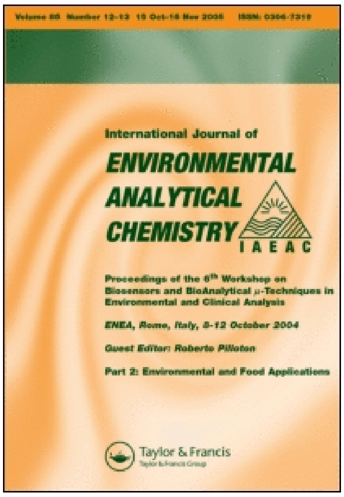

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Valerio, F. , Brescianini, C. , Lastraioli, S. and Coccia, S.(1989) 'Metals in Leaves as Indicators of Atmospheric Pollution in Urban Areas', International Journal of Environmental Analytical Chemistry, 37: 4, 245 — 251
To link to this Article: DOI: 10.1080/03067318908026901
URL: http://dx.doi.org/10.1080/03067318908026901

Intern. J. Environ. Anal. Chem., Vol. 37, pp. 245–251
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METALS IN LEAVES AS INDICATORS OF ATMOSPHERIC POLLUTION IN URBAN AREAS*

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(*Received 14 November 1988*)

The use of biological indicators to monitor atmospheric pollution is widely distributed.

The analysis of heavy metals in leaves is suggested as a method for a rapid identification of polluted areas.

Reproducibility and representativity of this method must be assessed.

We have verified if the concentration of lead, chromium, copper, nickel and manganese in "Quercus Ilex" leaves may be used to classify urban areas according to the level of their atmospheric pollution.

Particular emphasis was placed on reproducibility of sampling and the analytical method. Preliminary results show a linear correlation between concentration of metals in atmosphere (particularly lead) and in leaves collected in the same sampling areas.

KEY WORDS: Biomonitoring, durmast oak, metal compounds, manganese, lead, atmospheric pollution, leaves, ICP–AES, reproducibility, sample preparation.

INTRODUCTION

The use of vegetable tissues as indicators of atmospheric pollution appears to be an effective alternative to usual monitoring methods. In polluted areas significant decrease of population of lichens and specific pathologies as stomatic function alteration or photosynthesis inhibition were verified.[1]

Also the concentration of some metals in vegetable tissues appears to be linked to the atmospheric concentration of these metals. In fact higher concentrations of lead in trees bark and in mosses, collected in high traffic areas, were found and significant increase of Cu, Cr and Ni was verified in mosses sampled near a steel foundry.[2,3,4]

An accumulation of airborne heavy metals in leaves and bark suggests the possibility of a simultaneous and rapid collection of samples (for example, leaves) in a high number of sites to identify and possibly classify polluted areas according to their pollution level.[5]

We have asked if mean concentration of lead, copper, chromium, nickel, iron, cadmium, zinc, vanadium and manganese in leaves of "Quercus Ilex" may be correlated with their mean concentration in atmosphere.

*Presented at the 18th International Symposium on Environmental and Analytical Chemistry, Barcelona 5–8 September, 1988.

Leaves of "Quercus Ilex" were selected because this tree is an evergreen, and typical of mediterranean areas. It is resistant to air pollution and widely distributed in our town.

Particular emphasis was given to establish analytical conditions and to verify reproducibility of sampling.

METHOD

About 50 leaves were collected randomly at about 3 meters of height from 5 trees, grown in 5 different sites (urban, suburban and industrial areas) during the first week of June (Figure 1).[6]

These sites were the same where 213 samples of airborne particulate were collected and analysed for their metal content.[7]

The leaves of present year were separated from those of last year and separately analysed.

A preliminary work was carried out to verify the reproducibility of our analytical method.

The leaves collected were washed three times in an ultrasonic bath with 10% HNO3 and three times with doubly distilled water to remove all deposited dust and in order to measure only the concentration of metals adsorbed by vegetable tissue.

The samples were then dried at 105° for 48 hours and finely ground in a mortar.

One gram of sample was treated with 65% HNO3 at 200° for 10 hours and the residue was solubilised with 10% HNO3.

An ICP–AES (Jobin Yvon 38—Plasma Source JY3832) was used for the analysis of Pb, Cr, Cu, Ni, Fe, Cd, V, Zn, and Mn.

Operating conditions are shown in Table 1.

Results show that the content of metals in leaves collected in different positions on the same tree and collected from different trees growing in the same area is not statistically different.

Table 2 shows the values of reproducibility for each metal.

The "T" student and the "signed-rank" tests were used for statistical elaboration.

RESULTS

Significant differences in content of metals were found comparing the results obtained from "young" leaves (about two months old) respectively to "old" ones.

The lead concentration in "young" leaves appears in each site significantly lower than in "old" leaves (Table 3).

Only the Mn concentration in site 5 was particularly high both in "young" and in "old" leaves (Figure 2).

The lead concentrations in "old" leaves collected in studied areas are reported in Figure 3.

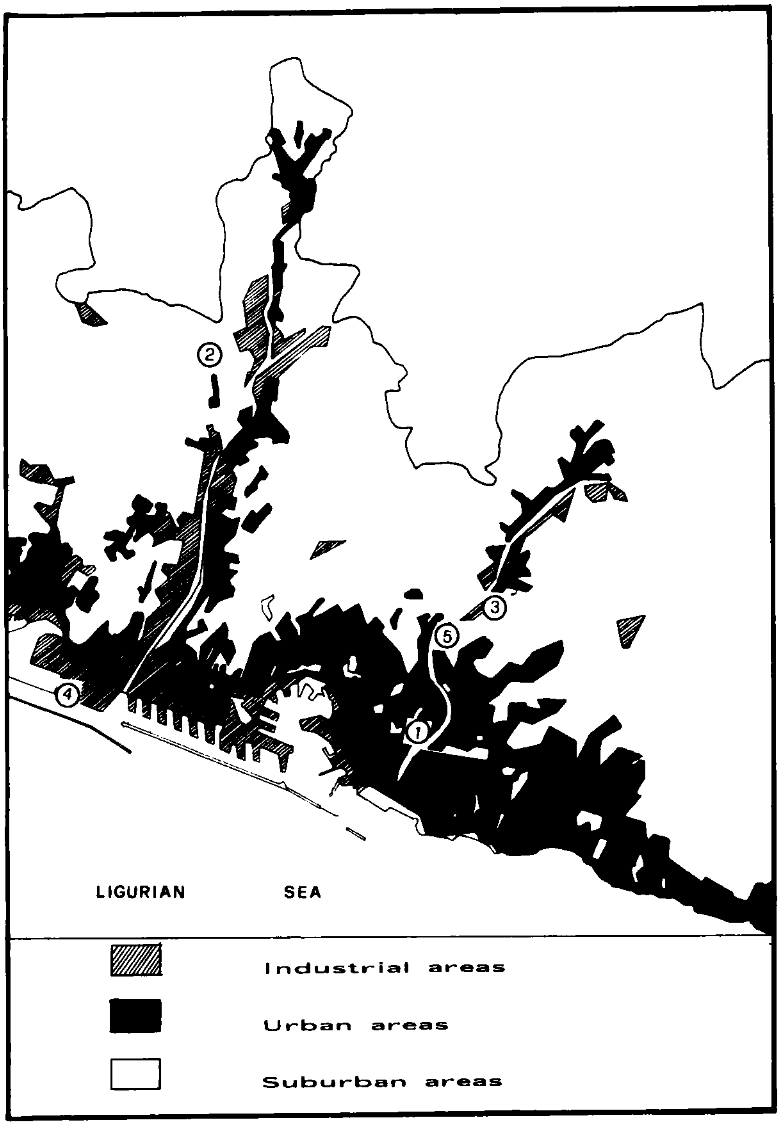

Figure 1 Map of the city of Genoa.

Table 1 ICP–AES operating conditions

Gas:	Plasma	18 l/min Ar
	Carrier	0.4 l/min Ar
	Coating	0.4 l/min Ar
Sample rate:		0.8 ml/min Ar (through perystaltic pump)
Power:		2 Kw
Entrance slit:		50 u
Exit slit:		50 u

Table 2

Reproducibility of analytical method for each metal	
Pb	89%
Zn	97%
Mn	96%
Fe	96%
Cr	80%
V	94%
Ni	88%

Table 3 Lead concentration (ppm) in "Quercus Ilex" leaves

Sites	*Old leaves*		*Young leaves*		*P*
	Mean	*SD*	*Mean*	*SD*	
1	5.23	±1.40	1.47	±0.38	≦0.01
2	2.14	±0.68	1.18	±0.27	/
3	4.27	±0.76	2.69	±0.54	≦0.05
4	2.21	±0.69	0.63	±0.18	≦0.01
5	2.28	±1.03	0.20	±0.06	≦0.01

Relative abundance of lead in samples collected in sites 1 and 3 (characterised by a high traffic density) appears to be significantly higher ($P<0.01$) than lead concentration in samples collected in sites 2, 4 and 5.

These values were compared with the geometric mean of lead, found in the atmosphere of the same areas and a good correlation ($P<0.05$) was found (Figure 4).

The relative abundance of Cu, Cr, Ni, Mn, Fe, Cd, V, and Zn between site 2 and sites 1, 3 and 4 was statistically different ("Signed-Rank" Test) (Table 4).

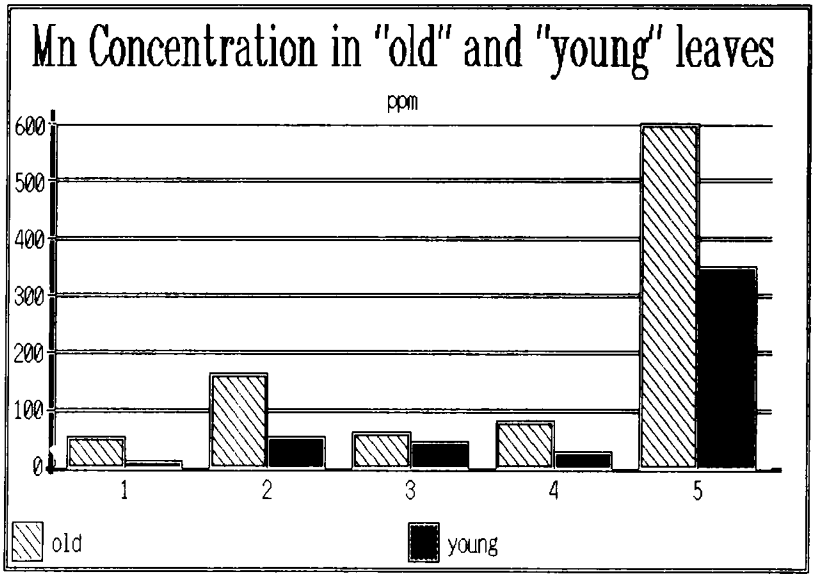

Figure 2 Mn concentration (ppm) in "old" and "young" leaves of "Quercus Ilex" in selected sites.

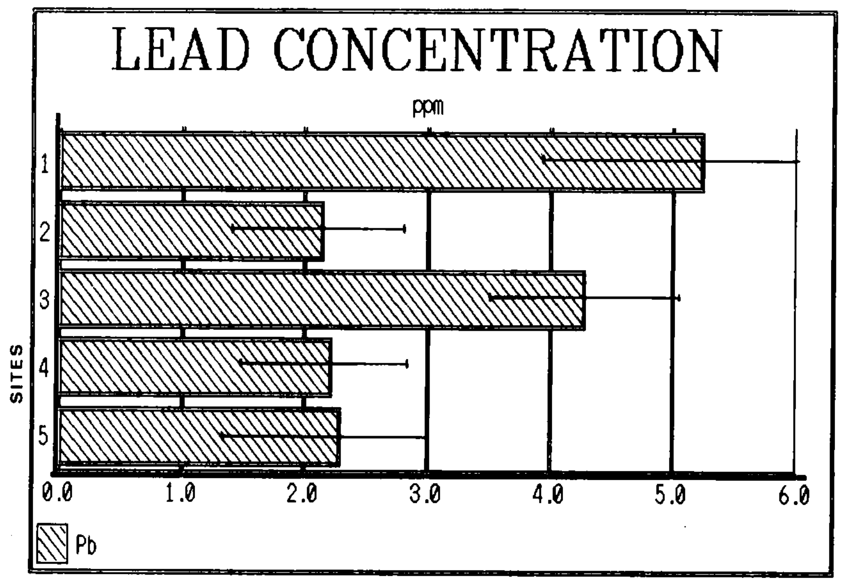

Figure 3 Lead concentration (ppm) in "old" leaves of "Quercus Ilex" in selected sites.

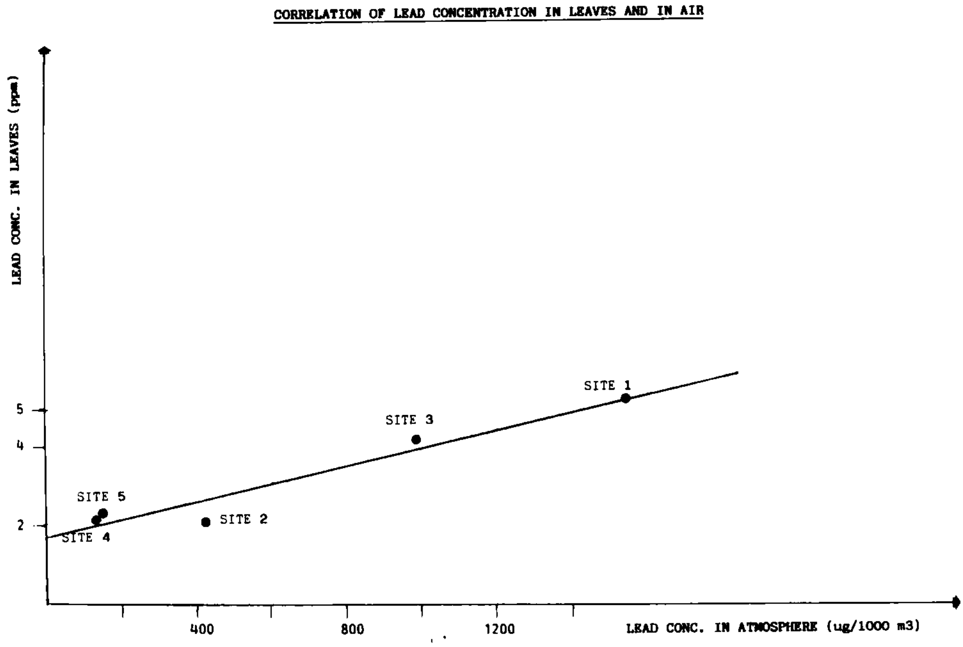

Figure 4 Correlation between lead concentration in leaves of "Quercus Ilex" and in airborne particulate collected in the same areas.

Table 4 Metals concentration (ppm) in "Quercus Ilex" leaves

	Sites			
	1	*2*	*3*	*4*
Cu	4.35 ± 0.20	5.32 ± 0.72	4.28 ± 0.33	5.10 ± 0.68
Zn	20.72 ± 5.55	27.38 ± 6.39	15.17 ± 0.41	14.73 ± 0.80
Cd	0.06 ± 0.02	0.12 ± 0.05	0.07 ± 0.04	0.04 ± 0.03
V	0.34 ± 0.13	0.27 ± 0.07	0.50 ± 0.14	0.31 ± 0.18
Ni	0.98 ± 0.54	2.63 ± 1.58	1.31 ± 0.51	1.36 ± 0.35
Fe	352.47 ± 76.57	369.51 ± 55.74	332.87 ± 64.01	285.14 ± 49.67
Mn	51.03 ± 17.62	161.40 ± 29.78	58.87 ± 12.34	78.69 ± 20.16
Cr	1.61 ± 0.53	1.44 ± 0.62	1.56 ± 0.23	1.07 ± 0.55

DISCUSSION

Heavy metals present in ecosystem may be naturally absorbed by plants, mainly by assimilation by the roots. In this case different factors, as vegetable species, chemical–physical nature of soil, may influence the equilibrium between concentration of metals in soil and in plants.

A passive adsorption of metals as airborne particulate by the leaves may also occur but the mechanism of this phenomenon is still unclear.

Preliminary results obtained in our study show that the accumulation by passive adsorption of heavy metals in leaves of "Quercus Ilex" is generally a slow phenomenon which probably needs months to reach the equilibrium.

Different results were found in site 5 where Mn concentration was particularly high both in "young" and in "old" leaves.

Moreover, in this area a relatively low content of manganese in airborne particulate was found. This phenomenon may be correlated with a larger concentration of manganese in soil of this area or with a higher bioavailability of this metal due to particular soil characteristics.

The good correlation obtained between the lead concentration in air and in leaves support the original hypothesis that maps suitable to identify areas affected by different degrees of atmospheric pollution produced by specific sources (traffic, foundries) may be simply carried out using concentration of this metal in leaves collected from trees grown in the studied areas.

Applying this method our results emphazised the importance of the sampling strategies, and particularly collection period and leaves age.

Acknowledgement

The authors are grateful to Dr. Roberto Costa for his suggestions and encouragement, and to Comune of Genoa for its collaboration.

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