



## Simultaneous electrochemical analysis of heavy metals in atmospheric deposits

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### Abstract

Technical difficulties and the high cost of instrumental sampling have caused few atmospheric studies to be conducted. Herein we present a study showing the potential use of tree leaves and adjacent soils as an alternative to direct monitoring of air quality. This work describes the detection and quantification of trace metal concentrations ( $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cu}^{2+}$ ) in an acid-soluble fraction of atmospheric deposits on tree leaves of *Ficus rubiginosa* and adjacent soils, sampled at different selected points in Mohammedia city (Morocco Kingdom), using the electrochemical technique of square wave anodic stripping voltammetry (SWASV). This method employs a rotating disk of glassy carbon electrode as a working electrode, modified with thin mercury film (RDGCE/TMF). This technique enhances the sensitivity of all the investigated heavy metals (HMs), with a detection limit of approximately 30 ppb. The range of heavy metal concentrations in dry tree leaves was 4-58, 4-60, and 2-18 mg/kg for  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cu}^{2+}$ , respectively. Concentrations in dry soil were 1.32-19, 1.5-36.26, and 0.75-8.75 mg/kg for  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cu}^{2+}$ , respectively. The concentrations of heavy metals in soil are lower in comparison to tree leaves.

## 1. Introduction

Air pollution is a universal emerging environmental hazard that threatens life on earth and is increasing in developed countries and large urban areas [1]. Atmospheric studies, especially on metallic pollution, have been conducted since the end of the last millenary [2]. However, because of the high cost of instrumental monitoring and the difficulties posed by the associated sampling methods, few studies have been reported [1].

The atmospheric concentrations of heavy elements and their availability and cycling have greatly changed due to anthropogenic activities, such as coal and oil combustion and domestic waste incineration, as well as road traffic [3,4]. The health effects associated with atmospheric particles are known to be dependent on their toxicity resulting from contamination with heavy metals (HMs). Numerous studies have shown that HM elements are cumulative [5], persistent, and widely dispersed in the environment and interact with various natural compartments [6,7,8,9].

HMs are carcinogenic and highly toxic and thus harmful to human life and disruptive to the biophysical environment. An examination of atmospheric deposition samples is useful in conducting environmental monitoring of HM concentrations in soil solution and plant leaves, which allows us to evaluate the state of metallic pollution in the air [10]. These samples are very important for ecological assessments as well as for understanding the relationship between plants and soil [7,11]. In urban areas, trees have been used as indicators or monitors of trace metal pollution because they are very efficient in trapping atmospheric particles. Trees thus constitute an efficient barrier to airborne particles, preventing them from reaching the ground under the effect of gravity. Studying tree leaves as accumulative biomonitors of trace metal pollution has attained great ecological importance [3,5,12,13,14]. Lead and cadmium are two frequently studied elements. Other trace elements (e.g., Cu, Cr, Zn, Ni) are also encountered.

Because people spend substantial time in urban environments, they can be significantly exposed to such emissions. Thus, it is important to quantify this exposure to airborne particles. It is evident that in Morocco, air monitoring via fixed stations does not capture the exposure of the entire population. This work will therefore contribute to characterizing the large urban area of Mohammedia city in terms of pollution by cadmium, lead, and copper.

Several methods have been proposed for the determination of metallic compounds in environmental samples (e.g., tree bark [14], lichen [15], and waters [1,16]), including spark source mass spectrometry, atomic absorption spectrometry, spectrophotometric methods, and electrochemical techniques [17,18]. This type of analysis is usually performed using spectrometric techniques, which are sensitive and accurate but expensive and time-consuming. In contrast, the proposed method, anodic stripping voltammetry (ASV), when associated with a simplified extraction procedure can minimize delays and potentially reduce costs of analysis [17]. The principle of ASV is well known [12,19,20]. The simultaneous detection of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cu}^{2+}$  with square wave ASV (SWASV) using a working electrode composed of a thin mercury film coated a rotating disk of glassy carbon developed by Florence replaced liquid mercury electrodes because of restrictions related to mercury toxicity [21]. A mercury film electrode (solid) is a thin layer of mercury ions plated on an electric transducer. The most commonly used conductive substrate for this electrode is glassy carbon [22]. Mercury ions are reduced on the surface of the substrate, making a film in which thickness is a function of time of deposition and the amount of mercury in solution [23].

The modification of solid electrodes such as glassy carbon electrodes (GCEs) using mercury films has offered various advantages, including a wide anodic polarization range; low residual current within this range; and generally greater sensitivity, stability of measurement, and selectivity toward trace HMs [24,25]. Therefore, this electrode, coupled with SWASV, has provided an efficient, inexpensive device for the simultaneous determination of Cd (II), Pb (II), and Cu (II) in soil [12], water [22], and clinical samples [26] in the microgram per litre/kilogram range.

The global aim of this work is to determine concentrations of metallic ions of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cu}^{2+}$  in filtered digested samples of the leaves of *Ficusrubiginosa* and the corresponding topsoils, collected in 14 sites in the urban area of “Mohammedia” city during January and February 2017. Both types of sample were digested and analysed as dried and calcined fractions using SWASV. The second aim is to show the impact of atmospheric deposits and the use of these data to make thematic maps. “Mohammedia” city was selected for this study because it represents a multi-polluted site that brings together industrial activities and major urban road traffic. The points that have been sampled are densely populated, enabling us to assess the risk to which the population is exposed.

## 2. Material and Methods

### 2.1. Solutions and reagents

$\text{HgCl}_2$ , suprapur grade of  $\text{HCl}$  and  $\text{HNO}_3$  acids were purchased from SOLVACHIM (Morocco). HMs stock solutions were prepared by diluting the nitrate salts  $\text{CdNO}_3$  and  $\text{PbNO}_3$  and the sulfate salt  $\text{CuSO}_4$  ( $1 \text{ gL}^{-1}$ ) in  $\text{HCl}$   $0.1 \text{ molL}^{-1}$  (Riedel-de Haën). All solutions and dilutions were prepared using ultrapure water from a Millipore Milli-Q purifying system.

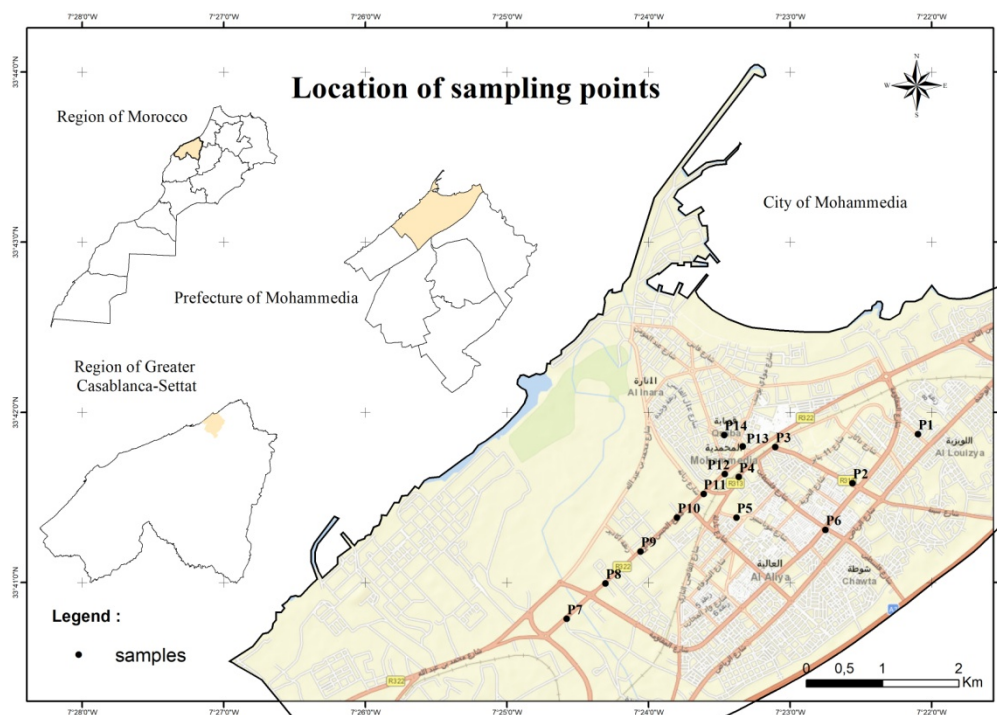
### 2.2. Apparatus and material

The setup used for analytic experiments was a three-electrode cell (25 mL) consisting of a rotating disk of GCE support (RDGCE) (3 mm diameter, OrigaTrod) connected to stirring speed controller (OrigaBox) and modified (ex situ) with a mercury film as the working electrode, a saturated calomel as the reference electrode (SCE) and lastly a glassy carbon as the auxiliary electrode. All experiments were carried out using a PalmSens portable potentiostat (Ecochemie, Utrecht, Netherlands) operated via the PStTrace 3.0 software for data acquisition and signal visualization. The electrochemical cell was cleaned before the experiments using the recommended procedures for trace analysis [27]. A precision balance OHAUS Pioneer PA214/0.1 mg with an accuracy of 0.1 mg was employed to determine humidity and organic matter levels. For the digestion of all samples, we used a muffle furnace at  $500^\circ\text{C}$ , a desiccator at  $110^\circ\text{C}$ , and an automatic digestion unit (VELP SCIENTIFICA) with Pyrex tubes.

### 2.3. Sampling site and methods

All samples were collected in “Mohammedia” city from different selected trees and the adjacent soils. Leaves were sampled from *Ficusrubiginosa*, a species commonly found in the study area (Figure 1). In order to reduce age variation among the samples trees, approximately the same sizewere selected. The leaves were takenfrom

trees at about 2 to 2.5 m height using clean stainless-steel scissors while wearing polyethylene gloves [13]. At each site, a number of fully developed and healthy leaves were randomly taken from all sides of the tree crown and immediately placed in paper envelopes to be transferred to the laboratory [9].



**Figure 1 :**Location map of Mohammedia city and sampling points.

The experimental topsoil (15-20 cm) samples were collected around the trunk of each tree by using a stainless-steel shovel. Samples were placed (five subsamples to make a composite soil sample per tree) in a polyethylene plastic bag and transferred to the laboratory, where each one was passed through a 2 mm plastic sieve and homogenized by the quenching technique [11].

Tree leaf samples were divided to uniform size using a stainless-steel scissors and digested in aqua regia. The scissors were thoroughly cleaned after each grinding to avoid any cross contamination between samples [28]. Both types of samples were dried at 110°C for 12 h in beakers. Some of the dry residues was calcined at 500°C for 8 h. In this procedure, the sample intake was (0.4 g) of dried or dried and calcined samples, carefully weighed on a polystyrene platform and transferred in 250 mL Pyrex digestion tubes. First, the pre-digestion step was done at room temperature for 16 h with 10 mL of a (3:1) mixture of HCl (37%) and HNO<sub>3</sub> (70%). The suspension was then digested at 110°C for 2 h in a reflux condenser. The obtained solution was filtered through a nitrate cellulose membrane filter of 0.45 µm size, diluted to 100 mL with ultrapure water and stored in polyethylene bottles at 4°C for analyses [29]. Those bottles were previously soaked in a solution of HNO<sub>3</sub> 10% during 24 h and then rinsed several times with milli-Q water. Finally, trace metal concentrations were determined in acidic medium (pH=1±0.1) for diluted samples with the selected electrochemical method (SWASV).

#### 2.4. Trace metal detection using SWASV

Using the conventional electrochemical technique of SWASV [12] with a mercury film electrode, it was possible to measure trace metal concentrations (Cd<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>) simultaneously in acid soluble fraction of deposits of both types of samples [19]. The mercury film was pre-plated from a stirred mercury (II) chloride solution, 80 mgL<sup>-1</sup>, prepared in hydrochloric acid 0.1 molL<sup>-1</sup> by holding the electrode at -1.2 V for 300 s. Before the electrodeposition of the mercury film, the surface of the GCE was cleaned and polished to a mirror-like finish with alumina slurries (0.3 and 0.05 µm, Buehler, USA) on polishing cloths (Micropolish II, Buehler, USA) and then rinsed with milli Q water and sonicated for 1 min [30]. The modified RDGCE coated with thin mercury film (RDGCE/TMF) thus obtained was ready for trace metal detection.

The simultaneous SWASV was performed with the standard addition method in HCl 0.1 molL<sup>-1</sup> at RDGCE/TMF for a range of concentrations between 0.1 and 4 mgL<sup>-1</sup> for Cd<sup>2+</sup>, Pb<sup>2+</sup>, and Cu<sup>2+</sup>. Deposition time at -1.2 V was set at 60 s followed by 10 s resting period in the window potential between -1.2 and 0 V. Data analysis and graphing were done with Origin 8.5 software.

### 3. Results and discussion

#### 3.1. Analytical performance evaluation of simultaneous determination of trace metal concentration by SWASV

##### 3.1.1. Trace metal calibration

Various optimizations of the experimental parameters of the technique were performed, and the analytical performance of the SWASV method was evaluated. The quantifiable stripping peaks were obtained with the optimized parameters of the technique used. Cd (II), Pb (II), and Cu (II) were quantified after calibration by the method of standard addition in the linear range between 0.1 and 4 mgL<sup>-1</sup>, which was done by adding increasing concentrations of these elements from standard solutions prepared daily from the stock solutions (1 gL<sup>-1</sup> in HCl 0.1 molL<sup>-1</sup>). The calibration plots show good analysis correlation coefficients (R<sup>2</sup>) of 0.988, 0.986, and 0.946 for Cd<sup>2+</sup>, Pb<sup>2+</sup>, and Cu<sup>2+</sup>, respectively. The sensitivity of the measurement system and the limits of detection (LODs) of the method and the limits of quantification (LOQs) were also determined.

The LOD was calculated as being equal to 3Sdb/a, where (Sdb) is the experimental standard deviation of five non-consecutive blank measurements and (a) is the slope calibration performed with the RDGCE/TMF in HCl 0.1 molL<sup>-1</sup>. The obtained LODs are 28, 35, and 34 ppb for Cd<sup>2+</sup>, Pb<sup>2+</sup>, and Cu<sup>2+</sup>, respectively, and the sensitivities are 121.05, 141.46, and 32.05  $\mu\text{A}/\text{mg L}^{-1}$  in the same order as indicated in Table 1.

##### 3.1.2. Accuracy of measurements

The determination of Cd<sup>2+</sup>, Pb<sup>2+</sup>, and Cu<sup>2+</sup> contents had no interference except for zinc, which forms intermetallic elements on the surface of the thin mercury film electrode [22]. We found a more marked effect on the copper response. However, some tree leaf samples show a zinc oxidation peak. Table 1 summarizes the analytical performance of the thin mercury film electrode (TMFE) chosen for simultaneous detection of the actual elements (Figure 2).

**Table 1:** Analytical performance of simultaneous detection of Cd<sup>2+</sup>, Pb<sup>2+</sup> and Cu<sup>2+</sup>.

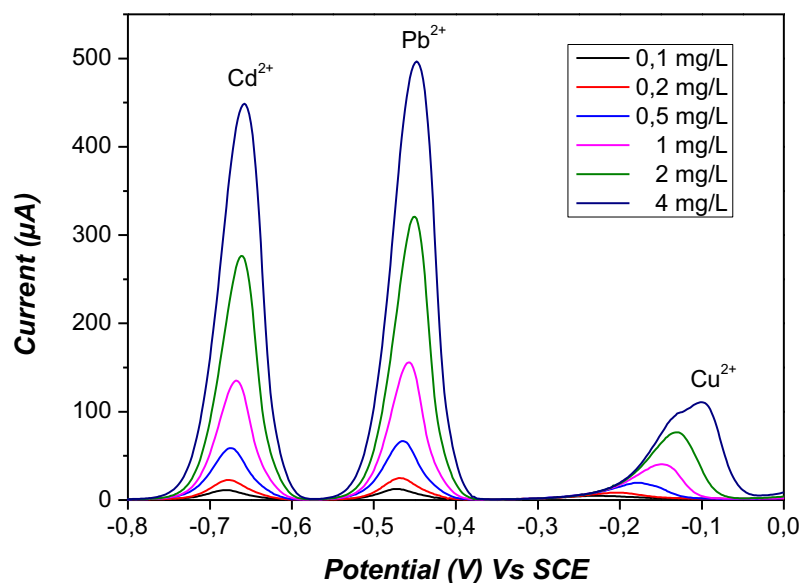
Analytical parameters*	Cd <sup>2+</sup>	Pb <sup>2+</sup>	Cu <sup>2+</sup>
Linear range (mgL <sup>-1</sup> )	0.1-4	0.1-4	0.1-4
Slope of the calibration plot ( $\mu\text{A}/\text{mgL}^{-1}$ )	121.05	141.46	32.05
Standard error of Slope ( $\mu\text{A}/\text{mgL}^{-1}$ )	5.79	7.46	3.38
Intercept ( $\mu\text{A}$ )	-0.02	-0.74	0.77
Standard error of Intercept ( $\mu\text{A}$ )	1.14	1.65	0.36
LOD (mgL <sup>-1</sup> )	0.028	0.035	0.034
LOQ (mgL <sup>-1</sup> )	0.094	0.116	0.112
R <sup>2</sup>	0.988	0.986	0.946

\*Average of five non-consecutive determinations: n=5

#### 3.2. Concentrations of soluble trace metals: application to reel samples

##### 3.2.1. Choice of tree leaves and soil samples

Copper and other metals are naturally present in plant leaves as constituents of the chloroplast protein and several enzymes [31], but some metals like cadmium and lead are considered non-essential in the life cycle of plants and thus are toxic when certain thresholds are exceeded.



**Figure 2:** SWAS voltammograms obtained for Cd (II), Pb (II) and Cu (II) at RDGCE/TMF in HCl 0.1 molL<sup>-1</sup> electrolyte. Experimental conditions E step: 0.002 V, E amp: 0.025 V, E Cond: 0.0 V, E dep: - 1.2 V, Freq: 25 Hz, t Cond: 120 s, t dep: 60 s, t eq: 10 s and stirring speed: 1500 rpm.

Tree leaves are considered a good indicator of air pollution in urban areas because they accumulate pollutants such as HMs and can be used as a surface for atmospheric dust deposition. Leaves are an alternative to direct sampling for air quality monitoring. Examining atmospheric deposition samples allows environmental monitoring of HMs concentrations in soil solution and plants leaves to be used to evaluate metallic pollution in the air [14]. Such samples are very important for ecological assessments as well as for understanding the relationship between plants and soil [7]. In urban areas, trees play an important role because they are very efficient in trapping atmospheric particles. Airborne particles are considered to be indicators of HMs pollution due to atmospheric deposition [3,12]. HMs in soil are analyzed because they show the impact of air pollution in urban areas. This type of analysis, when correlated with analysis of tree leaves, gives an idea of the accumulation factor from soil to plants [5,11].

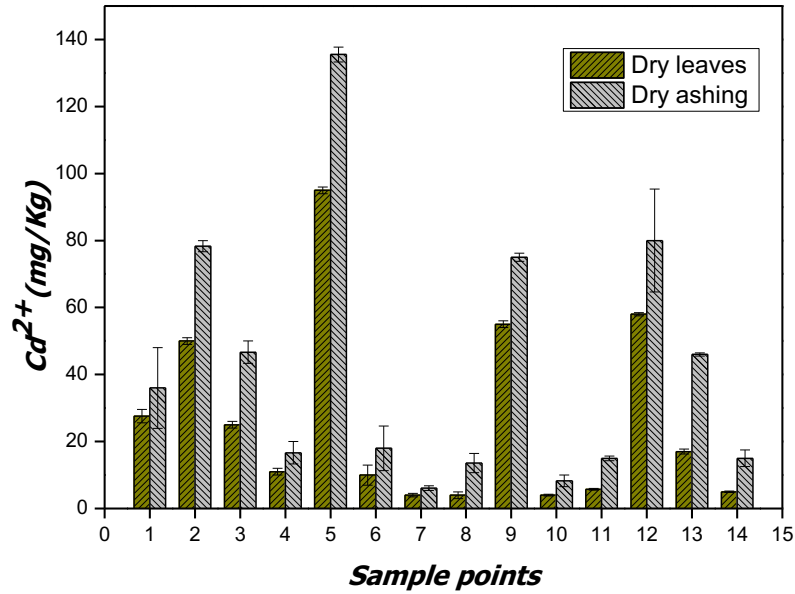
### 3.2.2. Choice of treatment method of samples

Both fractions of the dried and calcined samples were investigated. Comparatively to dried fractions, the calcined ones show substantial concentrations for all studied elements. Different forms of those elements are present in leaves. This is because the trace metallic compounds present in the leaves and soil are in the organic form in addition to particulate and inorganic forms. The metals can be retained as complexes, in which they are very energetically fixed. Treatment at 500°C makes it possible to release all the contents associated with the organic matter. The diagrams in figures 3 to 8 confirm that heavy metals concentrations in the calcined fractions are higher than those in the dry fraction. For the rest of the study, we chose the calcination treatment of the samples.

### 3.2.3. Heavy metal contents found in studied samples

#### - Cadmium in leaves

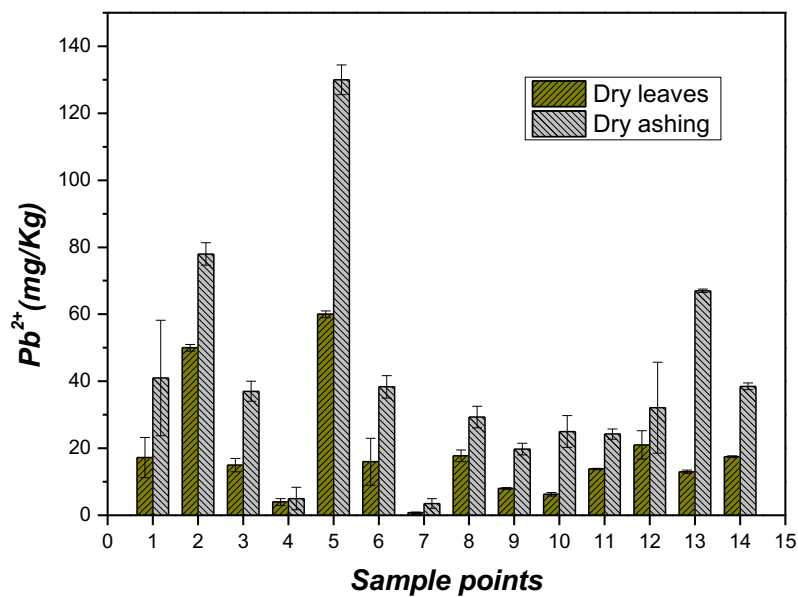
Concerning cadmium in dried leaf samples, it should be noted that most sampling points have significant concentrations (below 30 mg/kg), except for points 2 (dense road traffic, low flow, and narrow right-of-way), 5 (dense and non-fluid road traffic, parking, a school, and a daily market), 9 (a red light), and 12 (near the railway station and with heavy road traffic) (Figure 3). This is also valid for the calcined phase at 500°C, which presents higher concentrations of cadmium, taking into account the organic composition (ash). Cadmium does not exist naturally; it is a co-product of the refining of lead and copper. It combines with organic and mineral sulfur and chlorine and exists in different forms, such as oxides and sulphates. The presence of cadmium in tree leaves mainly results from the underlying soil due to cadmium's great mobility.



**Figure 3:** Concentration of Cd<sup>2+</sup> in dry and ash tree leaves.

*-Lead in leaves*

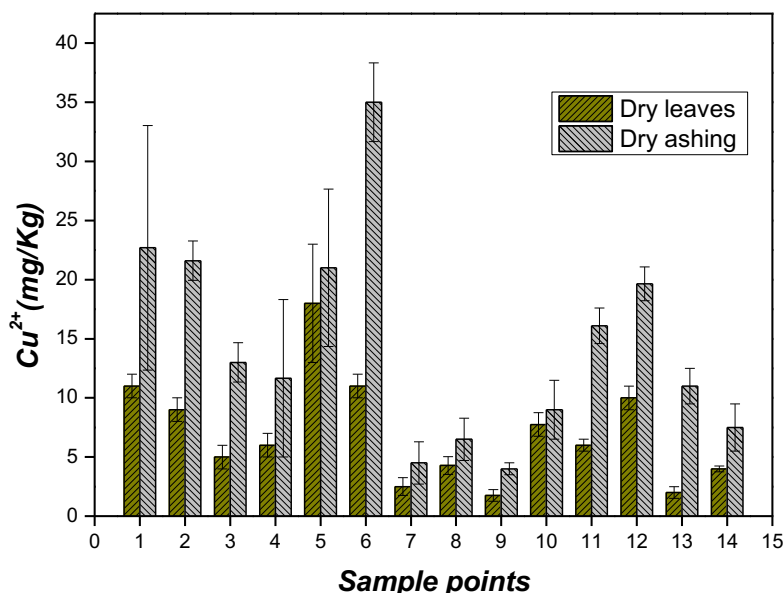
As a trace metal that is non-essential for biological functions, lead is highly toxic to plants and animals. It is naturally present and may also be originate from atmospheric deposition (resuspension of soil particles) and anthropic activity (industries). The concentration of Pb<sup>2+</sup> in the dry leaves phase for all samples is within the normal range (5-10 mg/kg), except at points 2 (50 mg/kg), 5 (60 mg/kg), 9 and 12, all of which exceed the threshold for toxicity (30 mg/kg). The calcined fraction contains concentrations are greater than dry ones. The maximum value was found at point 5 and the minimum at point 7 (Figure 4). Uptake of lead is passive, and its translocation from roots to other plant organs is generally low.



**Figure 4:** Concentration of Pb<sup>2+</sup> in dry and ash tree leaves.

*-Copper in leaves*

Copper is required in very small amounts, with about 5 to 20 mgL<sup>-1</sup> in plant tissue being adequate for normal growth. Less than 4 mgL<sup>-1</sup> is considered deficient, and above 20 mgL<sup>-1</sup> is considered toxic. We found that the concentration of copper in the dried leaves fluctuates significantly across the different sampling points, with a maximum of 18 mg/kg at point 5 and a minimum of 1.75 mg/kg at point 9. Compared to lead and cadmium, copper concentrations are very low, a finding that is justified by the absence of a potential source of pollution. The absorption by the leaves is a function of the pH and nature of the soil. When zinc, calcium, potassium, and ammonium are present, they have an antagonistic effect on copper absorption (Figure 5).



**Figure 5:** Concentration of Cu<sup>2+</sup> in dry and ash tree leaves.

It has been reported in the literature that the concentration of trace metallic elements differs according to the species of tree [13], the organs studied (e.g., leaves, bark, branch, fruit) [26], the location of sampling [11], and the season [28].

**Table 2:** Comparison between three metal concentrations (mg/Kg) in different countries.

Studies	n	Cd <sup>2+</sup>	Pb <sup>2+</sup>	Cu <sup>2+</sup>	Species and site samples
[9]	7	ND	0.71	18.97	Leaves of <i>Platanus orientalis</i> in Isfahan city Iran.
[11]	10	ND	5.79	15.60	Leaves of <i>Jacaranda Mimosifolia</i> at different points in Tshwane South Africa
[32]	37	0.64	2.49	6.54	Different organs of different trees Southeast Tavsanlı Turkey
[33]	5	ND	19.40	14.67	Leaves of <i>Aesculus hippocastanum</i> beginning and end of vegetation period Botanic Garden Belgrade
	5	ND	19.00	12.96	Leaves of <i>Corylus colurna</i> beginning and end of vegetation period Botanic Garden Belgrade
[5]	5	0.06	3.20	9.10	Green shoots of <i>Cupressus sempervirens</i> sarapium forest Egypt
	5	0.05	3.20	8.70	Green shoots of <i>Cupressus sempervirens</i> sadat forest Egypt
[34]	83	ND	99.38	19.46	Leaves of <i>Phoenix dactylifera</i> Aqaba Jordan
<b>Current study</b>	14	26.52	18.59	7.02	Leaves of <i>Ficus rubiginosa</i> Mohammedia Morocco

\*: Mean value, n: Number of samples, ND: Not defined

Table 2 shows the mean concentration of cadmium, lead and Copper in different tree samples from different locations: Iran, South Africa, Turkey, Egypt, and Jordan. In comparison to those studies, the results obtained in “Mohammedia” are similar to the lead value found in Belgrade and copper found in Turkey. However, the value of cadmium greatly exceeds that found in all the cited studies. Additionally, the results in “Mohammedia” city are slightly higher than the normal level for lead but they are at a toxic one for cadmium.

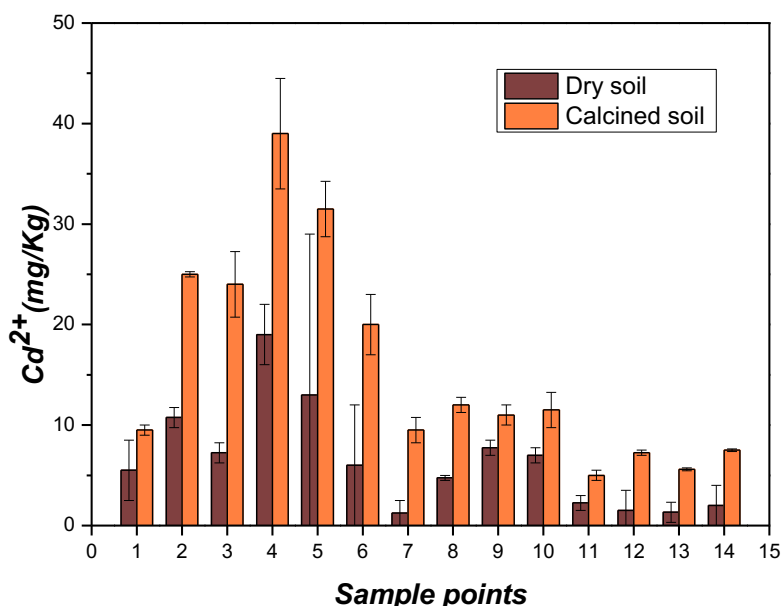
**Table 3:** Normal and toxic value of lead and cadmium in plants mg/Kg dry weight [35].

	<b>Cadmium</b>	<b>Lead</b>
<b>Normal value</b>	0.05-0.20	5-10
<b>Toxic value</b>	5-30	30-300

*-Cadmium in soil*

In the dried topsoil from near each tree, in the majority of the sampling points, the cadmium concentrations are low with a slight overrun for point 2 (10.75 mg/kg); point 4, near a taxi station (19 mg/kg); and point 5 (13 mg/kg), which is characterized by the presence of a taxi station and very frequent and non-fluid road traffic (Figure 6). This last site has the peculiarity of being the highest point of the study area. A slight increase in concentration is observed in the calcined fraction compared with the dried fraction (Table 3).

Cadmium is found in various forms such as oxides or is associated with chloride sulphates and sulphide. It may be in water-soluble form or in the form of an insoluble organic and inorganic complex. Cadmium is a very mobile and not very volatile element. The ubiquitous concentration of cadmium in soil is between 0.1 and 0.2 mg/kg.

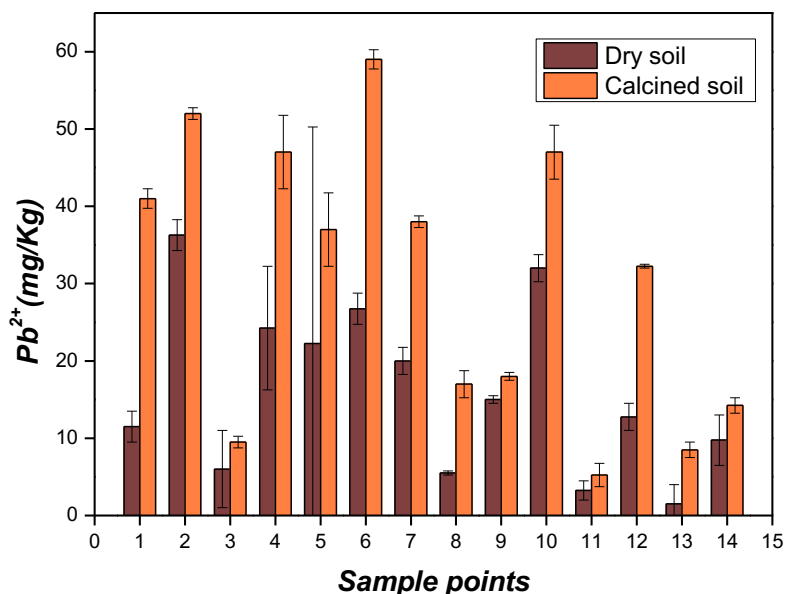


**Figure 6:** Concentration of Cd<sup>2+</sup> in dry and calcined soil.

*-Lead in soil*

Naturally present in the soil, lead is associated with sulphides (galena), sulphates (anglesite), or carbonates (cerusite). It can also be present as the result of human activity when combined with acetates or basic carbonates. Oxidized forms are also found. In the dried soil samples, nearly all sampling points are below the threshold for toxicity (Figure 7).

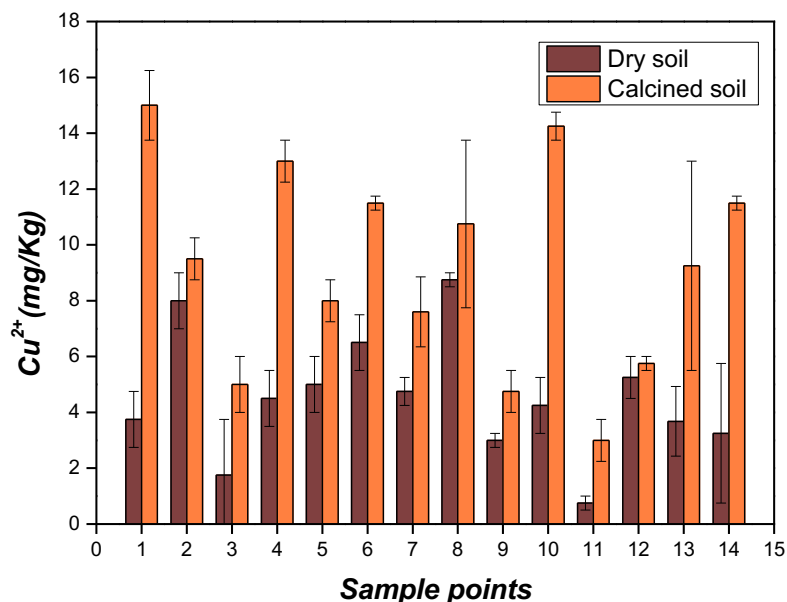




**Figure 7:** Concentration of Pb<sup>2+</sup> in dry and calcined soil.

*-Copper in soil*

The concentration of copper found in the dried soil is close to that found in dried leaves, with a maximum of 8.75 mg/kg at point 8 and a minimum of 0.75 mg/kg at point 11 (Figure 8). Copper is found in the soil in the native state and in the oxidation state. Cu (I) and (II) are associated with sulphates, carbonates, and sulphides. Copper is preferentially bound to organic matter, the oxides of iron and manganese, and clay. It also is strongly adsorbed in the upper few centimeters of soil.



**Figure 8:** Concentration of Cu<sup>2+</sup> in dry and calcined soil.

Some leaf samples show peaks of Zn (II). All peaks of the studied elements were very clean and well defined, and a peak separation was observed. Cd<sup>2+</sup> and Cu<sup>2+</sup> peaks in the reel samples were detectable but were not measurable, which led us to use the standard addition method to spike the samples. Pb<sup>2+</sup> and Cu<sup>2+</sup> peaks were repeatable, whereas the intensity of Cd<sup>2+</sup> peaks progressively decreased during scanning.

### 3.3 Mobility and bioaccumulation of metallic elements

Our goal is to measure the HMs content from air pollution, so we chose not to wash the leaves. Therefore, we cannot measure the accumulation factor. We found that the HM content measured in the unwashed leaves exceeded that measured in the soil. In addition, it has been mentioned in the literature that lead and copper ions have reduced mobility in soil. The physicochemical parameters characterizing the soil samples studied here prove that the accumulation of these elements from the soil is not favoured. We deduce that the contents recorded in the two types of samples are essentially of atmospheric origin (Tables 4 and 5).

**Table 4:** Heavy metal background values in soil (mg/Kg) [36].

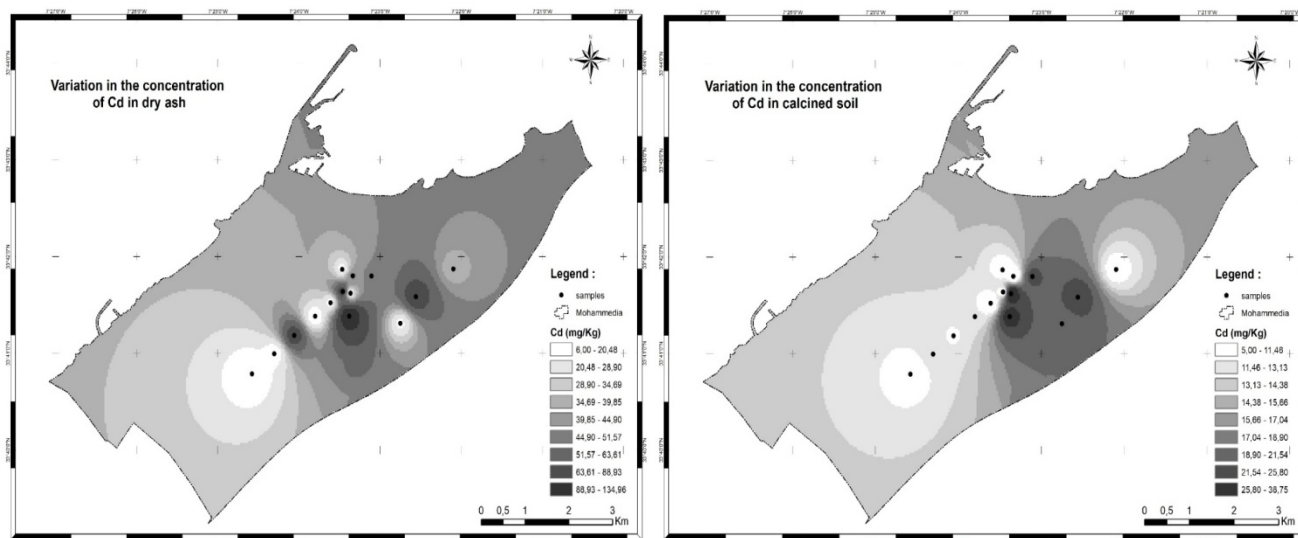
	1	2	3	4	5
<b>Cd</b>	0.35	0.10	0.05-0.45	0.2-1	-
<b>Pb</b>	35	17	9-50	10-30	25
<b>Cu</b>	30	14.3	2-20	20-30	14

1: Natural levels in the terrestrial crust (Bowen,1979);2: Mean levels in the continental crust (Wedepohl, 1995)  
3: Ordinary Soils (Baiz, 1997); 4: Alloway (1990); 5: Worldwide data (Kabata-Pendias and Pendias, 1999)

**Table 5:** Comparison between metal concentrations (mg/Kg) in different soils.

Studies	n	Cd	Pb	Cu	Nature of samples
[37]	9	2.42	ND	34.85	Urban soil Marrakech Morocco
[38]	94	ND	10.00	7.94	Soil province Cordoba Argentina
[39]	30	0.14	11.40	23.60	Municipal Catamarca Argentina
[40]	7	0.41	17.00	17.00	Agricultural topsoil Spain
[41]	39	2.92	54.8	41.58	Urban soil Changchun China
<b>Current study</b>	14	6.38	9.75	4.50	Urban soil Mohammedia Morocco

The natural background concentrations of these elements in soils can be used as a reference. The concentrations of lead and copper in the study area are similar to values found in Catamarca Argentina. We note that the concentration of cadmium is generally higher, but the concentrations of lead and copper are both normal. Moreover Rodriguez et al. (2008) showed that concentrations of Pb, Cu and Cd accumulated by soil respectively have concentrations of 17, 17 and 0.4 (mg / kg), which is still much lower than those found in the present study; Bermudez et al. (2012) showed varying concentrations of 18.9-133, 9.8-116.6 and 1.85-11.1 mg / kg, respectively, for Pb, Cu and Cd. The last ones are close to what we found in our study 26.5, 18.6 and 7 respectively for Cd, Pb and Cu. Figures 9 to 11 show the spatial distribution of the studied elements. Some variation in the concentrations of the elements between the different sampling points was observed.



**Figure 9:** Spatial distribution of Cadmium.

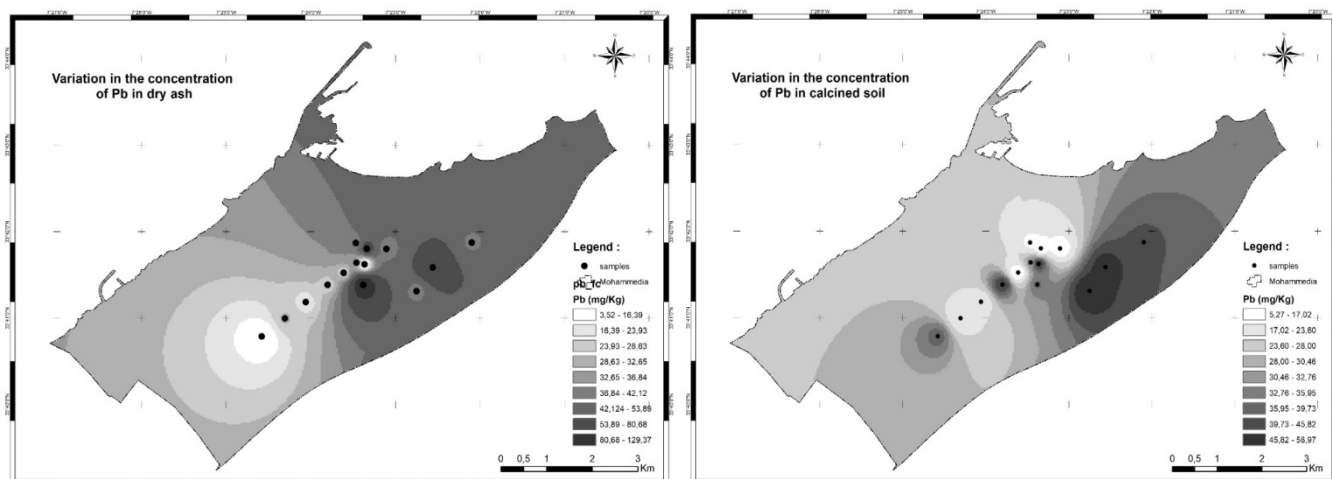


Figure 10: Spatial distribution of Lead.

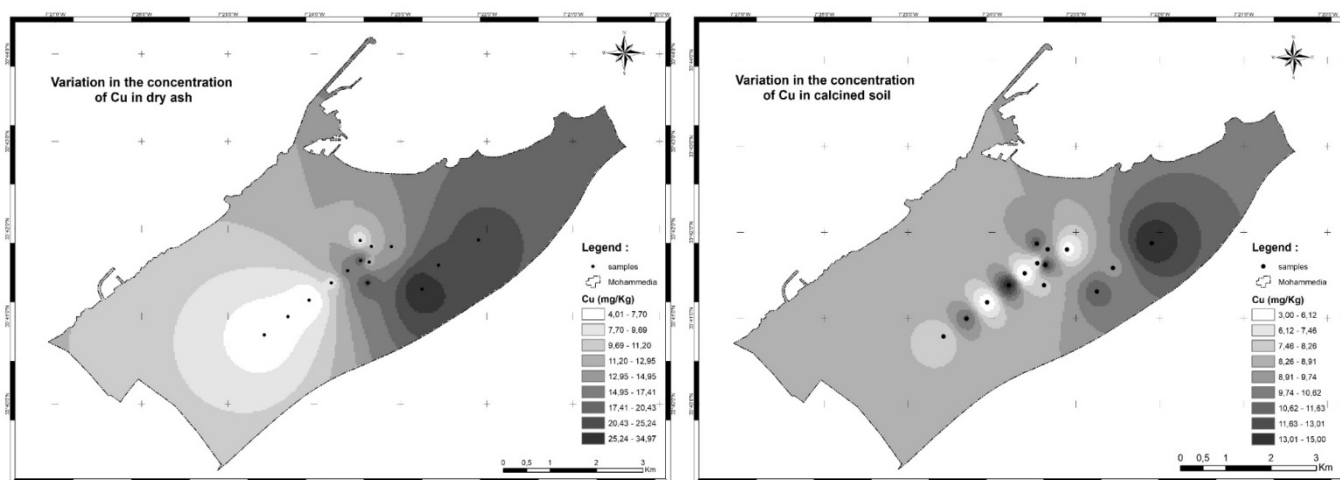


Figure 11: Spatial distribution of Copper.

These figures (6 maps) show clearly the most influenced points. The points that contain excessive concentrations of lead and cadmium are located in areas of the city with present high human density and traffic jam. This tree leaf sampling and corresponding soils technique allowed us to give an idea of the air pollution at Mohammediacity.

## Conclusion

In this study, the results show that determination of trace elements in soil and tree leaves has been achieved successfully. This passive dust sampling and pollution accumulating method appears to be an easy, inexpensive, and accessible approach for the detection of atmospheric heavy metals. In addition, the adopted analysis method (Square Wave Anodic Stripping Voltammetry) presents not only analytical performances similar to those of the spectral methods but also a simplicity of implementation and a low cost. Our results can complement the data provided by the air quality monitoring stations. The founded metallic concentrations in the studied samples reflect variation among sample points, and most samples exceed normal thresholds. Therefore, the local population certainly suffers the negative impact on the health of this form of pollution; this has already been proved by some epidemiological studies of other pollutants in the region of “Mohammedia” [42]. In addition to that, the determination of trace elements in airborne particulate matter is very important in air pollution studies: the elemental composition of particles as a function of size may lead to identification of emission sources. This topic will be the subject of our future work.

Taking into account the simplicity of the proposed method, it can be considered as an analytical tool for routine atmospheric pollution analysis.

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