International Journal of Geosciences, 2013, 4, 1267-1274
Published Online November 2013 (http://www.scirp.org/journal/ijg)
http://dx.doi.org/10.4236/ijg.2013.49121

Biogeochemistry of Plane Trees as a Tool to Detect Atmospheric Pollution

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Received July 14, 2013; revised August 16, 2013; accepted September 13, 2013

ABSTRACT

The plane tree, which is a valuable tool to detect atmospheric pollution, is one of the most common trees in European cities. Soil and leaf samplings were carried out in Barcelona and its environs (NE Spain) to establish the soil-plant relationship. Dry and ashed leaves and soils were analyzed by Instrumental Neutron Activation Analysis and Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP/OES) at the ACTLABS laboratories in Ontario, Canada. Given that diesel is the main fuel used in vehicles in Europe, we sought to establish the role of diesel in atmospheric pollution. Diesel samples were obtained from service stations and analyzed after preconcentration using ICP/MS at the geochemistry laboratories of the University of Barcelona. The average content of diesel oil shows high values of Pb, Cu, Cr, Ag, Cd and Mn. High values of Pb, Cu, Au, Hg and Sb in leaves and soils were detected downtown and along main roads outside the city, whereas low levels of these elements were observed in rural areas.

Keywords: Atmospheric Pollution; Biogeochemistry; Heavy Metals; Vehicle Emissions; Plane Trees

1. Introduction

The plane tree, which is a valuable tool to detect atmospheric pollution, is one of the most common trees in European cities, e.g. London, Paris, Berlin, Madrid, Rome, Athens, etc. Our study was carried out in Barcelona (NE Spain), a Mediterranean city with a large number of the plane trees.

Barcelona which has a population of 1,527,190, is located on the Mediterranean coast and occupies an area of 100.4 km^2 between the hills of the Collserola massif (which belongs to the Catalan Coastal Ranges, CCR) and the Mediterranean sea (**Figure 1**).

The traditional industries of Barcelona (chemicals, metallurgy, textiles, etc.) were transferred to industrial zones outside the city in the 1970s, and have been replaced by the service sector.

Atmospheric contamination in the city is similar to that described by [1-4] and is attributed to internal sources, *i.e.* transport, domestic heating, public works and construction, and to external inputs, *i.e.* particulate matter blown in by winds from North Africa [5] and marine aerosol.

According to data from the Municipality, Barcelona had more than 920,000 vehicles and the daily traffic involved approx 1,200,000 vehicles in the late 1990s (**Figure 2**). Traffic evolution in the last decade underwent considerable growth between 1992 and 1997, in which a daily traffic of 1,190,000 vehicles was achieved. This period was followed by a certain stabilization of the daily traffic during the period 1997-2005 (**Figure 2**). The average number of vehicles per day along this period was 1,180,000 (with an inter-annual oscillation of ±25,000 vehicles per day).

This study was undertaken in 1997, *i.e.* during the period in which the daily traffic was high, and in which an average maximum threshold of traffic pollution was achieved. The aim was to ascertain whether plane trees could be used to determine the different chemical elements responsible for pollution, and to pinpoint the areas of greatest pollution.

2. Materials and Methods

Barcelona is one of the towns in Europe with the highest

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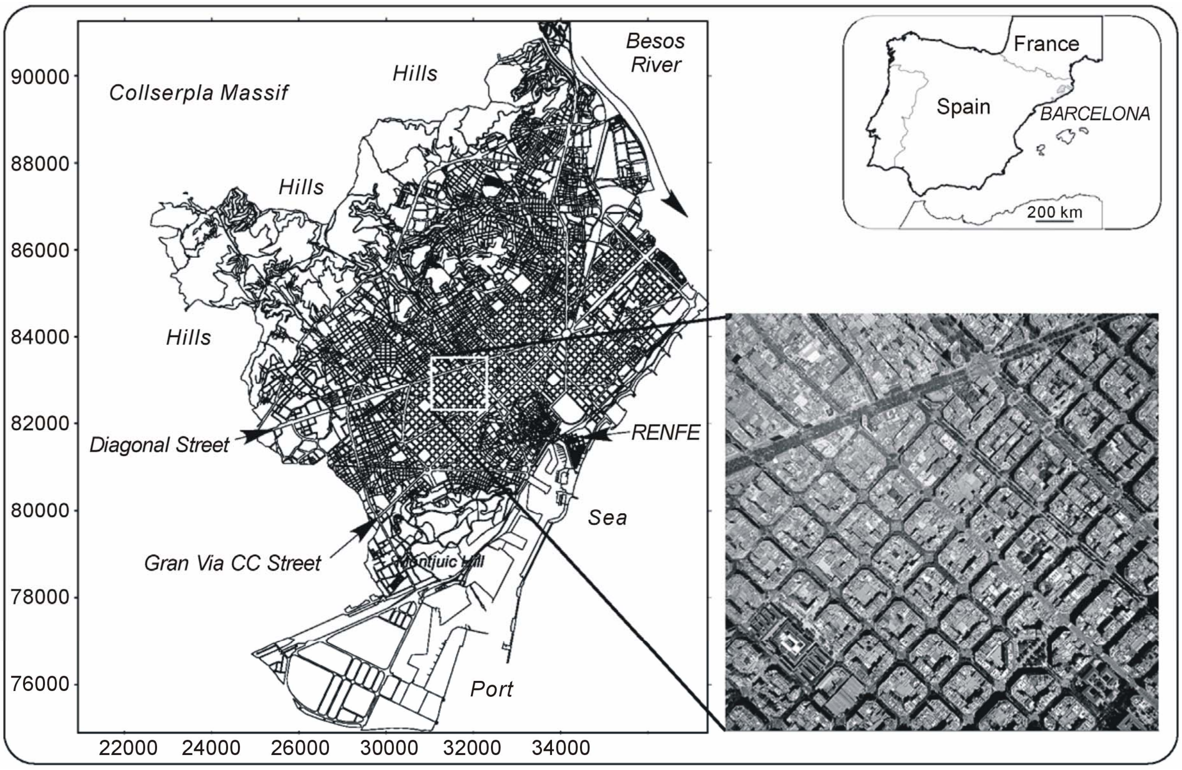

Figure 1. Plan of Barcelona with the references cited in the text: Gran Via CC street; Diagonal street; Port; railway (RENFE); Besòs river and Collserola massif. Aerial photograph corresponds to the "Eixample sector".

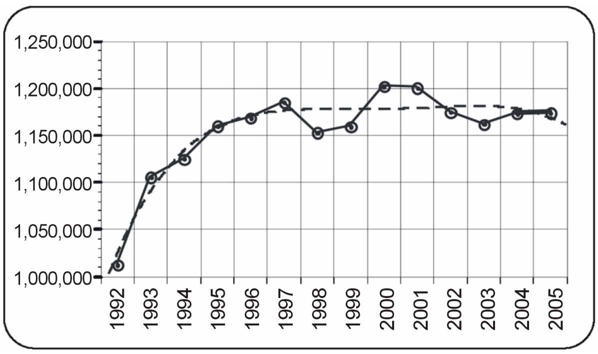

Figure 2. Temporal evolution of traffic in Barcelona (vehicles per day).

density of trees in its streets. The most common tree is the plane tree (*Platanus hybrida* or *Platanus x hispanica*). The reasons for the ubiquity of this species were summed up by [6], who cites an anonymous article in the "Revista del Institut Agricola Català de Sant Isidre in 1899", and are the following: 1) The tree should be hardy, *i.e.* it should demand little from the soil and much from the air, 2) It should be endowed with a majestic presence, a rapid growth, a straight trunk and a leafy top to provide maximum shade in summer, 3) It should shed its leaves in autumn, 4) It should not attract insects harmful to the tree or to humans, 5) It should not give off substances that are deleterious to the health of the citizens.

According to this anonymous author, the plane tree meets the top four of the five conditions. The fifth condition is not met because of its fruit, which might cause allergies in some people.

According to the Municipal Council, in the 1990s, 80% of the 150,192 trees in Barcelona were plane trees. However, in 2004, of the 155,541 trees in the streets of Barcelona the plane trees numbered only 54,354 (30%). They were planted along most of the streets, mainly in the area known as the "Eixample". This area was created when the old walls surrounding Barcelona were pulled down in the middle of the XIX century, enabling the city to expand (**Figure 1**).

The second most common species of tree in Barcelona is the *Celtis australis*, which is gradually replacing the plane tree since its fruit does not cause allergies. Other species, such as *Sophora japonica* and *Ulmus pumila* are currently being planted given their resistance to air pollution, and lower allergy levels. Notwithstanding, the plane tree continues to be the most ubiquitous tree in the city.

Owing to the scarcity of large parks in Barcelona, the exceptional number of trees in the streets constitutes a crucial environmental asset.

[7-10] have described the capacity of metal accumulation in vegetation. Likewise, [1,11-14] have provided evidence of soils and vegetation as indicators of urban pollution.

2.1. Sampling and Analysis

Sampling of plane trees was carried out at 53 sites in Barcelona (*i.e.* 53 composite samples of leaves) in autumn 1997 given that plane trees are deciduous. The sampling sites were located in the main thoroughfares of the town (**Figure 3**). Each sample consisted of four or five trees spaced in a maximum radius of 50 meters. In the area known as the "Eixample", on account of its square shape (**Figure 1**, sampling was performed on street corners).

Each sample contained 500 grams of leaves. The leaves were washed with distilled water, rinsed and dried in an oven at a temperature not exceeding 40˚C to avoid potential loss of mercury. Subsequently they were ground and prepared for analysis. Eight soil samples were taken from the area occupied by the plane trees to compare the soil and plant contents [15] and to determine the Plant Soil Coefficient (PSC). These samples were dried and sieved (80 mesh ASTM). All samples were analyzed at ACTLABS laboratories (Ontario, Canada).

The samples were ground and prepared for analysis by Instrumental Neutron Activation Analysis (INAA) [16] and Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP/OES) at ACTLABS laboratories (Ontario, Canada).

Vegetation samples were analyzed for Au, As, Ag, Ba, Br, Ca, Ce, Co, Cr, Cs, Eu, Fe, Hg, Hf, La, (K), La, Lu, Mo, Na, Ni, Nd, Rb, Sb, Sc, Se, Sr, Sm, Ta, Th, Tb, U, W and Yb by Instrumental Neutron Activation Analysis (INAA) [16]. Cd, Cu, Mn, and Pb (and also Ag and Ni) were analyzed by ICP/OES after *aqua regia* extraction on the ash vegetation.

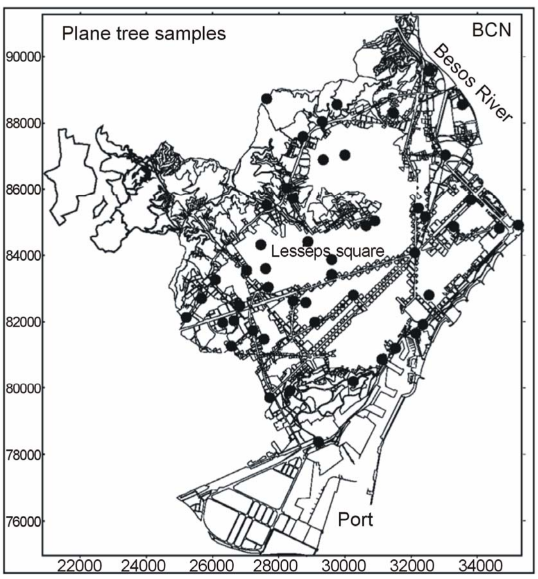

Figure 3. Distribution of samples of plane tree leaves in Barcelona. Dots depict a composite sample of a maximum of 5 plane trees in a radius of 50 meters.

Soil samples were analyzed for Au, As, Ag, Ba, Br, Ca, Ce, Co, Cr, Cs, Eu, Fe, Hg, Hf, La, Lu, Mo, Na, Ni, Nd, Rb, Sb, Sc, Se, Sr, Sm, Ta, Th, Tb, U, W and Yb by INAA. Ag, Cd, Cu, Mn, Ni and Pb were analyzed by ICP/OES after *aqua regia* extraction.

The soils of the plane trees sampled in Barcelona proceed from weathered granite soils of the Catalan Coastal Ranges (CCR) near Barcelona [17].

Moreover, on the suspicion that the contents of these elements could be attributed to vehicle emissions, eight diesel samples were obtained from service stations (selling different brands of diesel oil) in Barcelona. These samples were analyzed after preconcentration using ICP/MS in the laboratories at the University of Barcelona. In addition, mercury vapor from the exhaust emissions of of 28 diesel vehicles (buses, trucks and automobiles) was also analyzed. A "JEROME 431-X" (Arizona Instrument Corporation) vapor mercury analyzer was used. The determination of gaseous mercury was made in situ with a range between 0.003 $mg \cdot Hg \cdot m^{-3}$ and 0.999 $mg \cdot Hg \cdot m^{-3}$, a resolution of 0.001 $mg \cdot Hg \cdot m^{-3}$, and with a sensitivity of 0.003 $mg \cdot Hg \cdot m^{-3}$ [18] and [19].

Furthermore, sixteen additional samples were obtained from plane trees in different areas outside Barcelona. These samples were taken from plane trees located along main thoroughfares, at varying distances from the road.

2.2. Data Treatment and Data Presentation

Data obtained from leaves of plane trees and soils allowed us to carry out basic statistical treatment (**Tables 1-3**), correlation between plane trees and soils (**Figure 4**), multivariate statistical treatment with principal component analysis (**Table 4**), and kriging interpolation of Pb, As, Hg, Fe, Cu, Cr, Au and U (**Figures 5-12**).

3. Results and Discussion

High content of chalcophile elements such as Pb, Cu, Zn and Sb, and siderophile elements such as Fe, Cr and Au were detected in the plane tree leaves and soils (**Tables 1** and **2**). By contrast, weathered granite soils of CCR tend to present lower values in these elements (**Table 3**). Moreover, the average contents of diesel fuels (**Table 5**) showed high values of Pb, Cu, Cr, Ag, Cd and Mn. The mercury vapor in the exhaust emissions from vehicles ranged between 0.032 and 0.125 $mg \cdot Hg \cdot m^{-3}$.

The plant-soil coefficients (PSC) in **Figure 4** show medium to high values for Cr, Pb, Au and Cu; therefore, the plane tree would constitute a non-barrier to these elements after [15].

The principal component analysis (**Table 4**) shows the principal factor (Factor 1) with a very high factorial load for Pb, Zn, Fe, Cr, Sb, Cu and Au and Factor 2 with high load for U and a medium load for As (cumulated variance for both factors is high).

Table 1. Statistical data of the most significant results of samples of plane trees.

	Mean	Std. Dev.	Minimum	Maximum	Median
As (ppb)	276.5	267.0	10.0	1400.0	205.0
Au (ppb)	20.7	21.4	3.7	111.0	11.9
Ba (ppm)	20.1	8.2	1.0	42.0	19.5
Br (ppm)	44.7	22.9	6.5	100.0	43.5
Ca (%)	2.3	0.6	0.9	3.4	2.2
Co (ppm)	0.8	0.4	0.2	2.0	0.8
Cr (ppm)	2.4	1.9	0.1	9.6	1.7
Cu (ppm)	14.3	8.3	4.0	40.0	12.5
Fe (ppm)	378.7	195.7	170.0	1100.0	300.0
Hg (ppb)	162.5	179.6	10.0	800.0	155.0
La (ppm)	0.3	0.1	0.1	0.8	0.3
Mn (ppm)	120.0	77.2	46.0	408.0	96.5
Mo (ppm)	0.8	2.3	0.1	17.0	0.5
Pb (ppm)	12.3	7.1	4.0	35.0	10.0
Rb (ppm)	2.3	1.8	0.5	10.0	2.0
Sb (ppm)	1.1	0.9	0.1	5.1	0.9
Sr (ppm)	88.3	31.3	5.0	160.0	90.5
Zn (ppm)	30.4	15.3	13.0	83.0	26.0
U (ppb)	71.3	85.6	10.0	410.0	30.0

Table 2. Statistical data of 8 soil samples taken from the area occupied by plane trees.

	Mean	Std. Dev.	Minimum	Maximum
Au (ppb)	175.5	167	32.0	555.0
As (ppm)	5.1	3.2	0.5	11.9
Co (ppm)	7.6	2.2	5.0	11.0
Cr (ppm)	33.6	8.5	22.0	44.0
Fe (%)	2.8	0.6	1.2	8.8
Sb (ppm)	4.0	2.5	1.2	8.8
Th (ppm)	19.6	7.0	10.0	32.0
U (ppm)	2.7	0.4	2.2	3.3
Cu (ppm)	37.0	11.6	16.0	55.0
Pb (ppm)	133	40.8	71.0	216.0
Zn (ppm)	165.6	48.2	93.0	251.0
Ni (ppm)	12.6	2.6	8.0	16.0
Mn (ppm)	572.4	168.3	378.0	854.0
Cd (ppm)	0.6	0.5	0.1	1.6
V (ppm)	43.5	14.1	18.0	60.0

Table 3. Content of elements in 30 weathered granite soil samples from the CCR near Barcelona.

	Mean	Std. Deviation	Minimum	Maximum	Median
Au (ppb)	2.7	2.4	1.0	10.0	1.5
As (ppm)	3.8	6.2	1.0	36.0	2.0
Hg (ppm)	>0.5	>0.5	>0.5	>0.5	>0.5
Fe (%)	3.8	0.8	1.7	5.5	3.9
Cu (ppm)	27.8	31.6	3.0	189.0	23.0
Pb (ppm)	26.2	8.9	12.0	53.0	23.0
Cr (ppm)	15.4	5.5	2.0	31.0	15.5
U (ppm)	3.9	1.3	1.4	6.7	3.8

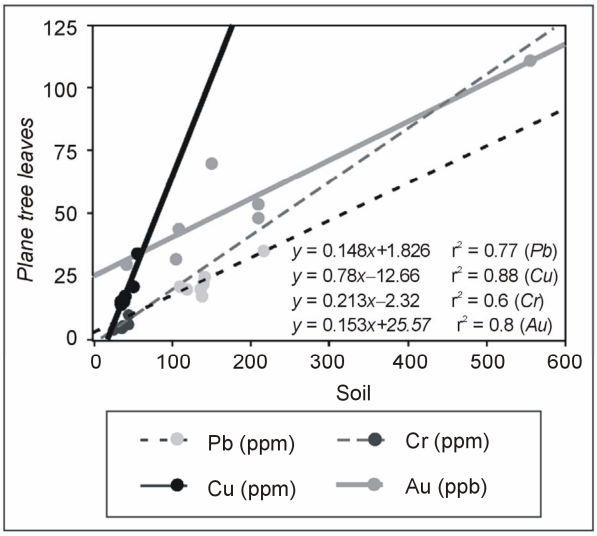

Figure 4. PSC for Cr, Pb, Au and Cu.

Table 4. Loading-factors matrix of principal component analysis (orthogonal solution) of leaves of plane trees in Barcelona.

	Factor 1	Factor 2	Factor 3
Pb	0.9	0.1	−0.003
Zn	0.9	0.1	−0.2
Fe	0.9	0.2	−0.1
Cr	0.9	0.2	−0.2
Sb	0.8	−0.03	−0.2
Cu	0.7	−0.1	0.3
Au	0.7	−0.3	−0.3
As	0.3	0.6	−0.3
Mn	−0.1	−0.1	0.9
U	−0.1	0.9	0.04

The area with the highest lead content in plane trees is located near the Port and the Railway Station (RENFE), and along the main thoroughfares, *i.e.* the Diagonal Street and the Gran Via de les Corts Catalanes (CC) Street (**Figures 1** and **5**).

The area with the highest anomalous arsenic content in plane trees is situated along the coast, which includes the Port zone. Another anomalous area is the former industrial zone in the proximity of the river Besòs delta (**Figures 1** and **6**).

Mercury anomalies are detected in the city center and a along the inner ring road and the port area (**Figures 1** and **7**).

The iron content of the plane trees shows an anomalous area near the Railway Station (RENFE) and along the two railway tracks (coastal and interior tracks, **Figures 1** and **8**).

Table 5. Different elements (in ppb) found in diesel oil from service stations in Barcelona.

Au	Pb	Cu	Sb	Cr	Cd	Mn	Mo	Ag	Co	Se
4.43	2 139.6	886.8	7.96	659.5	17.5	237.4	58.0	108.3	14.73	8.37

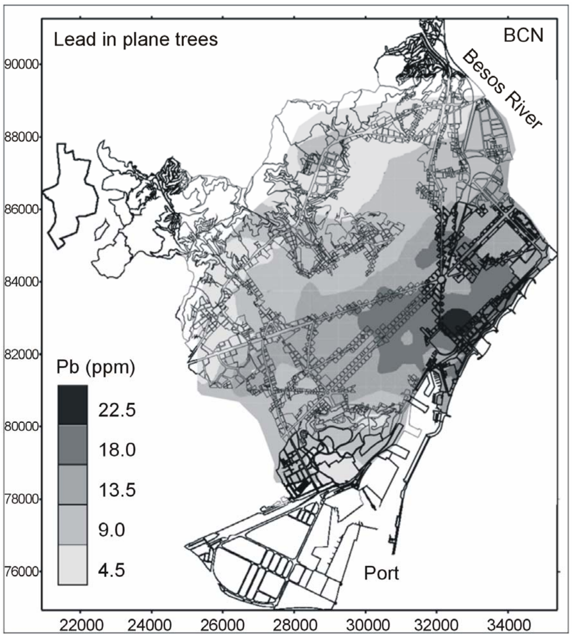

Figure 5. Map of the main anomalous lead content in the leaves of plane trees. The higher contents are located near the Port, Railway Station (RENFE) and along the main thoroughfares, *i.e.* the Diagonal street and the Gran Via CC street (Figure 1).

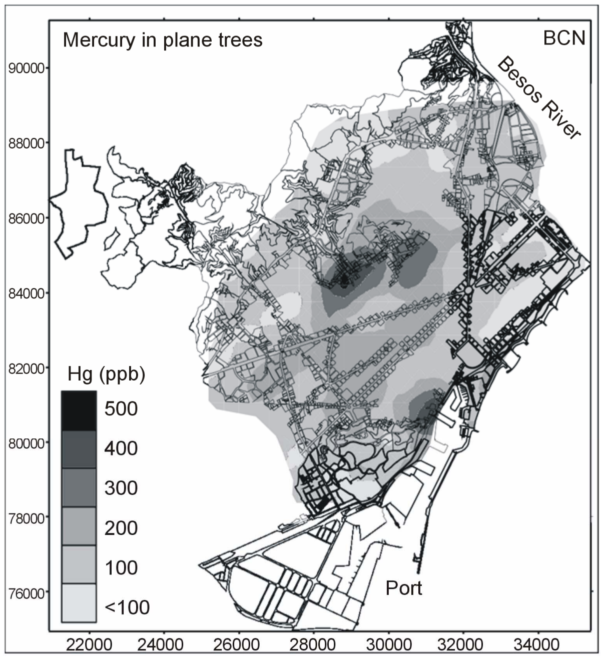

Figure 7. Map of the main anomalous mercury content in the leaves of plane trees. The higher contents are located in the vicinity of Lesseps Square and along the central ring road and the Port area (Figure 1).

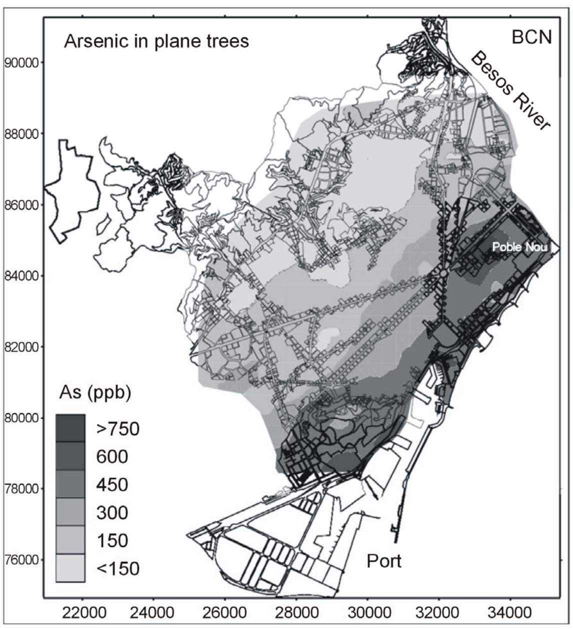

Figure 6. Map of the main anomalous aresenic content in the leaves of plane trees. The higher contents are located along the coast, which includes the Port. Another anomalous area is the former industrial zone of "Poble Nou" in the proximity of river Besòs delta (Figure 1).

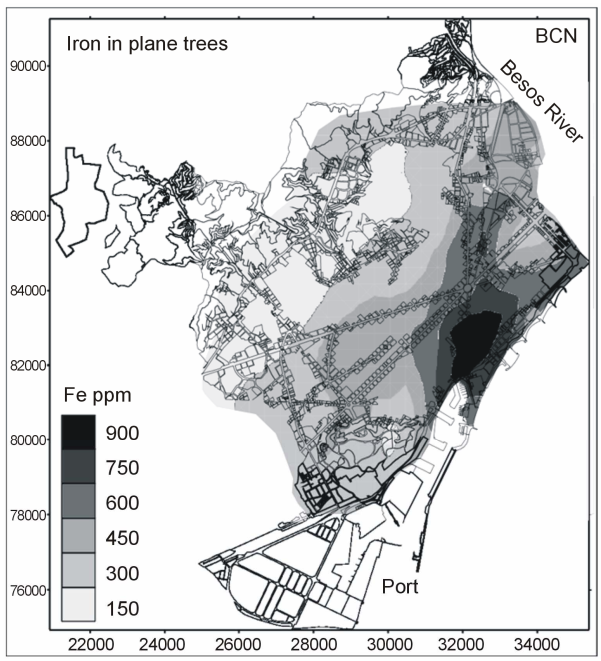

Figure 8. Map of the main anomalous iron content in the leaves of plane trees. The higher contents are located in the proximity of the Port and the Railway Station (RENFE in Figure 1) and along the railway track.

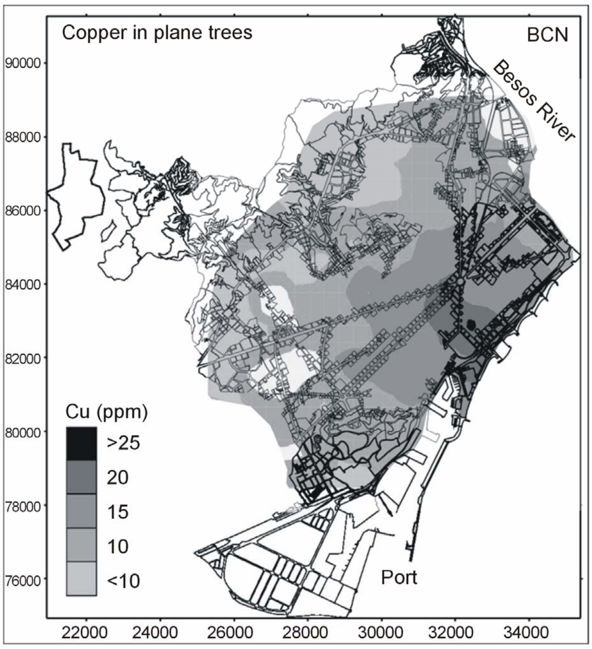

Figure 9. Map of the main anomalous copper content in the leaves of plane trees. The highest content is located in the proximity of the Port and the Railway Station (RENFE in Figure 1).

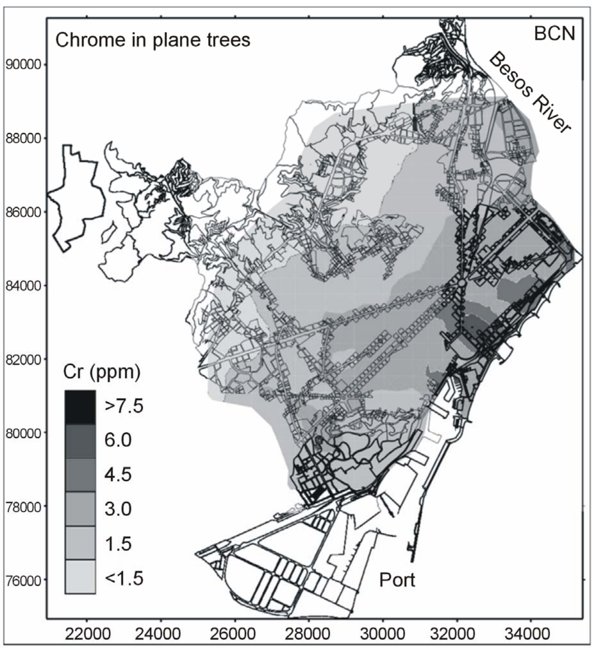

Figure 10. Map of the main anomalous chromium content in the leaves of plane trees. The highest content is located in the same area as copper (Figure 9).

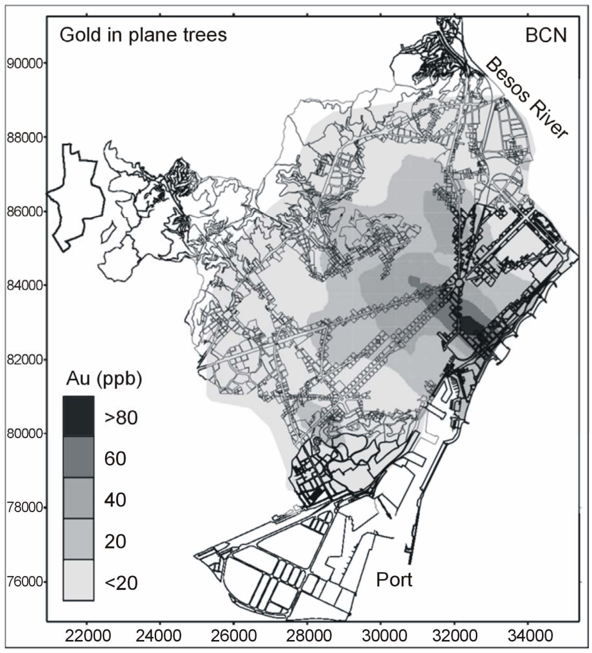

Figure 11. Map of the main anomalous gold content in the leaves of plane trees. The highest content is located in the same areas as Cu and Cr (Figures 9 and 10).

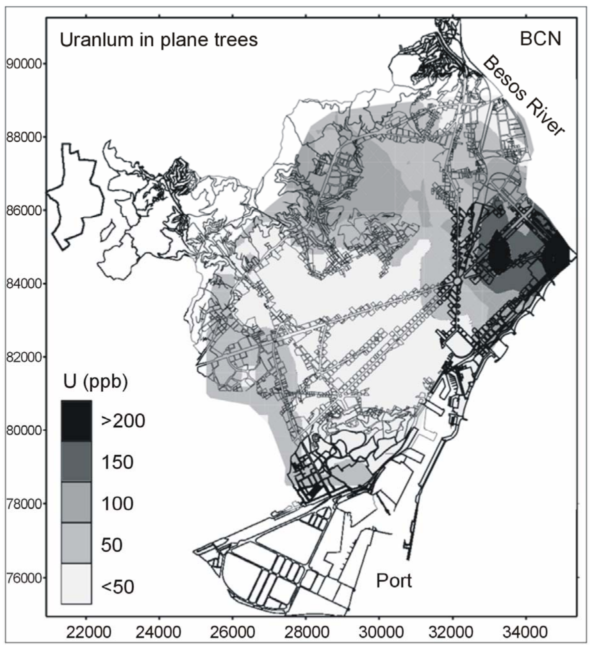

Figure 12. Map of the main anomalous uranium content in the leaves of plane trees. The higher contents are located in NE Barcelona, mainly near the power plants in the vicinity of the Besòs river (Figure 1).

The area with the highest Cu, Cr and Au contents is located in the proximity of the port and the Railway Station (RENFE) and penetrates the interior of the city in a NW direction (**Figures 1**, **9**, **10** and **11**). Phytoaccumulation of gold in plane trees (**Figure 11** and **Table 1**) and gold accumulation in soils (**Tables 2** and **3**) are very high, with values that approach vegetation and soil gold contents near gold deposits [10].

The area with the highest anomalous uranium content is in the North Eastern part of Barcelona, mainly near the power plants in the vicinity of the river Besòs (**Figures 1** and **12**).

Lead content in diesel fuels was higher than that found (0.017 $g \cdot Pb \cdot L^{-1}$) by [20]. Analysis of the additional plane trees sampled in areas outside Barcelona (**Figure 13**) showed that the greater the distance between plane trees and the road, the lower the concentration levels of these elements. High levels of Au, Pb, Cu, Hg and Sb were detected along main roads whereas much lower levels of these elements were observed in rural areas.

After comparing the average contents of plane trees located within the city of Barcelona with those located outside (**Table 6**), we could observe a high enrichment factor (EF) (exceeding 100%) for Sb, Pb, Au, Mo, W, Cr, Co, As, Ni, Hg, Zn, Mn and Fe in the former. It is therefore reasonable to assume that these anomalous elements in plane tree leaves can be attributed to vehicle emissions.

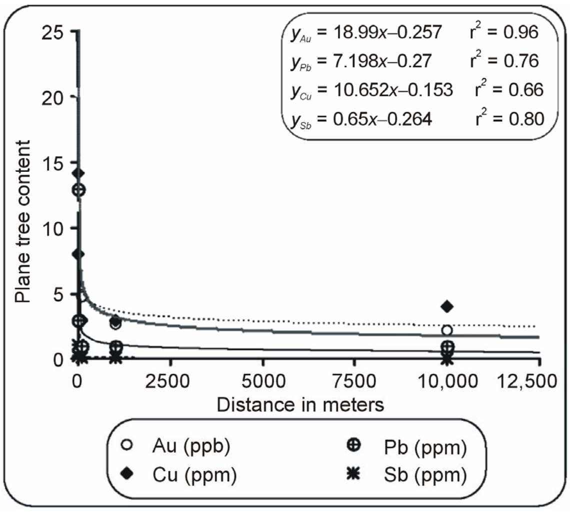

Figure 13. Distance (m) between plane tree sampled and principal road.

Table 6. Average content in 53 plane tree samples in Barcelona (BCN) and 16 outside Barcelona (Out BCN) and enrichment factor (EF).

	BCN	Out BCN	EF (%)
Sb (ppm)	1.13	0.10	1130
Pb (ppm)	12.45	1.75	711
Au (ppb)	20.97	4.30	488
Mo (ppm)	0.78	0.17	459
W (ppm)	0.04	0.01	400
Cr (ppm)	2.45	0.73	336
Co (ppm)	0.79	0.24	329
Cu (ppm)	11.03	4.00	276
As (ppm)	0.28	0.12	233
Ni (ppm)	1.79	0.88	203
Hg (ppm)	0.25	0.13	192
Zn (ppm)	30.51	16.50	185
Mn (ppm)	77.34	52.25	148
Fe (%)	0.04	0.03	133

4. Conclusions

The studies carried out on different elements in fossil fuels such as diesel show high levels of Au, Pb, Cu, Sb, Cr, Cd, Mn, Mo, Co, Se and Ag. The leaves of plane tree are enriched in these elements but not in Cd, Se and Ag, which could be attributed to a high detection limit in the INAA analysis of dry leaves.

Fe, Pb, As, Cu and Cr show anomalies in the main streets and at the Railway Station (RENFE) and in the proximity of the rail tracks. Gold shows a strong anomaly in plane trees and soils, which resembles the gold content in vegetation and soil adjacent to gold mineral deposits.

The content of these elements in plane trees depends on the proximity of the trees to traffic. Phytoaccumulation in plane trees proves to be a reliable tool for detecting atmospheric pollution.

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