The composition and relationships between trace element levels in inhalable atmospheric particles (PM_{10}) and in leaves of *Nerium oleander* L. and *Lantana camara* L.

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ABSTRACT

In order to evaluate the influence of air pollutant influx on inhalable atmospheric particles (PM_{10}) metal composition and study the relationship between trace element levels in PM_{10} and in leaves of two plant species, the concentration of Ba, Cu, Fe, Mn, Pb, Ti and V were analysed in PM_{10} and in *Nerium oleander* L. and *Lantana camara* L. leaves from 3 sites of the city of Seville. In the PM_{10}, Cu, Fe and Mn content was significantly lower ($p<0.05$) in the control site than in the other sites. Atmospheric pollution level of the city of Seville can be generally considered not dangerous for human health. No correlation between leaf content and air content was found for none elements in *L. camara*. By contrast positive and significant correlations ($p<0.05$) were found between leaf content of *N. oleander* and PM_{10} content for Cu and Fe. The data suggest that *N. oleander* can be used in atmospheric biomonitoring studies, being especially useful for Cu and Fe and much indicate than *L. camara*.

Keywords: Biomonitoring; Leaf; Particles; Trace elements

INTRODUCTION

Interest on the effect of atmospheric particles and especially in the inhalable fraction (PM_{10}) increased during the last years. PM_{10} are considered to be harmful for human health since they can cause respiratory and cardiovascular disease. Association between asthma attacks and coughs with particulates have also been reported (Freer-Smith et al., 1997). In large urban areas, the considerable amount of particulate matter in the air is a very crucial problem. The primary source of airborne particulate matter is agricultural practises, vehicle traffic, industrial processes and fossil fuel stations (Beckett et al., 1998). On the other hand, plants are known to capture trace elements and can be used in biomonitoring studies (Markert, 1996; Rossini Oliva and Valdés, 2003). Several studies have been done on the contamination by particulate matter in the city (Janssen et al., 1997; Monaci et al., 2000; Fernández et al., 2001), and on the useful of plant species as biomonitors (Barghigiani et al., 1991; Sawidis et al., 1995; Aksoy and Öztürk, 1997; Bargagli et al., 2003; Rossini Oliva and Valdés, 2003, 2004, Rossini Oliva & Rautio, 2004). Nevertheless, whether a relation between PM_{10} composition and trace elements in plants exists was insufficiently studied. An attempt to study the relation between Hg content in rosemary and broom leaves, *Abies alba* needles and pine needles in relation to those in atmosphere was done in Italy (Barghigiani et al., 1991; Barghigiani and Bauleo, 1992; Barghigiani and Ristori, 1995).

Seville is the most densely populated city of Southern Spain, with 716.937 inhabitants, situated only 10 m above the sea level on an extensive plain crossed by the Guadalquivir River. The city has a Mediterranean climate with an annual average temperature of 19 °C and rainfall of 580 mm. Traffic represents the most important pollution source since industries are rather scarce and metallurgic products represent only 15% of this industries. Important contributions of crustal particles in Seville and in the south of Spain are well known by the local scientific community and the Spanish and the regional governments.

The aim of this study was to compare trace element levels between the content in PM_{10} and leaves of *Nerium oleander* L. (oleander) and *Lantana camara* L. (lantana) to evaluate if a direct correspondence between the metal content of pollutants in air and in plant exists. These species were chosen because they are widespread in the city of Seville (S of Spain), both are perennial and Oleander is know to be an useful biomonitor (Sawidis et al., 1991; Aksoy and Öztürk, 1997; Rossini Oliva and Valdés, 2003). In addition, the composition of inhalable atmospheric particles was studied to establish the atmospheric contamination level of Seville.

MATERIALS AND METHODS

Samples of particles smaller than 10 μm (PM_{10}) and adult leaves of *N. oleander* and *L. camara* were collected simultaneously in three sampling sites from autumn 2003 to spring of 2004. A total of 22 samples of PM_{10} were collected together with the samples of both species of plants at the same day. Samples were usually taken on different days of the week, obtaining samples of every day of the week, therefore, in different meteorological and environmental conditions. Sampling periods for airborne particles were from 0:00 a.m. to 23:59 p.m. According to the local authorities information, one of the sampling site represents the area of Seville affected by the highest vehicular emissions (Torneo, TRN) and the other is a less contaminated areas with low traffic density (Porvenir, POR). The third sampling site (BLK), was chosen as a control site; it is located at about 40 Km far from Seville, in Sierra Morena, away from any traffic emissions but with similar climatic characteristics.

Several branches from three healthy-looking plants were cut off from sides of the canopy at 1.5 m for *N. oleander* and at 0.5 m for *L. camara*. Once in the lab, about 300 g of fresh mature leaves (including the petioles) were mixed to provide a unique sample. Samples were dried overnight at 70 °C, ground to a fine powder.

Atmospheric particulate matter was collected with a standard high-volume sampler MCV, model CAV-A/HF equipped with a PM_{10} inlet (MCV, model PM_{10}/CAV). PM_{10} inlet was used to collect all particles less than 10 micrometers (aed) and the MCV mark was inter-compared with the reference PM_{10} inlet of the EN 12341 European Norm. The sampling system was set at a flow rate of 68 $m^{-3}h^{-1}$, according manufacturing specifications. Glassfibre filters were used as collection media (Whatman GF/A, 24.5 x 20.3 cm). Before the analysis of airborne samples, filters used for particle collection were dried, before and after weighing, in a high-volume desiccator under 3% R.H. for a 48-h period. Operations of conservation, drying and weighing took place in a dark room at 50±5 % R.H, a temperature of 20±1 ºC was controlled by a heating-cooling system. Care was taken in handling the sampled filters and plants in order to avoid contamination problems using a vertical laminar airflow cabinet with a HEPA filter INDELAB, model IDL-48V, thereby ensuring air cleanliness standards of class 100 according to the US-Federal Standard 209E (FED.STD-209E, 1988).

Filters and plants were placed in closed teflon vessels with 15 ml of HNO_3-$HClO_4$ v/v (3:1) and digested in a microwave oven Millestone, model Ethos 900 with a specific digestion programme. After digestion and cooling, sample solutions were transferred into sterile tubes.

Since individuals blanks were not available for each filter used for sampling, a set of unexposed filters for each type of filter was analysed as blanks using the same procedure used for samples. The mean unexposed filters value were determined and subtracted from each sample to obtain the best estimate of each element in the particulate matter.

The accuracy of the determinations were previously checked by analysis of a NIST reference material (SRM 1648) for airborne particles and a GBW 07604 (poplar leaves) reference material for plants. A gold solution was used as internal standard to spike samples, blanks and reference material and to check the correct quantification of the elements. Previously, it was studied that gold was not presented in urban air and plants and its presence within the teflon vessel had no influence on analytical determinations of the other metals. All ultrapure reagents and standards were supplied by Merck and distilled water was of Milli-Q grade obtained from a Waters-Millipore apparatus, model Plus. The concentration of Ba, Cu, Fe, Pb, Mn, Ni, Ti and V have been determined simultaneously by inductively coupled plasma atomic emission spectrometry (ICP-AES), using a Fisons-ARL 3410 sequential multi-element instrument. The standard operational condition of this instrument are summarised as follows: the carrier gas, coolant gas, and plasma gas is argon at 80 psi of pressure, the carrier gas and plasma gas flow rate are 0.8 l min^{-1}, the coolant gas flow rate is 7.5 l min^{-1} and the integration time is 1 s. One mini-torch consumes argon gas at a radio frequency power of 650 W. Consequently, it is capable of consuming a few millilitres of sample at a flow rate of 2.3 ml min^{-1}. In order to avoid errors in results due to the effect produced by the different viscosity and density of the acid matrix of samples on the ICP nebulisation, calibration curves have been made with the same acid matrix.

Statistical analyses were carried out using the CSS:STATISTICA (StatSoft) software package. Summary statistics were used to calculate the mean values and standard deviation and, one-way analysis of variance (ANOVA) to detect significant differences of mean content between sites and species ($p<0.05$). Relationship between metal concentration in particles and in both species was tested by the Pearson correlation coefficients (r). The interpretation of the correlation results consist in assigning a common source to the metal fractions correlated, in relation to the main sources of this city, such as the traffic, the land particles and the industrial activities. In our case, when one metal increases their concentration in the air, parallelly to other metal through different sampling sites and different days, one can consider that these metals come from the same emission source. Because a high correlation coefficient does not necessarily imply linearity, linearity was verified by graphical examination. Any non-linear case was discarded.

RESULTS AND DISCUSSION

The studied elements mean concentrations found in PM_{10} and in plants in different sites are reported in Table 1. The values of particles metal concentration for all sampling sites can be consider not dangerous for human health, since their values showed lower concentrations than those indicated by the Unit Risk (UR) values on cancer of the WHO (World Health Organization). Only for Ni, the mean value was close to the UR limit (2.5 ng m^{-3}), indicating the potential risk of harmful for this element. The result of Cu and Pb is also according to Ross (1994) criteria, since the concentration of these two elements in both studied species did not exceed the upper limit of values considered toxic or present in contaminated plants.

The ANOVA results showed that the air pollutant concentrations were not significantly different between the various sampling sites, except for Mn, Cu and Fe. The Mn concentration was significantly low in the control sites respect to POR and TRN and, this was also the case of Cu and Fe only comparing to TRN. The TRN site represents the zone of the city more influenced by the vehicular traffic as it was above mentioned, suggesting that atmospheric pollution by both elements is higher due to the traffic or soil re-suspension (Fernández et al., 2004).

In relation to the plants, in both species the mean concentration of Pb, Ni, Mn, Cu (except for lantana en POR), Fe (except for lantana in POR) and Ba were below than the reference values given by Markert (1996). On the other hand the V and, mainly the Ti mean values in both species were always higher than the reference values, including the samples from the control site, suggesting that they come mainly from the soil.

Leaves of oleander showed a mean concentration of Cu, Pb, Fe and Ni lower than that reported by Rossini Oliva and Valdés (2003) in Palermo. Sawidis et al. (1995) found higher values of Cu and Pb in control site and in city roads of Tessaloniki than those found in Seville and the same results were reported by Aksoy and Öztürk (1997) in Antalya (Turkey), confirming the data of PM_{10} above discussed.

In the case of *N. oleander*, differences of Pb, Ni and V concentration in the control site with respect to the other sites were not find, whilst a lower Cu, Fe and Mn concentration were found in the control site. For *L. camara* pollutant concentrations were significantly different between the various sampling sites, except for Ni. The Pb, Ba, Cu, Fe and V concentrations were significantly lower in the control sites only with respect to POR and, Mn concentration in the control site was significantly higher than in both sites; significantly higher Ba and V concentrations in the control site with respect to TRN were also found. In addition, the Ti concentration in the control site was significantly higher than in the other sites. This means that lantana is not useful as biomonitor since it does not reflects the pollution environmental conditions.

Correlation between content in PM_{10} and plants was only found in one species, *N. oleander* and only for Cu and Fe (Fig. 1), indicating that oleander can be a more useful biomonitors of these two elements than *L. camara*. This is in accordance with Jones et al. (1985) stating that high positive associations between the pollutant concentrations in plants and their environment suggest the potential use for pollution monitoring in general and for the examined metals in particular. Barghigiani and Ristori (1995) did not found any relationship between Hg concentration in rosemary and broom leaves and in air, indicating that one of the reasons could be the low Hg air concentration. Since atmospheric pollution in the sampling sites can be considered low, this can be the reason because the absence of relationship in lantana, indicating therefore that it is less sensible than oleander to detect atmospheric pollution variations by Cu and Fe.

Although lantana has a rougher leaf surface than oleander, that it is known that this characteristic increases the dust deposition, this study shows that this property look likes than does not affects the capacity to retain and trap more pollutants, since the ANOVA results showed that significant differences ($p<0.05$) between the two species only exists for Cu and Fe contents, in addition oleander leaves accumulates more Ba than lantana. On the other hand like Farmer reported (1993) that this characteristic is important for particle greater than 10 µm, therefore this can be the reason because the null correlations found in lantana.

CONCLUSIONS

The atmospheric pollution by metals of the Seville City can be considered low and generally not dangerous for human health except for Ni. Iron and Cu were specially differentiating between the control site and the urban sites. These two metals were the only correlated between particles and oleander leaf concentrations, indicating that this species is more useful biomonitor of atmospheric Cu and Fe than lantana. Lantana is able to accumulate a high amount of pollutants by leaves, but it is not useful to reflect quantitative aspect of atmospheric quality.

The content in PM_{10} of the road sites contain concentrations of Cu, Fe and Mn in amount higher than the value in the control site, suggests that their source come from the traffic emissions.

Acknowledgement

The authors would like to thanks Prof. Miguel Ternero and Prof. Benito Valdés for their valuable help to the organisation of the field job. We would also like to thank the Council of Castilblanco de los Arroyo for their facilities during the sampling at the control site.

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Table 1
Measured and certified element concentrations (mg kg^{-1}) in reference materials

Element	Certified value	Experimental value	Recovery (%)	AOAC criteria[a] (%)
GBW 07604 (poplar leaves)				
Pb	1.5 ± 0.2	1.3 ± 0.3	84.7	80–110
Ni	1.9 ± 0.2	1.6 ± 0.2	83.9	80–110
Mn	45 ± 2	42.4 ± 2.6	94.3	80–110
Cu	9.3 ± 0.5	8.5 ± 0.8	91.5	80–110
Fe	274 ± 10	283 ± 11	103.1	90–107
V[b]	(0.64)	0.5 ± 0.1	72.0	–
Ti	20.4 ± 1.7	17.3 ± 2.2	85.0	80–110
Ba	26 ± 2	21.8 ± 2.5	83.7	80–110
SRM 1648 (urban particulate matter)				
Pb	6550 ± 162	6242 ± 170	95.3	95–105
Ni	82 ± 6	70 ± 3	86.0	80–110
Mn	786 ± 34	777 ± 18	98.9	90–107
Cu	609 ± 55	561 ± 8	92.1	90–107
Fe	39100 ± 2020	39960 ± 821	102.2	97–103
V	127 ± 14	122 ± 3	96.1	90–107
Ba[b]	(737)	713 ± 23	96.7	90–107

Recovery values were compared with the criteria of the American Organisation of Analytical Chemists (AOAC).

[a] AOAC (1993).

[b] Value not certified.

Table 2
Mean concentrations of pollutant elements (±SD) in airborne particles (PM_{10}, ng m^{-3}) and plants (mg kg^{-1}). P, PM_{10}; N, *Nerium oleander*; L, *Lantana camara*

Sampling sites and sample type	Pb	Ni	Mn	Cu	Fe	V	Ti	Ba
P, POR ($n = 8$)	4.76 ± 3.01	2.29 ± 0.92	5.79 ± 2.27	22.62 ± 3.46	238.6 ± 89.47	4.10 ± 1.83	10.81 ± 4.94	–
P, TRN ($n = 9$)	4.15 ± 2.44	2.45 ± 1.07	6.50 ± 2.72*	28.88 ± 8.40*	277.2 ± 120.6*	3.76 ± 2.01	11.58 ± 6.74	–
P, BLK ($n = 5$)	1.14 ± 0.70	1.66 ± 0.48	2.60 ± 0.97	13.45 ± 5.04	85.05 ± 46.55	2.16 ± 1.36	10.13 ± 7.47	–
N, POR ($n = 8$)	0.71 ± 0.49	0.17 ± 0.12*	42.38 ± 4.96*	4.83 ± 0.62*	108.3 ± 12.20*	0.72 ± 0.30	9.06 ± 1.96*	22.89 ± 4.63
N, TRN ($n = 9$)	0.91 ± 0.60	0.09 ± 0.06	18.26 ± 2.12	7.04 ± 1.29*	109.5 ± 15.78*	0.61 ± 0.22	8.44 ± 2.26*	32.97 ± 3.85*
N, BLK ($n = 5$)	0.27 ± 0.35	n.d.	23.79 ± 8.66	2.60 ± 1.13	63.97 ± 14.65	0.49 ± 0.18	14.19 ± 2.93	22.88 ± 6.04
L, POR ($n = 8$)	1.28 ± 0.43*	0.13 ± 0.11	17.75 ± 2.18*	11.88 ± 1.92*	222.1 ± 48.52*	1.29 ± 0.38	15.89 ± 2.93*	10.54 ± 2.32*
L, TRN ($n = 9$)	0.47 ± 0.41	0.15 ± 0.14	23.53 ± 9.17	5.94 ± 0.81	70.98 ± 12.61*	0.42 ± 0.23	4.75 ± 1.43*	5.81 ± 1.79
L, BLK ($n = 5$)	0.77 ± 0.14	0.04 ± 0.02	33.47 ± 3.67	7.79 ± 0.80	119.0 ± 24.15	0.88 ± 0.09*	25.81 ± 5.40	3.73 ± 1.77
Particle limit values[a]	500	2.5	150			1000		
Elemental conc. in plants[b]	1	1.5	200	10	150	0.5	5	40

In PM_{10} Ba was not possible to measure. POR, Porvenir; TRN, Torneo; BLK, background.
* Differences between the means from BLK and sampling sites are statistically significant (Schefflé test, $p < 0.05$) n.d., not detected.
[a] Unit Risk (UR, ng m^{-3}) values based on cancer of the WHO (World Health Organization).
[b] Markert (1996) (mg kg^{-1}).

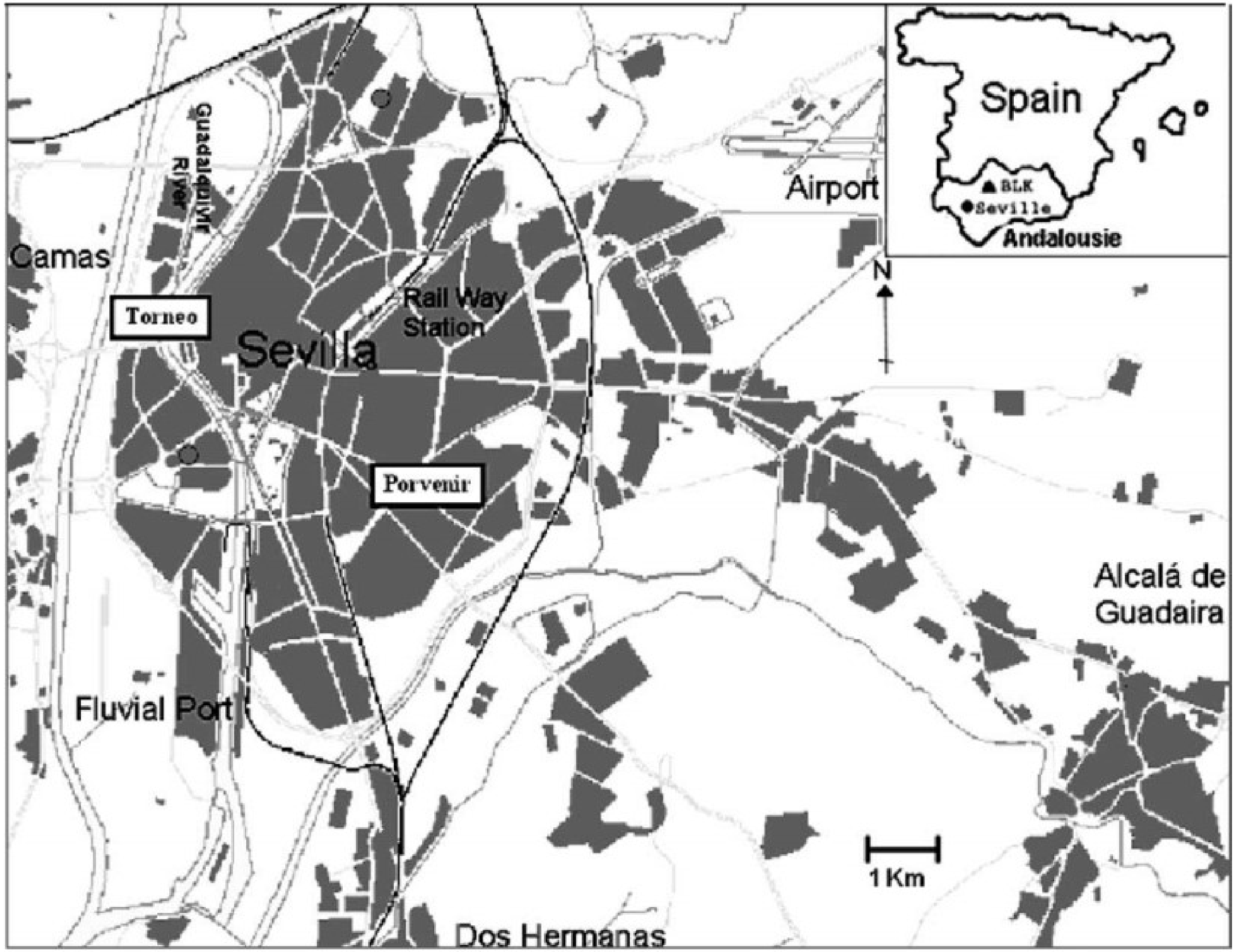

Fig. 1. Map of Seville with the location of the sampling site. BLK indicates the control site.

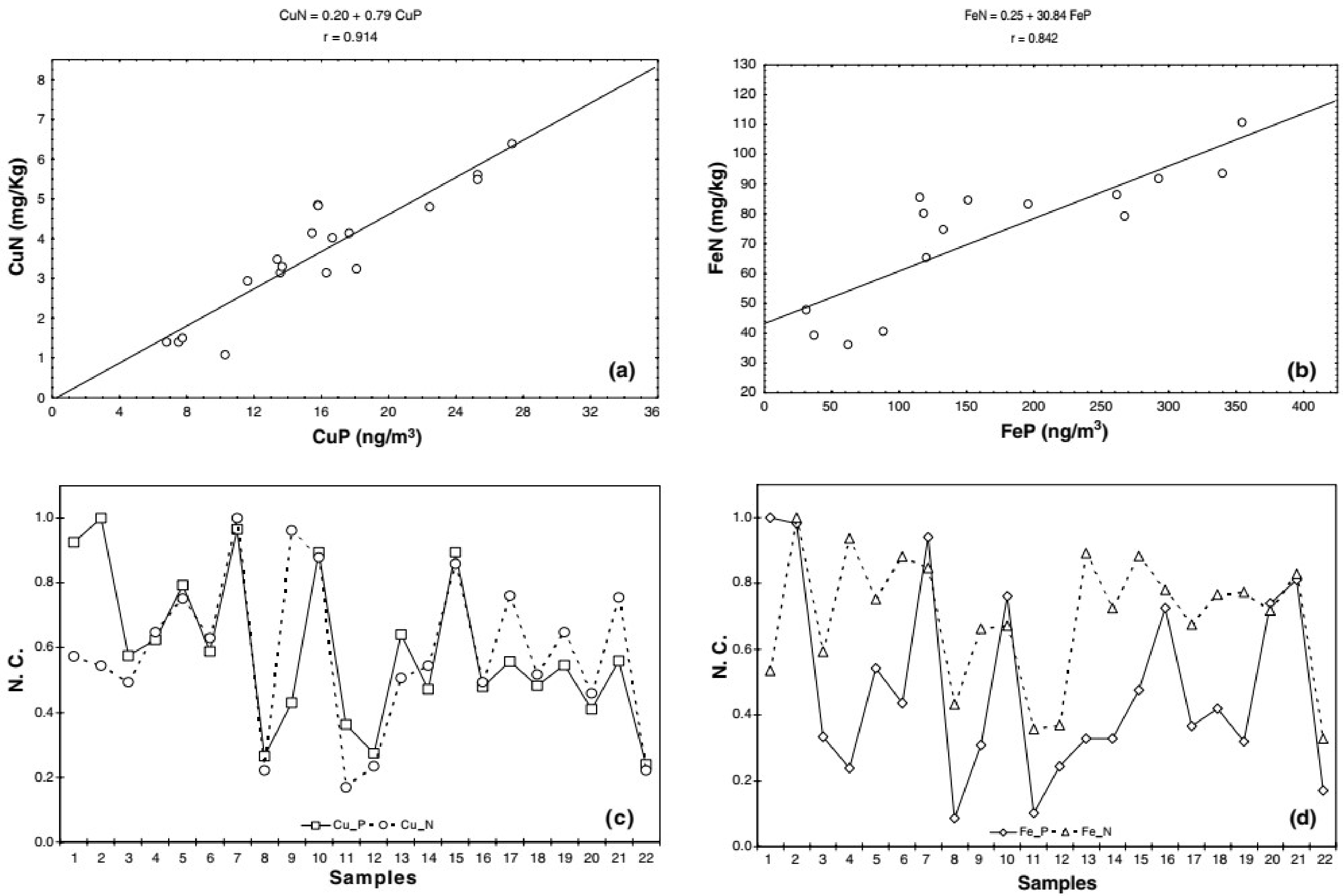

Fig. 2. Statistical correlations between particles (indicated by P) and *N. oleander* obtained for Cu (a) and Fe (b). Sequential variation of Cu (c) and Fe (d) concentrations in *N. oleander*. NC, normalised concentration.