits fall to the soil, dissolve, and metals may later enter the plant system through its roots. The total metals deposited in the 3 parts of the plant, FSL, was 200 mg Kg^{-1} day^{-1} in the strawberry pots and mg Kg^{-1} day^{-1} in the tomato pots.

4. **Discussion**

4.1. Differentiation in metal accumulation between species and among fruits, leaves and the soil of pots

As described above, once the contamination experiments were effective and reproducible, the next objective was to study whether there exist differences in the accumulation of metals in the different parts of the FSL system. In addition, metals that accumulate on the surface by dry Stokes deposition and surface adsorption (sPM) need be discriminated from metals that enter the leaves by internal sorption through the stomata or into the fruits through their cuticles (*i*PM). Discrimination was studied by estimating the highest differences between the proportion of metal in the FSL plant system ($\%C_P$, Table 4) and that of the synthetic particles SS ($\%C_{SS}$, Table 2), which are due to internal sorption by leaf stomata or fruit cuticle. For this, the ratios $\%C_P/\%C_{SS}$ = *R*, were calculated for fruits R_F, leaves R_L and the soil R_S and for the ensemble FSL system, R_{FSL} (Table 4).

Initially, it was observed that the metals Al, Fe, B, Cu and Zn had the highest ratios in both plant species (Group A), all of which are essential elements (EEs). The remaining metals, Cd, Co, Cr,

K, Mg, Mn, Ni and Pb are essential and non-essential elements (Group B), such as the potential toxic elements (PTEs) Cd, Cr, Ni and Pb. Thus, the metals over-accumulated in the FSL system of cherry tomatoes were found in the order Zn (R_{FSL} = 1.9) > Al, Fe (1.5) > B, Cu (1.3). In the strawberry pots, the over-accumulated metals were the same Zn (1.6) > Fe (1.4) > Al (1.3) > B, Cu (1.2), and the over-accumulation of these metals were slightly higher in cherry tomato pots than in strawberries (+11%), but not significant ($p > 0.05$). These initial results lead to propose that, in addition to some metal particles deposited on the surface (*s*PM), other metal particles directly enter the interior of the plant (through leaves and fruits, (*i*PM), increasing the proportion of the metal in FSL relative to the proportion in SS.

For the remaining metals, Group B, the ratios for Cd, Co, Cr, K, Mg, Mn, Ni and Pb were 1.0 or slightly lower (Table 4) for the whole FSL system in both species, and the over-accumulation of the PTEs Cd, Cr, Ni in cherry tomatoes was also slightly higher than in strawberries (+7%), but not Pb. Nevertheless, considering the leaf ratios (R_L), the PTEs showed over-accumulations significantly higher than 1.0, R_L = 1.7 - 1.6, especially in cherry tomatoes (+41%), Ni, Cr (1.7), Cd, Co, K (1.6) and only K in strawberry leaves with a ratio of 1.2. Meanwhile, metals of Group A showed the highest ratios in cherry tomato leaves (+22%), such as Zn (R_L = 3.2), Fe (2.0), Cu (1.7), Al (1.6) and B (1.5). For example, there was 6.0% Zn in the contaminated tomato leaves, compared to 1.9% in the SS (x 3.2). $R_L > 1$ values were also observed in strawberry leaves, but lower than in tomato leaves (Zn 2.1, Al 1.6, Fe 1.5, B 1.4 and Cu 1.2).

For fruits, cherry tomatoes did not over accumulate metals above the normal deposition $R_F \sim 1$ or less, however, strawberry fruits over accumulated metals ($R_F > 1.1$) for Al (R = 1.2), Zn, Cu, B, Cd, Fe, Cr, and Ni (R = 1.1), but lower than leaves. Thus, over-accumulation was the highest in strawberry fruits +15.0% for EEs of Group A and +5.8% for PTE metals of Group B. Pb, Mn and Mg (0.5 - 1.0) showed no accumulation rates in leaves, fruits, or soil in both species, fortunately due to the toxicity of lead, which has shown here a different behavior than the other heavy metals, as also reported by other authors (Hogan, 2011). In summary, the study discriminated the process of internal overaccumulation of metals from that of surface deposition, with leaves being the part

552 of the plant system that produced the greatest differences between the two food plant species,
553 with significantly higher metal overaccumulation in cherry tomato leaves +29.9% (EEs + PTEs)
554 than in strawberry leaves, while in fruits it was only slightly higher in strawberries than in
555 tomatoes +10.3% (EEs + PTEs). Therefore, the metals that entered the F+L system were Zn (4.1)
556 > Fe (3.0), Ni, Cr (2.7) > Cu (2.6), K, Cd, Co, Al (2.6) > B (2.5) in cherry tomato species and Zn
557 (3.2) > Al (2.7) > Fe (2.6) > B (2.5) in strawberry species. In addition, it is alarming that the PTEs
558 Cd, Ni and Cr in cherry tomato leaves and strawberry fruits had a higher presence in the interior
559 of the plant system.

560 Finally, the cherry tomato was the food plant species that differs from strawberries in their ability
561 to incorporate metals through their leaves, such as the toxic metals Cd, Ni and Cr, whereas it was
562 the strawberry species that incorporate metals to a greater extent through its fruit, unlike the round
563 and smooth mini cherry tomato. Furthermore, it should be noted that if we calculate the sum of
564 the concentrations of the essential elements Al, Fe, B, Cu and Zn and the non-essential metals Cd,
565 Cr and Ni for fruits and leaves of both species, the concentrations of the EEs exceed the PTEs by
566 25% and also follow the same order observed above *to*L > *st*L ≅ *st*F >> *to*F.

567 *4.2. Multivariate statistical analyses of metal pollutants*

568 In this section, the interrelationships of the 13 metal pollutants and their distribution in the plant
569 system among fruit, leaf and the soil were studied by multivariate analysis, such as principal
570 component analysis (PCA), cluster analysis (CA) and linear discriminant analysis (LDA). This
571 statistical study was done to corroborate the different accumulations of EEs and PTEs found in
572 the different parts of the FSL system and to find new correlations between metals that will enrich
573 the knowledge about the behavior and response of the plant to exposure to these air pollutants
574 typical in urban gardens of large cities.

575 *Principal component analysis*. Prior to the PCA, the Pearson correlations was checked,
576 confirming that all correlation coefficients obtained were higher than 0.80, $p < 0.01$, as an obvious
577 result since all metals come from the same synthetic set of particles. A first result, PCA_1, was
578 obtained for the matrix of data formed by the 13 metals and 24 cases (fruit+leaf+soil x 4 pots x 2

579 species): two PCs accounted for 95.5% of the total variance (Fig. 4-a), where PC_2 (8.9% of
580 variance) was associated with the metals that did not over accumulate in fruits and leaves, as
581 already detected in the previous section, Mg, Mn, and Pb with high positive loadings (0.88-0.92).
582 After discarding these three elements, the second PCA (PCA_2) showed two PCs that explained
583 the overaccumulation of 10 metals in the different parts of the two plant species assayed (Table
584 5, Fig. 4-b). According to the loadings of the variables in the first PC, the descriptors that
585 contributed the most were Cd, Cr, Ni and Co. PC_1 accounted for 86.2% of the total variance and
586 appeared grouping of the heavy metals of Group B, Cd, Cr, Ni, Co, Cu and the alkali metal K
587 with high positive loadings (0.72-0.88). Cd and Ni are two of the four elements regulated by the
588 directive 2004/107/EC European Parliament. The scores of these metals of PC_1 were associated
589 with the leaves of cherry tomatoes and the fruits of strawberries, mainly of cherry tomatoes. Thus,
590 this PC represent the potential toxic elements that enter the plant system by the metal sorption
591 process (*i*PM).

592 PC_2 accounted for 11.2% of the total variance and appeared grouping of the essential metals Al,
593 B, Fe, Zn, the metals of Group A, with high positive loadings (0.73-0.88). The scores of these
594 metals of PC_2 were associated with the leaves of both species, mainly of strawberries, representing
595 in this case the essential metals that are deposited on leaves surface (*s*PM). Thus, the non-essential
596 heavy metals Cd and Cr themselves and also Ni and Co explain the observed variance and can be
597 considered the most discriminant variables between both type of uptake process. In addition,
598 samples of soils were not significant in the current system and constitute a different class.

599 *Cluster analysis*. A first cluster analysis with all variables (CA_1, Fig. 5-a) showed at a low linkage
600 distance, 8%, a separation between the metals that did not accumulate in the FSL system, Mg, Mn
601 and Pb, and the others, as already found in PCA_1. A second cluster analysis without Mg, Mn and
602 Pb (not shown) reveals the same separation of CA_1 between essential metals of Group A (right,
603 $C2_2$) and the potential toxic elements of Group B (left, $C2_1$) of metals. This dendrogram reveals
604 in C2 that the pairs Cr and Ni as PTEs, Fe and Al as EEs and especially B and Cu were the most
605 similar when particles contact to the FLS system. It must be mentioned that previous studies on

606 Nerium Oleander collected in an urban environment (Rossini & Fernández, 2007) revealed a
607 relationship between Cu content in leaves, soils and PM_{10} particles.

608 According to the PCA_2 results, Cd, Cr and Ni, Co were found to be the descriptors with highest
609 contribution (Table 5 and Fig. 4-b), as it was confirmed by $C2_1$ clusters of Fig. 5. Accordingly,
610 the cluster analysis of cases was applied by using these PTEs as variables and with no soil
611 samples. The tree dendrogram CA_2 reveals three clusters at 21% distance, one (left, C1) group
612 the round and smooth cherry tomato fruits, which accumulate the least contaminants (Fig. 5-b)
613 and do not appear in PCA_2. The other (right, $C2_2$) represents the tomato leaves and the strawberry
614 fruits, which accumulate the most pollutants and is the PC_1 of the PCA that accumulate
615 contaminants by *i*PM. In the middle ($C2_1$) are the strawberry leaf samples, which is also the PC_2
616 accumulating metals by *s*PM. Thus, CA_2 clearly separates the parts of the FSL system that
617 accumulate the most contaminants from those that do not, while it also discriminates tomato
618 leaves from strawberry leaves.

619 *Discriminant analysis*. If a descriptive LDA is done for the 6 sample classes, F+S+L in the two
620 species, strawberries and tomatoes are well discriminated for both the essential and the potentially
621 toxic elements. Al, B, Fe, Zn, Cr and Ni (Fig. 6-a). At the top of the graph, the strawberry fruits
622 and their leaves, well differentiated from each other, appear in the same grouping and separated
623 from the grouping at the bottom. where the round and smooth tomato fruits are entirely separated
624 from their leaves. In addition, the soils of both species, particularly strawberries, are more closely
625 associated with the tomato fruit group than with the leaves, which are completely discriminated.
626 When 3 classes were defined, tomato samples (leaves and fruits), strawberry samples (leaves and
627 fruits), and soil samples (strawberry and tomato) the variables Al, Cr, Fe, and Ni are the ones that
628 discriminate the classes formed by the 2 plant species and the soil (Fig. 6-b).

629 Finally, the following 4 classes were defined: first, tomato leaves and strawberry fruits that uptake
630 metals by over-accumulation (*i*PM), second, strawberry leaves which accumulation of metals
631 carried out by surface deposition (*s*PM), third, the soil samples from both pots where few particles
632 arrive, and fourth, the tomato fruits where particles slip away, and no metals are deposited, both

633 with no-acumulation. In this case, the diagram clearly shows (Fig. 6-c) that cherry tomato fruits
634 accumulate practically no metals and are grouped with the soil in the pots that receive few
635 particles, as they are deposited earlier on leaves and strawberry fruits. on the other hand, the
636 samples that have the greatest capacity to carry metals into the plant (tomato leaves and strawberry
637 fruits) are totally discriminated from those that only accumulate metals on the surface (strawberry
638 leaves).

639 5. **Conclusions**

640 The synthetic metallic particles were successfully prepared in the laboratory, and it was verified
641 that the composition of elements deposited on the contaminated plant parts and filters was similar
642 to the final composition of the synthetic particles injected (%C_{SS}, Table3). The experimental
643 design of the closed chamber worked efficiently, and positive and significant contamination for
644 both food species was verified statistically by ANOVA, hypothesis tests and measurement of
645 intermediate precision comparing blanks and contaminated samples.

646 This work has satisfied the objective of differentiating the rate of metal accumulation between the
647 two vegetal food species and between the different parts of the plant, with cherry tomato leaves
648 accumulating more amount of metals than strawberry leaves, with a special attention to the over-
649 accumulation of the toxic metals Ni, Cr, Cd and Co (+41%) and the essential metals Zn, Fe, Cu,
650 Al and B (+22%) by internal sorption (iPM) into stomata leaves. The strawberry fruits over-
651 accumulated (+15%) into it edible matrix much more metals (Al, Zn, Cu, B, Cd, Fe, Cr, and Ni)
652 than the mini and round cherry tomatoes, which due to their shape and texture do not allow particle
653 deposition. The study reveals the poor capacity of Mg, Mn and Pb elements for accumulation
654 inside the plant leaves and fruits. The accumulation capacity of fruits and leaves of both species
655 followed the order *to*L ≅ *st*F > *st*L >> *to*F, so, differences between the two plant species in terms
656 of metal uptake were only significant (>>) for the cherry tomato fruits, with a much lower capture
657 capacity, fortunately, as this is the edible part of the plant. However, in a fresh weight basis it was
658 a significant difference for the strawberry fruit (*st*F >> *st*L > *to*L >> *to*F), with an higher metal
659 uptake capacity, being now the edible part.

Multivariate analyses confirm by PCA the differentiation between the accumulation of the essential elements in plants by surface deposition for Al, B, Fe and Zn and that of internal sorption of the potential toxic elements Cd, Cr, Ni and Co. Likewise, the clustering found similarities between the pairs of elements Fe-Al, Cr-Ni and B-Cu. They highlighted the separation between the tomato fruit cluster from the other parts of both plant species due to the low metals cumulated in cherries, also differentiating the tomato leaves-strawberry fruits cluster (*i*PM) from the strawberry leaf samples (*s*PM). LDA showed clearly the difference between the *i*PM and *s*PM mode of metal uptake, and different from the soil samples and the tomato fruit.

If a long-term exposure of these plants occurs in a dry climate with few rainfall events and near sources of air pollutants, the entrance of metals into the plant by surface deposition/adsorption or internal absorption will be mostly through the leaves, especially in tomato, and through the fruit of strawberry (not in the case of cherry tomato), while the amount of particles deposited on the soil just below the plant is much smaller. During rainfall events it is to be expected that much of the particles fall to the ground and the entry of pollutants occurs via the roots by translocation, which constitutes a current research project.

In relation to the use of these food species in urban gardening, in summary, when quantifying the total deposited pollutants in a fresh weight basis, tomato pots accumulated less metals than strawberry pots, while, according to particles deposited in quartz filters, strawberries were the best at removing particles from the indoor air. Therefore, in relation to the use of food species on indoor vertical gardens, conclusions on the cleaning effect of the polluted air by the growing plants during each weekly experiment showed that strawberry plants reduced the amount of particulate matter in the air better than tomato plants.

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833

834

835 **Table 1**

836 Results of the recovery study using BCR-062 (concentrations in mg kg^{-1}) for n = 6 replicates

Element	Certified	Obtained	Recovery(%)	F_{calc}	F_{crit}	t_{calc}	t_{crit}
Al	260*	238 ± 15	91.4				
Cd	0.10 ± 0.02	0.11 ± 0.03	107.2	2.25	3.66	0.94	2.08
Cu	46.6 ± 1.8	44.3 ± 3.1	95.1	2.97	3.66	1.98	2.08
Fe	280*	232 ± 17	82.7				
K	3100*	3278 ± 235	105.7				
Mg	1200*	1188 ± 44	99.0				
Mn	57.0 ± 2.4	54.2 ± 4.6	95.1	2.25	3.66	1.95	2.08
Pb	25.0 ± 1.5	25.2 ± 1.6	100.7	1.14	3.66	0.29	2.08
Zn	16.0 ± 0.7	15.6 ± 1.2	97.8	2.94	3.66	1.01	2.08

837 *: not certified values; F_{calc}: calculated F_{Fisher}; F_{crit}: tabulated F_{Fisher}; t_{calc}; calculated $t_{Student}$; t_{crit}: tabulated $t_{Student}$

838

839 **Table 2**

840 Determination of concentrations (mg g^{-1}) obtained (n = 3) and final composition of synthetic particles, SS.

841 Comparison with the theoretical values (calculated).

Element	metallic salt	Mw (g mol^{-1})	Mp (ºC)	calculated	obtained (%C_{SS})
Al	$Al(NO_3)_3 \cdot 9\ H_2O$	375.13	73	1.89	1.82(2.6)
B	$Na_2B_4O_7 \cdot 10\ H_2O$	381.37	742	1.06	3.45(4.9)
Cd	$3CdSO_4 \cdot 8\ H_2O$	769.54	> 40	5.81	4.53(6.4)
Co	$Co(NO_3)_2 \cdot 6\ H_2O$	291.03	55	2.90	2.14(3.0)
Cr	$CrCl_3 \cdot 6\ H_2O$	266.45	83	3.13	1.84(2.6)
Cu	$CuSO_4$	159.61	110	3.39	3.37(4.8)
Fe	$Fe(NO_3)_3 \cdot 9\ H_2O$	404.00	47	2.28	1.91(2.7)
K	KCl	74.55	770	3.42	3.21(4.6)
Mg	$MgCl_2$	95.21	714	1.65	33.88(48.0)
Mn	$MnSO_4 \cdot H_2O$	169.02	700	4.59	4.09(5.8)
Ni	$Ni(NO_3)_2 \cdot 6\ H_2O$	290.79	56	2.89	1.91(2.7)
Pb	$Pb(NO_3)_2$	331.21	470	10.20	7.06(10.0)
Zn	$Zn(NO_3)_2 \cdot 4\ H_2O$	261.45	45	1.61	1.32(1.9)

842 M.w.: molecular weight; M.p.: melting point; in brackets %C_{SS}: final composition in percentage

843

Table 3

Weighted sum (*WS*) values (%) of metals for the four (1 – 4) pot experiments over the indoor air, fruits, leaves and the soil for the cherry tomato and the Strawberry plant species. Results of *t*-Student and *F*-Fisher-Snedecor tests comparing blanks and samples show significant [+] or not significant difference [–].

	Indoor air	Fruits			The Soil			Leaves		
Pot*	PM***	blank	sample	H_2O%/n	blank	sample	H_2O%/n	blank	sample	H_2O%/n
					Cherry tomato					
1	273	959	1155	94.6/29	698	1114	80.6	551	1140	90.4/115
2	384	895	1099	94.9/25	687	1127	83.3	568	1185	90.7/125
3	305	973	1180	94.8/23	707	1147	78.9	604	1225	91.0/110
4	262	945	1136	93.2/24	707	1142	61.3	527	1148	91.1/105
Mean	306	943	1143(**199**;1.2)**	94.4***	700	1133(**433**;1.6)**	81.0	563	1174(**612**;2.1)**	90.8
SD	55	34.12	34.07	0.79	9.4	14.8	1.82	32.3	38.8	0.32
RSD(%)	18	3.62	2.98	0.84	1.34	1.31	2.25	5.74	3.30	0.35
F_{calc}			1.0[–]			2.5[–]			1.4[–]	
F_{crit}			15.4			15.4			15.4	
p			0.50			0.23			0.39	
t_{calc}			8.3[+]			49.4[+]			24.2[+]	
t_{crit}			1.9			1.9			1.9	
p			$8.4 \cdot 10^{-5}$			$2.3 \cdot 10^{-9}$			$1.6 \cdot 10^{-7}$	
					Strawberry					
1	257	587	1255	93.3(8)	805	1241	79.7	510	1207	81.9(90)
2	232	653	1258	92.6(6)	804	1233	80.4	564	1170	81.3(88)
3	133	545	1199	91.8(9)	847	1239	82.3	702	1109	81.6(89)
4	200	706	1221	93.1(7)	787	1189	80.1	571	1177	80.9(94)
Mean	205	623	1233(**611**;2.0)	92.7	811	1226(**415**;1.5)	80.6	587	1166(**579**;2.0)	81.4
SD	54	71.2	28.2	0.67	25.6	24.6	1.15	81.3	41.1	0.43
RSD(%)	26	11.43	2.29	0.72	3.16	2.01	1.43	13.86	3.53	0.52
F_{calc}			6.36[–]			1.1[–]			3.9[–]	
F_{crit}			15.4			15.4			15.4	
p			0.08			0.48			0.15	
t_{calc}			15.9[+]			23.4[+]			12.7[+]	
t_{crit}			1.9			1.9			1.9	
p			$1.9 \cdot 10^{-6}$			$2.0 \cdot 10^{-7}$			$7.3 \cdot 10^{-6}$	

H_2O%: water content of fruits, leaves and the soil. n: number of fruits or leaves per pot; SD: standard deviation; RSD(%): relative standard deviation; F_{calc}: calculated F_{Fisher}; F_{crit}: tabulated F_{Fisher}; t_{calc}; calculated $t_{Student}$; t_{crit}: tabulated $t_{Student}$; p: probability

*: blanks were not subtracted from the samples;

: in brackets (*nWS***;*r*): in bold, difference *nWS*, net weighted sum 'sample–blank'; ratio *r*, 'sample/blank'

***: WS(%) of the 'reference' was 1300.

Table 4

Metal concentrations (mg Kg^{-1} day^{-1} dry weight) deposited (samples – blanks) in the four experiments over the fruit, the soil and leaf for the two plant species.

	Fruits				The soil				Leaves				
Element	mean	%C_PF	RSD(%)	R_F	mean	%C_PS	RSD(%)	Rs	mean	%C_PL	RSD(%)	R_L	R_{FSL}
Solanum lycopersicum (Cherry tomato)													
Al	0.18	2.5	7.2	1.0	1.77	4.6	12.5	1.8	5.40	4.2	10.6	1.6	1.5
B	0.35	4.8	6.2	1.0	2.65	6.9	4.9	1.4	9.68	7.5	4.3	1.5	1.3
Cd	0.46	6.3	7.5	1.0	1.75	4.5	7.4	0.7	13.50	10.4	10.2	1.6	1.1
Co	0.22	3.0	7.9	1.0	0.99	2.6	19.0	0.8	6.31	4.9	12.4	1.6	1.1
Cr	0.20	2.7	8.7	1.0	0.57	1.5	12.9	0.6	5.57	4.3	8.8	1.7	1.1
Cu	0.34	4.6	8.7	1.0	2.26	5.9	18.5	1.2	10.26	8.0	13.9	1.7	1.3
Fe	0.21	2.8	8.5	1.0	1.62	4.2	7.8	1.6	6.84	5.3	8.7	2.0	1.5
K	0.33	4.5	8.5	1.0	1.12	2.9	16.4	0.6	9.54	7.4	10.3	1.6	1.1
Mg	3.51	48.0	4.8	1.0	17.90	46.4	7.0	1.0	35.60	27.6	15.8	0.6	0.8
Mn	0.42	5.8	7.7	1.0	2.80	7.3	4.5	1.3	4.51	3.5	19.0	0.6	1.0
Ni	0.21	2.8	11.5	1.0	0.48	1.3	25.6	0.5	6.06	4.7	10.1	1.7	1.1
Pb	0.77	10.5	9.2	1.0	3.56	9.2	19.6	0.9	7.99	6.2	16.2	0.6	0.9
Zn	0.13	1.8	10.1	0.9	1.05	2.7	11.9	1.5	7.75	6.0	3.9	3.2	1.9
overall	sum	100%	median	mean	sum	100%	median	mean	sum	100%	median	mean	mean
	7.3		8.5	1.00	38.50		12.5	1.06	129.00		10.3	1.54	3.60
ANOVA	F_{calc}	F_{crit}		*p*	F_{calc}	F_{crit}		*p*	F_{calc}	F_{crit}		*p*	
	0.50	2.87		0.69	1.06	2.87		0.38	0.48	2.87		0.70	
Fragaria x ananassa (Strawberry)													
Al	2.57	2.9	17.4	1.2	0.64	3.1	29.8	1.2	3.82	4.1	13.1	1.6	1.3
B	4.75	5.4	14.6	1.1	1.12	5.5	15.9	1.1	6.40	6.8	7.8	1.4	1.2
Cd	6.24	7.1	11.9	1.1	1.10	5.4	17.2	0.8	3.64	3.9	13.8	0.6	0.9
Co	2.57	2.9	10.4	1.0	0.75	3.7	12.0	1.2	2.44	2.6	22.2	0.9	1.0
Cr	2.49	2.8	10.3	1.1	0.56	2.7	16.8	1.1	2.26	2.4	35.6	0.9	1.0
Cu	4.67	5.3	7.1	1.1	1.15	5.7	7.1	1.2	5.26	5.6	24.0	1.2	1.2
Fe	2.62	3.0	15.8	1.1	0.79	3.9	18.8	1.4	3.87	4.1	24.4	1.5	1.4
K	3.93	4.5	8.0	1.0	0.79	3.9	21.4	0.8	4.87	5.2	14.3	1.1	1.0
Mg	38.90	44.6	7.5	0.9	8.97	44.0	8.3	0.9	42.60	45.5	10.3	0.9	0.9
Mn	4.93	5.6	6.6	1.0	1.34	6.6	9.3	1.0	4.09	4.4	21.1	0.8	1.0
Ni	2.57	2.9	7.4	1.1	0.53	2.6	15.4	1.0	2.31	2.5	13.9	0.9	1.0
Pb	9.19	10.5	8.7	1.0	2.05	10.1	12.3	1.0	8.34	8.9	16.1	0.9	1.0
Zn	1.83	2.1	11.0	1.1	0.60	2.9	14.7	1.6	3.65	3.9	12.2	2.1	1.6
overall	sum	100%	median	mean	sum	100%	median	mean	sum	100%	median	mean	mean
	87.2		10.3	1.06	20.40		15.4	1.11	93.50		14.3	1.14	3.32
ANOVA	F_{calc}	F_{crit}		*p*	F_{calc}	F_{crit}		*p*	F_{calc}	F_{crit}		*p*	
	1.36	2.87		0.27	0.42	2.87		0.74	1.32	2.87		0.28	

RSD(%): relative standard deviation along 1-4 pot experiments; %C_P: percentage composition in the three parts of the P-pot, F-Fruits, S-the Soil and L-Leaves; F_{calc}: calculated F_{Fisher} from ANOVA; F_{crit}: tabulated F_{Fisher} from ANOVA; *p*: probability; sum: sum of 13 elements of averaged concentration; median: represents the central value of RSD along 13 elements

867 **Table 5**

868 Result of the PCA_2 of metals deposited in the fruits, leaves and the soil of cherry tomato and strawberry.

PCn	Eigen.	% Var.	Variables (loadings)	Cases	Interpretation
PC_1	8.6	86.2/86.2	Cd(89), Cr(86), Ni(80), Co(79), K(74), Cu(72)	*to*L_2, *to*L_3, *to*L_4, *to*L_1 // *st*F_1, *st*F_2	PTEs in tomato leaves, also strawberry fruits, Group B. Metal sorption *i*PM
PC_2	1.1	11.2/97.4	Al(88), B(83), Fe(80), Zn(75)	*st*L_4, *st*L_3 / *to*L_4, *to*L_1, *st*L_1	EEs in strawberry leaves and tomato leaves, Group A. Surface deposition *s*PM

869 Eigen.: Eigenvalue; % Var.: Percentage of the total variance explained/cumulative variance

870

a) Cherry tomato pot b) Strawberry pot

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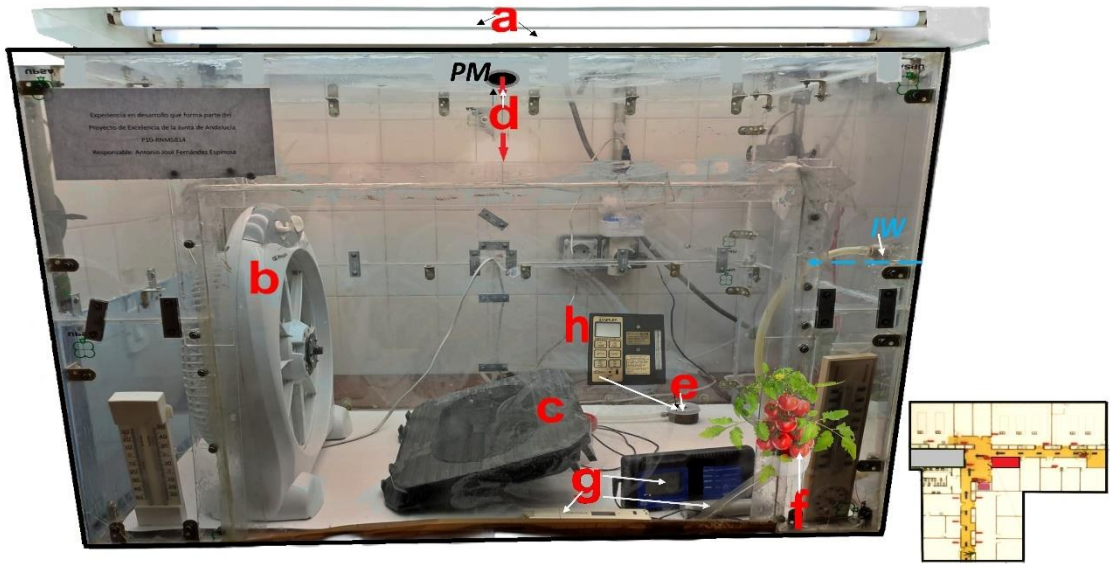

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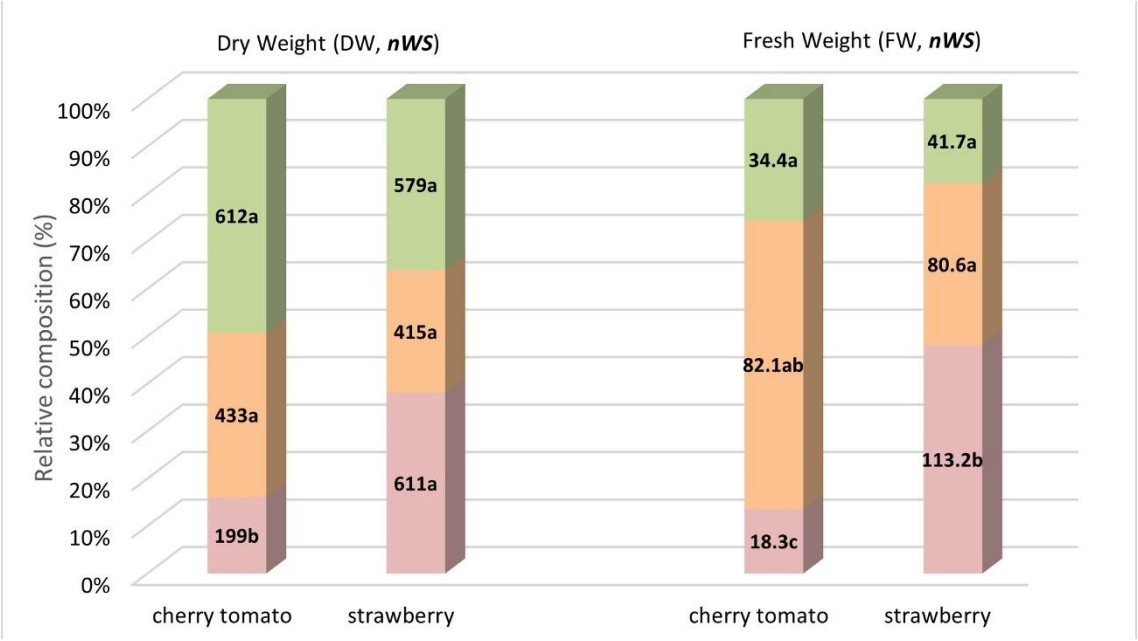
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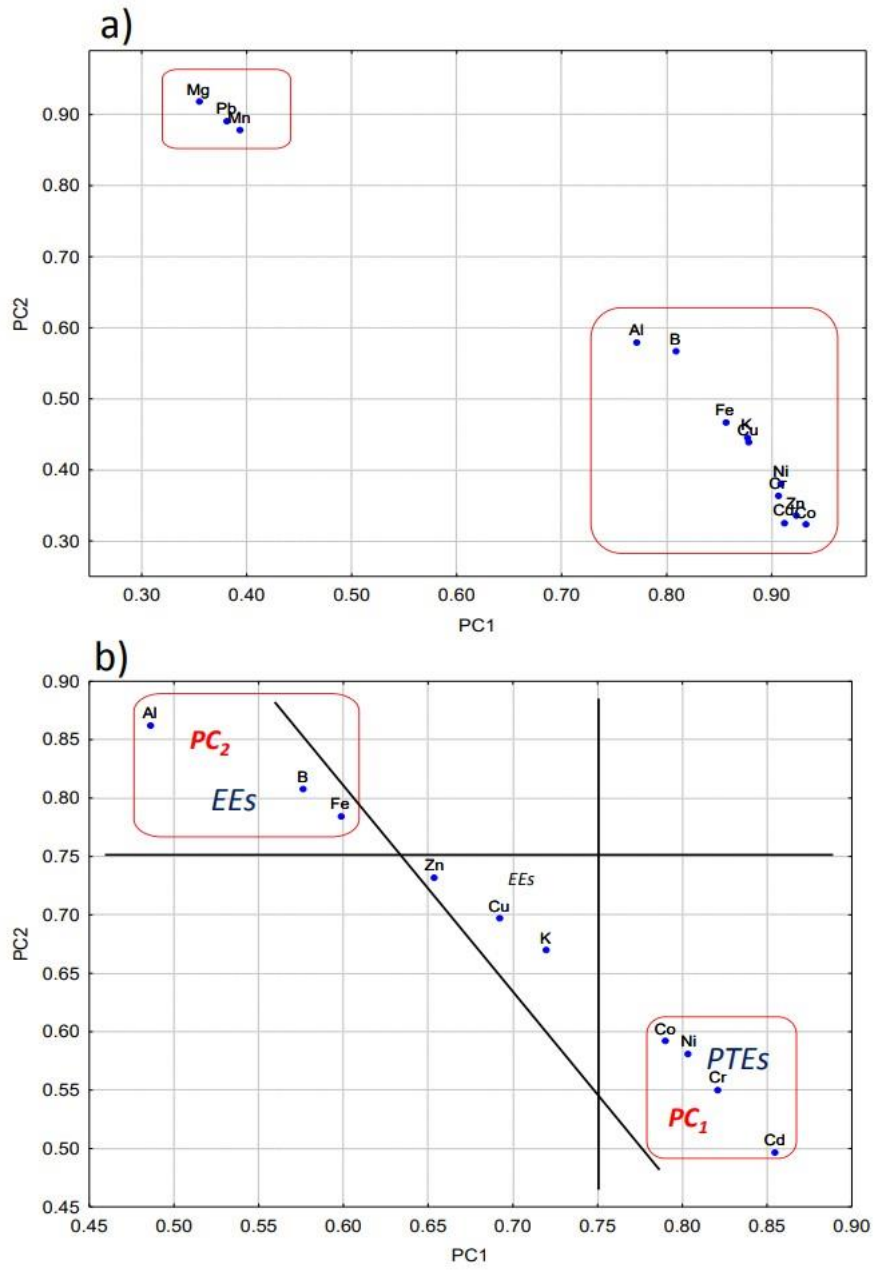
Fresh Weight (FW, nWS)
Relative composition (%)
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
612a
433a
199b
579a
415a
611a
34.4a
82.1ab
18.3c
41.7a
80.6a
113.2b
cherry tomato
strawberry
cherry tomato
strawberry

875
876


a)
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877

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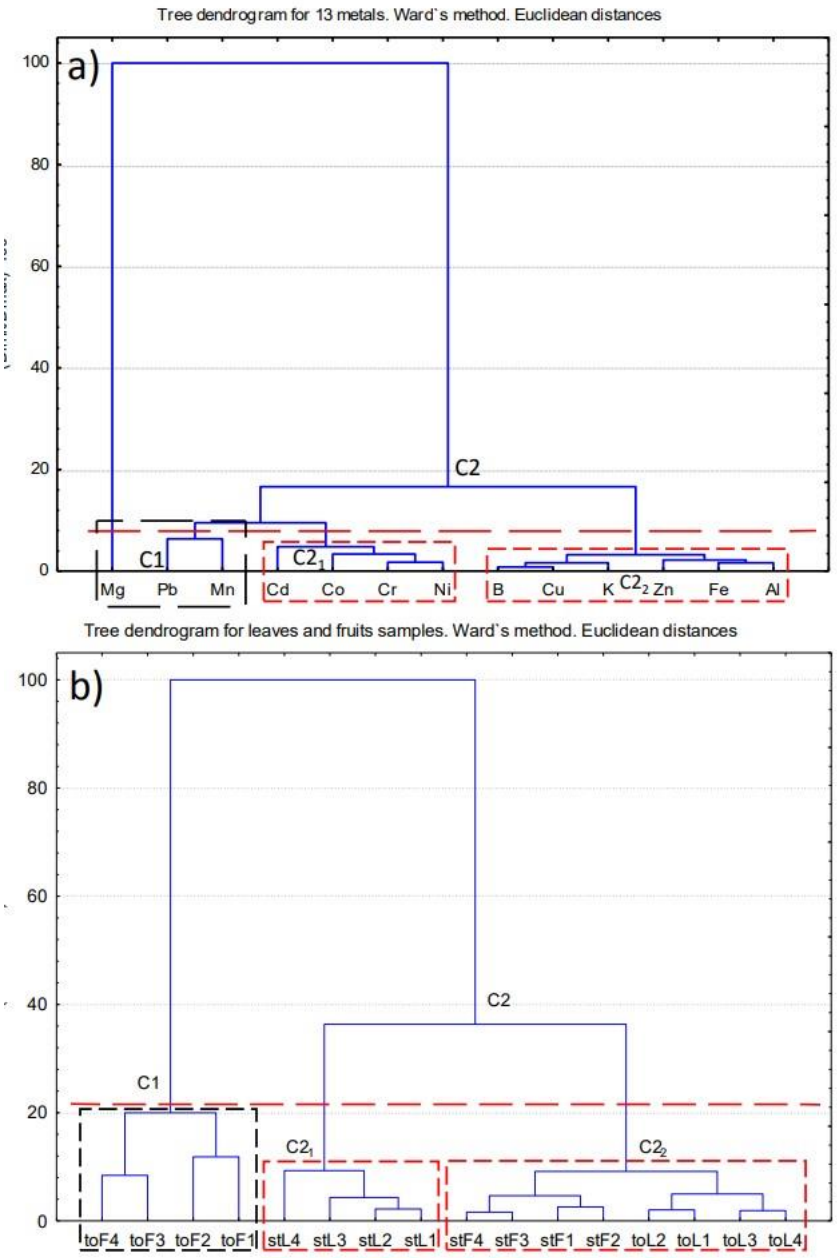
Tree dendrogram for 13 metals. Ward`s method. Euclidean distances
a)
100
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C1
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Tree dendrogram for leaves and fruits samples. Ward`s method. Euclidean distances
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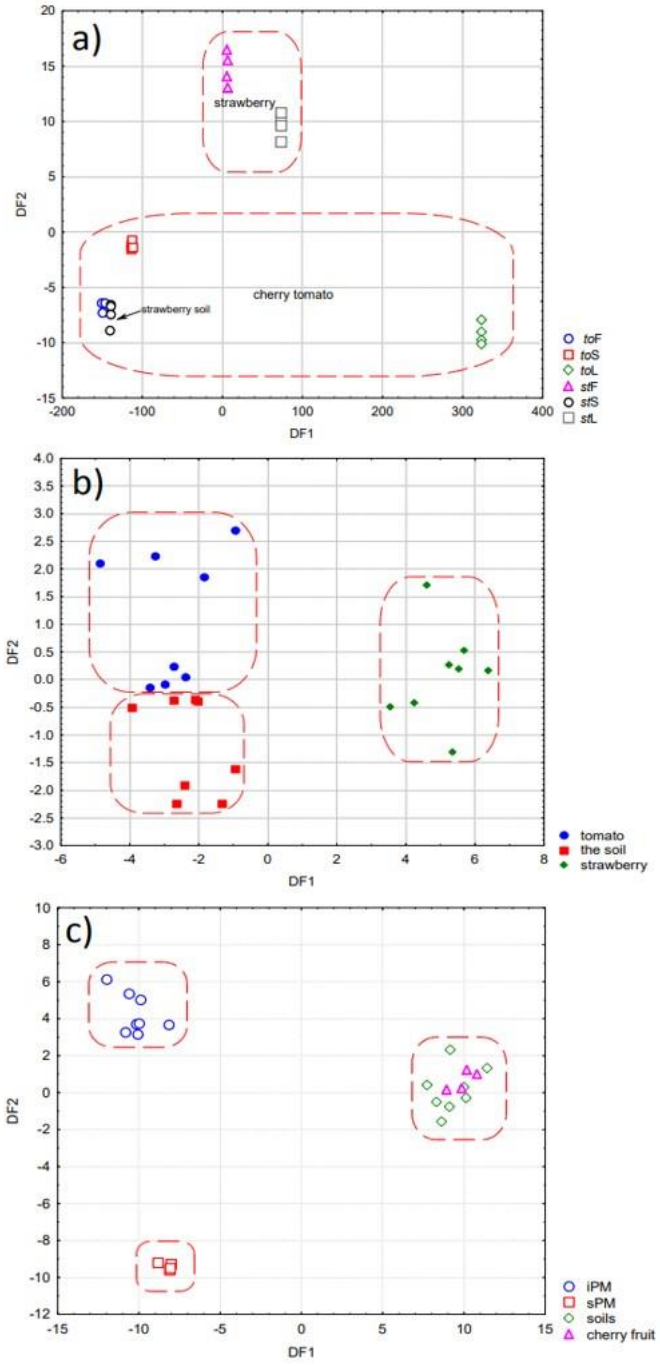
toL4

879
880


a)
strawberry
cherry tomato
strawberry soil
DF1
DF2
toF
toS
toL
stF
stS
stL
b)
DF1
DF2
tomato
the soil
strawberry
c)
DF1
DF2
iPM
sPM
soils
cherry fruit

881

882