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LEAF WASHING AS AN ASSESSMENT TOOL TO CHARACTERIZE DRY ATMOSPHERIC DEPOSITION

CARACTÉRISATION DES DEPOTS ATMOSPHERIQUES A TRAVERS LE TEST DE LAVAGE DE FEUILLES

CARATTERIZZAZIONE DELLE DEPOSIZIONI ATMOSFERICHE ATTRAVERSO IL TEST DEL LAVAGGIO FOGLIARE

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Abstract

The aim of this work was to characterize dry atmospheric deposition after the washing of broad leaves and conifer foliage. To assess this method different sites chosen on the basis of different exposure to both point (e.g. waste incinerator plant (WIP), local crafts) and widespread (e.g. roads, agricultural practices) sources of anthropogenic pollution.

The principal components analysis (PCA), performed on the major and trace elements identified after leaf washing, extracted four factors. F2 was lithogenic while the other three were anthropogenic. The enrichment factor (EF) highlights that Cd, Cu and Zn had a purely anthropogenic origin. The sites were grouped according to the predominant source of exposure and the synthetic index of enrichment (SIE) showed a decrease as follows: downwind from WIP > max exposure to WIP > min exposure to WIP > road > craft > rural zone.

The leaf area allows to calculate the annual flow of elements and the deposition flux in the study area varied for Cd from 0.07 to 0.55 mg m^{-2}, for Co from 0.1 to 0.48 mg m^{-2}, for Cr from 0.63 to 3.7 mg m^{-2}, for Cu from 14.5 to 32.27 mg m^{-2}. The Cd flux in the Bologna area was lower than in some industrial zones of the World and the lowest values were found in the rural zones and under a minimum exposure to the incinerator plant, while the highest values were near the roads and under maximum exposure to the incinerator.

The direct analysis of the leaf-washing water allows to discriminate the anthropogenic or geogenic metals deposited on the leaves using multivariate statistical analysis. It is also possible to predict the flow of metals in different areas of investigation.

Key words: *environmental quality, leaf-washing water, incinerator plant, enrichment factor, flux of pollutants*

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Résumé

Le but de ce travail était de caractériser les dépôts atmosphériques par le lavage des feuilles d'arbres à feuilles larges et de conifères. Pour évaluer la méthode, plusieurs sites ont été choisis sur la base de l'exposition à différentes sources de pollution aussi bien ponctuelle (par exemple, incinération de déchets (WIP), artisanat) et diffuses (par exemple routes, pratiques agricoles).
L'analyse en composantes principales (ACP) effectuée sur les éléments les plus importants et les traces déterminées après lavage des feuilles, a extrait quatre facteurs. F2 était lithogène tandis que les trois autres étaient d'origine anthropique. Le facteur d'enrichissement (EF) a montré que Cd, Cu et Zn étaient d'origine purement anthropique. Les sites ont été regroupés en fonction du mode principal d'exposition et on a calculé l'indice synthétique d'enrichissement (SIE), qui décroissait comme suit: sous le vent de WIP > exposition maximale à WIP > exposition minimale à WIP > route > zone artisanale > zone rurale.
La surface foliaire permet de calculer le débit d'éléments au cours de l'année et le flux de dépôt dans la zone d'étude variait pour le Cd de 0,07 à 0,55 mg m^{-2}, pour le Co de 0,1 à 0, 48 mg m^{-2}, pour le Cr de 0,63 à 3,7 mg m^{-2}, pour le Cu de 14,5 à 32,27 mg m^{-2}. Le flux de Cd dans la région de Bologne était inférieur à celui observé dans des zones industrielles du monde et les valeurs étaient plus faibles dans les zones rurales et sous exposition minimale à l'installation d'incinération, tandis que les plus élevées étaient localisées à proximité des routes et sous exposition maximale à l'incinérateur.
Une analyse directe de l'eau après lavage permet, par analyse statistique multivariée, de discriminer les métaux d'origine anthropique et / ou géogène déposés sur les feuilles. Il est également possible de prévoir les flux de métaux dans diverses aires d'investigation.
Mots-clés: *qualité de l'environnement, eau de lavage des feuilles, centre d'incinération, facteur d'enrichissement, flux de polluants.*

Riassunto

Lo scopo di questo lavoro è stato quello di caratterizzare la deposizione atmosferica nell'acqua di lavaggio delle foglie degli alberi di latifoglie e conifere. Per valutare il metodo diversi siti sono stati scelti sulla base della diversa esposizione a fonti di inquinamento sia puntuali (es. impianto di incenerimento dei rifiuti (WIP), artigianato) che diffuse (ad esempio strade, pratiche agricole).
L'analisi delle componenti principali (PCA), eseguite sugli elementi più importanti e in traccia determinati dopo il lavaggio delle foglie, ha estratto quattro fattori: F2 di origine litogenica, mentre gli altri tre erano di origine antropica. Il fattore di arricchimento (EF) ha evidenziato che Cd, Cu e Zn hanno un'origine prettamente antropica. I siti sono stati raggruppati secondo la principale fonte di esposizione ed è stato calcolato l'indice sintetico di arricchimento (SIE), che ha evidenziato una

flessione nel modo seguente: WIP sottovento> WIP max esposizione> WIP min esposizione> strada> zona artigianale> zona rurale.
La superficie fogliare ha permesso di calcolare il flusso di elementi nel corso dell'anno che nell'area di studio varia per il Cd da 0,07 a 0,55 mg m-2, per il Co da 0,1 a 0,48, per il Cr da 0,63 a 3,7 e per il Cu da 14,5 a 32,27. Il flusso di Cd nell'area bolognese è risultato inferiore a quello evidenziato in zone industriali del Mondo ed i valori sono più bassi nelle zone rurali e nella minima esposizione al dominio dell'impianti di incenerimento, mentre i più alti sono in concomitanza deghli assi viari e sotto la massima esposizione al dominio dell'inceneritore.
L'analisi diretta dell'acqua dopo il lavaggio fogliare ha permesso di discriminare l'origine antropica e/o geogenica dei metalli depositati sulle foglie con analisi statistica multivariata, con la possibilità di prevedere il flusso di metalli in diverse aree di indagine.
Parole chiave: *qualità ambientale, acque di lavaggio delle foglie, impianto di incenerimento, fattore di arricchimento, flusso di inquinanti*

Introduction

The atmospheric depositions in urban areas from scattered and point sources (Shi et al., 2012) affect the environmental quality and they constitute a risk for human health, depending on their characteristics (e.g size, surface and density) and on those of site (position and height of the emission point, local ventilation, prevailing wind direction and topography). Organic and inorganic particles may be transported in the atmosphere over long distances whereby only a fraction possibly recovered in the vicinity of the source and its deposition may be related to both wet and dry deposition (Galarneau et al., 2000).
High deposition of gaseous pollutants and particulates are intercepted by woodlands (Fowler et al. 1989) because trees, having a great leaf area, create a more turbulent mixing of the air compared to other types of vegetation. The urban trees can remove part of the particles from the air (Freer-Smith et al. 1997) and the amount of pollutants airborne becomes specific site (McPherson et al., 1994 and Beckett et al., 2000a). Beckett et al. (2000b) showed that the PM10 load on the foliage of various tree species were ranged between 70 and 490 mg m^{-2} depending on species, site and exposure conditions. Heavy metals concentration determined in water after leaves washing test can indicate the load of dry and wet atmospheric deposition of a specific site.
The metals concentration deposited on the leaves can be determined by subtracting the amount determined in the leaves washed and unwashed (Rossini Oliva and Ratio 2003; Gherardi et al., 2009) and much attention was also addressed to the technique, timing and cleaning of leaves (Rossini Oliva and Ratio 2003; Vittori Antisari et al., 2010).
Aim of this work was to assess the chemical composition of pollutants deposited on the leaves through the analysis of leaf-washing water. The hypothesis was that

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the collection of pollutants into water could be extremely sensitive tool to discriminate the sources of pollutants emission. The study area is close to the city of Bologna, situated in the centre of the Emilia-Romagna region in the southeast portion of the Po Valley, in Northern Italy. The Po Valley is characterised by high emissions from industrial, urban, agriculture and traffic sources and represents one of the European regions with the worst air pollution. Furthermore, the topography, geographic location and prevailing synoptic circulation of the area favour frequent low wind speeds, fog and inversion layers that occur consistently during winter seasons. Therefore, weather-climatic factors play a large role in determining the critical conditions that lead to the high pollution situation in the area (Vittori Antisari et al., 2009).

The aim of this work was assess the chemical composition of dry deposition in sites chosen on the basis of different exposures to both point (waste incineration plants, craft activities) and widespread (road and rural areas) sources of pollution.

Material and Methods

Study area, and sampling

The different PM_{10} fallout due to incinerator emission and other sources as well as industries, traffic, agriculture was defined by a dispersion model from Agency of Environmental Protection of Emilia Romagna Region (Italy) and in this way the monitoring sites were characterized.

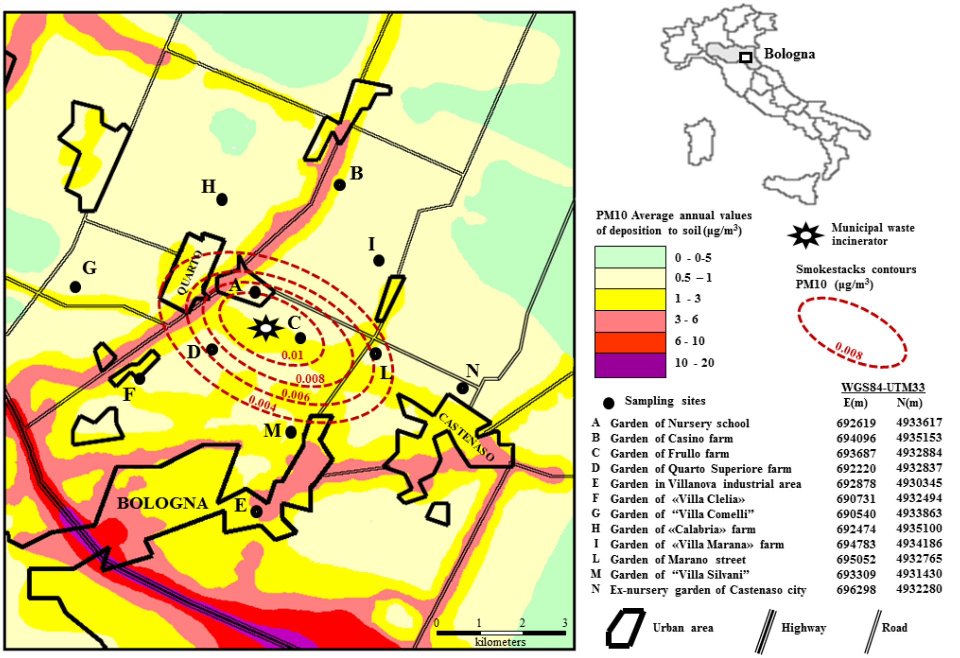
The sites, defined in Figure 1 by capital letters, are selected from gardens of ancient house. In addition, the sites A, C, D, L, M and N are in the fallout area of incinerator emissions (PM10 range 0.003-0.019 ng/m^3) namely: A and D located at the contrary to the prevailing wind direction (downwind stations), C and L under the direction of prevailing wind (C is the maximum expected fallout by incinerator) while N and M are under mild domain of incinerator. The sites B, and F are exposed to roads, site E is within an craft area, while the sites G, H and I are in rural area.

The leaves of three or four trees for each of twelve of selected gardens were collected away from rainfall. The leaves were collected at midi-canopy of each tree (about 2-3 m) for broadleaves and sprigs for conifers. The samples were replicated four time during a year. 50 leaves were carefully removed by the petiole and placed directly into acid cleaned 500 mL wide-mouth Teflon bottles and taken directly in laboratory. Three sets of 50 leaves were collected from each tree species for each sites. An additional set of 20 leaves was collected from each sampled branch for determination of leaf area and dry weight.

Analytical data

Leaf washing test. After 1 hour from collecting, the leaves samples were dipped in acidulated water (pH ~ 5.3, with 35% Suprapur HCl) and then shaken for 15 minutes. Steubing (1982) reported that washing with distilled water for 1 min removes only a minor proportion of the pollutants, but washing for 15 min considerably increases the yield, on the contrary increasing the washing time to 30 min do not removes any more pollutants (Steubing, 1982). The water samples after the leaching tests were collected in polyethylene beakers, evaporated in ventilated oven, brought to 100 mL, furthermore the samples were filtered, acidified with HNO_3 (65 % Suprapur, E. Merck, Germany; 1:100 v/v) and stored at 4°C until analysis.

Figure 1 – *PM10 year deposition map from widespread sources and municipal waste incinerator plant.*



The major and trace elements were determined by Inductive Coupled Plasma Optical Emission Spectrometry (ICP-OES, Spectro Ametek, Arcos). The ICP-OES setting followed multi-standard solutions (CPI-International-Amsterdam) that reproduce the matrix effect present in samples and allow the lowering of Detection Limits (DL). Instrument response was assessed by measuring a standard sample (CRM 609 - Community Bureau of Reference – BCR). The analytical method was validated by repeating the measures of concentrations present in the different standards used for ICP-OES setting.

Statistical analysis. The experimental data were treated statistically using software packages (i.e. Excel, Statgraphic plus 5.0, Systat 12.0). The one-way analysis of variance (ANOVA) test (Tukey's test ($p<0.05$)) is a general technique that can be used to test the hypothesis that the means among two or more groups are equal. This is a non-parametric test used to determine if one of several groups of data tends to have more widely dispersed values than the other. Principal component analysis (PCA) is one of the most common multivariate statistical methods used in

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environmental studies. PCA is widely used to reduce data and extract a small number of latent factors for analyzing the relationship among the observed variables. The principal components are orthogonal new variables that will account for most of the variance in the observed variables.

The principal component loadings may show relationships between variables. To make the results easier to interpret, the PCA with Varimax normalized rotation was applied, which can minimize the variances of the factors loading across variables for each factor. Factor loading values >0.71 are typically regarded as excellent and <0.32 very poor.

Results and discussion

The ammount of elements deposited on the leaves of trees was determined in leaf-washing water and a statistical summary of the major and trace elements concentrations was shown in table 1.

Elements	Min	Max	Mean	S.D.
			$mg\ L^{-1}$	
Al	0.1	5.4	1.7	±1.2
Ca	5.4	153.8	50.8	±13.3
Fe	0.2	13.4	3.3	±2.5
K	0.8	68.6	10.9	±8.3
Mg	0.8	33.4	7.2	±4.2
Na	0.1	18.2	4.8	±1.4
P	0.1	28.7	2.5	±4.7
S	1.8	17.3	6.7	±3.7
Si	0.1	6.8	1.8	±1.1
Zn	0.1	6.2	1.0	±0.4
			$\mu g\ L^{-1}$	
Ba	11.8	420.0	105.1	±74.9
Cd	0.3	9.6	1.6	±0.8
Co	0.4	9.5	2.3	±1.2
Cr	1.4	146.0	11.6	±23.4
Cu	36.2	454.1	167.3	±87.9
Mn	56.5	1141.0	379.5	±139.2
Ni	4.5	52.9	21.0	±11.5
Pb	3.1	181.9	47.1	±21.3
V	0.7	24.0	6.7	±4.7

Table 1

Major and trace element concentration determined after leaf-washing test.

Min = minimum value
Max = maximum value
S.D. = standard deviation

The major elements that have high concentrations have the following distribution: Ca>K>Mg>Na. Though Cesari et al. (2012) showed that high amount of Ca and Mg in urban dust was due to their abundant presence in asphalt and cement (Vega et al., 2001; Chow et al., 2004; Galindo et al., 2011), we believe that the high Ca concentration is due to high carbonate amount in the soil of the Po Valley. Indeed, a crustal contribution at PM10 has been observed in various sites in Europe with significant spatial variability ranging from 5% up to 37% on long-term averages and this source could originate from long-range transport, from eolian re-suspension of local soils but also from anthropogenic contributions due to agricultural activity and also road dust (Vianna et al., 2008). High amount of phosphorus and sulphur may be due to both geogenic and anthropogenic sources. The concentrations in trace elements decrease as follow: Zn>Mn>Cu>Ba>Pb>Cr. The higher concentrations of Zn than the other trace elements are found in air (from 0.05 to 0.2 µg/m3) because the major source is vehicular traffic (Kemp, 2002) with particular regard to wear particles (Councell et al. 2004) and industrial and commercial activities (Tippayowong et al., 2006). The soil sources contribute to a high fraction of Mn in the atmosphere (Gunawardena et al., 2012), while the wear of tires and brake pad can be source of Pb (Sansalone et al., 1996) even if the hypothesis that the dust from soil, possibly enriched with Pb, used in large amounts in the past decades as an additive of gasoline, can be re-suspended into the atmosphere, must be taken into account (Maher et al., 2008). Indeed, the soil dusts play an important role in the adsorption of pollutants (e.g. heavy metals), in the re-suspension and transport into the atmosphere.

No statistical difference in major and trace elements were found in relation to the exposure of sites, while a high variability due to both season and different characteristics of tree leaves were observed. The high amount found in winter time can be due to both a highest metal concentration in air (data ARPA not shown) but also a complex structure of the conifer foliage could be explain their much greater effectiveness in capturing particles (Beckett et al., 2000b) considering that the turbulent air flows is the main mechanisms resulting in the deposition of particles on the tree. Beckett et al., (2000b) highlighted greater capture efficiency to the tree shoots of more complex structure with smaller (conifers needles) or hairier leaves.

Principal component analysis (PCA) tries to reduce the original multidimensional space to a new one in which lower dimensions are calculated to explain the relationships and association among the variables. Four factors, which explain 80% of the total variability, were extracted by PCA analysis (Table 2). The most significant factor (F1), which explains 42.2% of the total variability, includes two typical soil geogenic tracers (Al and Fe) and some trace elements (Ba, Co, Cu, Ni, Pb; V) that may be due to both anthropogenic or lithological sources. Therefore, this factor can be thus interpreted as of geogenic origin – mainly wind blowing soil dust (González-Miqueo et al. 2010) even if 60% to 80% of the Fe is removable by leaf washing test (Rautio, 2000) because the Al and Fe concentration in plant species tissues is affected by washing (Lin and Schuepp, 1996; Rossini Oliva and Valdes, 2004) this can result from contaminants deposition (Ataabadi et al., 2012). Furthermore the Fe/Al ratio in the earth's crust is variable and depends both by lithology and anthropogenic sources. The Fe/Al ratio in the soil surface of the sites (data not shown) ranges from 0.31 to 0.81 highlights an anthropogenic origin of Fe in dusty deposited on the leaves can be suggest (Azimi et al., 2005) because the Al/Fe ratio measured in water after leaf leaching test is higher than 1, the dust was enriched by Fe. It has the evidence that Fe concentration was related to Ba, Pb and

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Mn amount, which derive from the engines of vehicles (Monaci and Barbagli 1997).

Ni and Pb was anthropogenic as established by a decrease of Ni concentration after leaf washing treatment in Pine needles tissues (Salkl and Maeda, 1982) as well as Pb in leaves of Lantana camera L. (Romano and Abate, 1995). The anthropogenic prevalent of the F1 of the PCA can then be established. The second factor (F2) consists of Ca, K, Mg, P that are mainly geogenic tracers, extremely abundant in soil (Rossini et al., 2005) as well as in the dust of cement and asphalt (Cesari et al 2012). The anthropogenic contribution of metals to atmospheric deposition is represented by F3 and F4. The third factor (F3) is characterized by Cd, Cr, and S, which are linked to anthropogenic atmospheric emission (Fujivara et al., 2011a), as well as the fourth factor (F4) that corresponds to Zn amount in pollutants deposition into the leaves. Many authors (Heal et al., 2005; Haggins et al., 2000; Karthikeyen et al., 2006) showed that Cu and Zn are present in airborne particulates as water-soluble sulphate salts, then it not excluded that soluble sulphate salts of Cd may be present in atmosphere. The concentrations of Zn in the atmosphere are high and it is ubiquitous, underlining the high concentration in the air.

Table 2

Principal component analysis (PCA) varimax rotation obtained by major and trace elements in water after leaf washing processing..

	F1	F2	F3	F4
Al	**0.96**	0.15	0.02	0.01
Ba	**0.78**	0.46	- 0.02	0.24
Co	**0.93**	0.09	0.08	- 0.02
Cu	**0.83**	0.24	- 0.04	0.1
Fe	0.95	0.21	- 0.02	0.04
Ni	**0.75**	0.46	0.11	0.10
Pb	**0.8**	0.26	0.15	0.29
V	**0.95**	0.15	0.18	0.11
Ca	0.40	**0.82**	- 0.06	0.21
K	0.11	**0.75**	0.14	- 0.25
Mg	0.27	**0.89**	- 0.10	0.13
Mn	0.32	**0.76**	0.30	0.05
P	- 0.09	**0.87**	0.01	- 0.02
Cd	**0.52**	- 0.23	**0.63**	0.39
Cr	0.22	0.04	**0.62**	0.38
S	0.29	0.22	**0.66**	0.27
Zn	0.02	0.07	0.06	**0.81**
Percent of total variance				
	42.2	24.12	7.76	6.89

A possible way to identify the anthropogenic or geogenic origin is the use of enrichment factor (EF). EF is a measurement of the accumulation extent of metals in environments which is useful for the discrimination of anthropogenic interference and specific sources of metals. These factors have been used to assess the enrichment of topsoil, moss, rainwater and atmospheric concentrations (Dragović and Mihailović 2009; Zhang et al., 2008). Generally, the average concentrations of upper crust composition are used in accordance with scientific literature (e.g. Taylor and McLennan, 1995), but in this case, the values determined in the topsoil of monitoring sites are used (Vittori Antisari et al., 2011). The use of characterization of topsoil mitigates the local variations and the local contamination of soil. The EF was calculated by ratio from element concentration in water normalized at crustal elements (e.g. Al, Fe, Zr, Ti etc) to the analogous ratio in soil (EF= (X/Al)water/(X/Al)soil).

Because it was not possible to obtain diversification across sites, the processing was performed by grouping the various stations according to the predominant source of exposure, as above described. A and D, downwind for emission from the chimney (Downwind); C and L maximum exposition of the incinerator domain (Max); M and N minimum exposition of the incinerator domain (Min); B and F are exposed to road (road); G, H and I are located in rural area (rural) and then E in a craft area (craft).

The EF is shown in table 3, and significant variability among enrichment of some trace elements was observed. As expected, the EF of Ca, Na, K, Mg, and P are low (less than 1), underlying the crustal effect as interpreted by F2 of PCA. Friction is highlighted for the S concentration, which is a geogenic source according to the EF, while contributing to F3, it can be attributed to an anthropogenic origin.

Table 3

Enrichment factors (EF) calculated as follows: [EF= (X/Al)water/(X/Al)soil] and the concentrations of elements are these of reference soils (data no shown).

	Incinerator domain			**Road**	**Craft**	**Rural**
	Downwind	**Max**	**Min**			
Ba	7.2	3.9	8.7	5.9	7.5	5.0
Ca	0.1	0.0	0.1	0.1	0.1	0.1
Cd	218.5	144.8	94.6	125.6	179.8	43.9
Co	6.4	3.6	2.9	4.1	5.4	4.1
Cr	2.7	1.1	5.0	2.2	8.0	1.9
Cu	56.1	26.7	108.2	52.3	45.9	34.6
Fe	15.3	2.6	16.1	11.0	11.2	8.3
Mn	14.2	5.7	15.9	8.9	9.8	6.4
Na	0.4	0.6	0.7	0.7	0.3	0.1
Ni	11.0	8.5	14.9	10.1	7.9	5.9
P	0.1	0.0	0.1	0.0	0.0	0.1
Pb	12.7	8.4	19.3	15.5	16.5	8.4
S	0.3	0.2	0.4	0.3	0.3	0.2
V	3.3	1.5	3.8	2.8	2.7	1.8
Zn	115.1	244.0	158.1	76.7	129.9	183.7

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The threshold to evaluate the crustal contribution varies according to the authors and it ranges from 1 to 10 (Alleman et al., 2010; Lonati et al., 2005) while the anthropogenic threshold can be higher than 5 or 50 or 100.
Cd, Cu and Zn have an remarkable anthropogenic origin. If the synthetic index of enrichment (SIE) is calculated, determining the EF sum for otherwise exposed sites, a decrease of SIEvalues is observed as follows: downwind > max esposure> min esposure> roads > craft > rural.
Excluding the values of the leaf washing of conifers, the average deposition flux on the leaves of broadleaf trees was calculated and is shown in table 4.

Table 4

Fluxes of major and trace elements concentrations analyzed after leaf washing test (mg m^{-2} y^{-1})

	Incinerator			**Road**	**Craft**	**Rural**
	Sub	**Max**	**Min**			
Al	230.20	256.69	280.16	208.40	310.18	96.49
Ba	12.24	17.42	12.64	13.47	10.79	7.59
Ca	4915.31	7135.95	6365.29	8310.26	4249.46	3962.69
Cd	0.23	0.37	0.10	0.55	0.36	0.07
Co	0.33	0.48	0.40	0.46	0.39	0.10
Cr	0.89	3.70	0.98	1.01	0.63	0.87
Cu	21.06	20.62	16.95	20.47	14.48	32.27
Fe	399.24	456.40	366.47	504.54	125.27	245.63
Mn	42.67	52.31	37.25	61.62	36.78	32.05
Na	1014.22	476.03	156.92	480.96	1090.73	383.60
Ni	3.00	2.63	2.15	2.96	3.39	1.85
P	144.50	182.53	354.79	634.21	170.66	303.78
Pb	6.71	7.98	4.46	4.99	4.94	3.52
S	822.39	890.43	799.93	867.38	718.51	561.80
V	0.91	0.99	0.71	0.97	0.67	0.52
Zn	69.08	130.43	201.29	126.37	295.98	59.64

The flux of Ca in the Bologna district, ranging from 3962 to 8310 mg m^{-2} y^{-1}, was in agreement with Rossini et al (2005) who calculated it in Venice (Italy). Also the flux of Fe is in agreement with those determined in the Lagoon of Venice (Rossini et al., 2005; 2010) and in Serbia (Mijić et al., 2010) emphasizing the anthropogenic origin, while higher values are found in Argentina and Turkey (Bermudez et al., 2012; Yatkin and Bayram 2010). Ridame et al. (1999) found in a remote site in Corsica a range for Al flux from 171-270 mg m^{-2} y^{-1} and for Pb flux 1.1-0.7 mg m^{-2} y^{-1}, while the Al flux is the same order of magnitudes, the Pb flux in this study is higher than 4-5 times. The deposition flux in the study area varies for Cd from 0.07 to 0.55 mg m^{-2}, for Co 0.1 to 0.48, for Cr 0.63 to 3.7, for Cu 14.5 to 32.27, respectively. The deposition flux of Cd in different regions of the world ranges from 0.047-12.8 mg $m^{-2}y^{-1}$ and higher values are found in the domain of the Porto

Marghera industry pole (12.5 mg $m^{-2}y^{-1}$) (Rossini et al.,2005), in India (1.38 and 6.3 mg m^{-2} y^{-1}) (Sharma et al 2008;).
In the Bologna area the lowest values are in rural zones and under a minimum exposure to the domain of incinerator plants, while the highest are in roads and under maximum domain exposure. This distribution is also found for the other trace elements. The highest values of Cu flux are found in agricultural areas due to probably to the use of Cu containing pesticides (e.g. Cu sulphate and Cu oxycloride).

Conclusion

The proposed leaf washing method has proved to be a powerful investigative tool. In fact it was possible to discriminate the anthropogenic or geogenic metals deposited on theleaves with multivariate statistical analysis, as it is possible to predict the flow of metals in different areas of investigation.

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