

## HEAVY METALS DETECTION IN ATMOSPHERIC FALLOUT AND AMBIANT AIR

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**Abstract:** The air quality-monitoring network in Morocco does not cover all regions and occasionally gives data on atmospheric metallic particulate pollution. This work makes it possible to find a simple, inexpensive and available method for monitoring this type of pollutants. In this paper, we report an effective, simple, sensitive and low-cost electrochemical method for heavy metals monitoring in rainwater and airborne particulate matters. The glassy carbon electrode modified ex-situ with a thin mercury film (GCE/TMF) was used as a sensor to detect  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  by square-wave anodic stripping voltammetry (SWASV). The developed sensor showed a linear response in the concentration range of  $0.1\text{--}2.0\ \mu\text{mol}\cdot\text{L}^{-1}$  in  $\text{HCl}\ 0.1\ \text{mol}\cdot\text{L}^{-1}$  for both  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  heavy metal ions. The calculated limits of detection were 12 and 16  $\text{nmol}\cdot\text{L}^{-1}$  for  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  respectively. Moreover, the proposed electrochemical sensor was successfully applied to monitor  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  in total atmospheric fallout (TAF) and particulate matter (PM10) samples collected in Mohammedia city. The obtained results showed some exceedances of the limit standards preconized for cadmium and lead elements.

**Keywords:** *air quality, electrochemical analysis, heavy metals ions, particulate matters, rainwater, thin mercury film electrode*

## INTRODUCTION

During the last decades, the world has been influenced by the uncontrolled development in several fields such as transport, urbanization and agriculture. This has a negative impact on the ecosystem by polluting air, soil and water.

Air pollution is a recognized scourge and its effect is spreading more and more in developing countries, like in Africa [1]. It's considered as a real danger facing people mainly in urban areas [2] and which may have a negative impact on the ecological balance of the planet [3, 4].

Actually, transports, garbage incineration, domestic heating and uncontrolled development of industries are considered the main sources of urban pollution by atmospheric particles [5 – 7]. These particulate matters are of different sizes and compositions and remain suspended in the air at some point before reaching the ground under the gravity effect [8 – 10]. However, these particles can penetrate deeply into the respiratory system and may cause lung damage, bronchitis, asphyxia and death [11]. Recently, this subject has been of a great concern within the scientific community since the determination of heavy metals for example in airborne particulate matter is very important in air pollution studies. Because of the very low concentrations of some toxic heavy metals and the complexity of the airborne particulate matrix, sensitive and accurate methods are required for their analysis, as well as suitable pretreatment methods for the samples. Therefore, tremendous studies have been conducted for metrology of atmospheric pollutants [12, 13], identification of emission sources [14, 15], simulation of scenarios of dispersion of pollutants [6, 16 – 18], epidemiology [19, 20] and mapping [21, 22].

The study of particulate matters pollution consists of trapping atmospheric particles via samplers on filters for analysis often by sophisticated and expensive analytical techniques [3, 14]. Rainwater also plays an interesting role in understanding air quality due to the contact of rain with aerosol and gases of the atmosphere (wash out phenomena) [9, 10, 23]. Moreover, it was reported that 90 % of the total amount of metallic pollutants present in the air are lixiviated by wet deposition [9, 24]. Heavy metals and others pollutants are present in particulate matters composition which indicate their origin [9, 13]. Copper, zinc, lead, cadmium, and other trace metals are commonly found in urban atmospheric particles [25, 26].

Heavy metals are potentially dangerous to human health because they are cumulative and non-biodegradable [26]. Therefore, the study of these toxic metals in airborne particulate matters concerns also Moroccan researchers [12, 27 – 35]. Thus, the development of fast, low cost material and simultaneous analytical methods are required in order to fulfill the information gap. Indeed, many analytical methods were reported for trace metals detection such as ICP-MS, ICP-AES, DRX, IC, XRF and GF-AAS [2, 5, 6, 26, 27, 29, 31 – 35]. These methods are robust and accurate however, they require expensive equipment.

The electrochemical methods offer many advantages such as low-cost, easy use, wide dynamic range, and high sensitivity compared to the classical analytical methods. Schroeder et al. reported the use of differential pulse anodic stripping voltammetry (DPASV) and showed that DPASV has been listed as the most sensitive technique for  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  detection in particulate matters samples [25, 39]. Anodic stripping

voltammetry is suitable to determine trace heavy metals in different sample matrix [40] such as clinical [41], environmental [3, 39, 43 – 47], food [48] and industrial [49, 50]. Herein, we present the application of square-wave anodic stripping voltammetry SWASV technique at glassy carbon electrode coated with thin mercury film GCE/TMF for the simultaneous determination of total soluble trace of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  ions in particulate matters PM10 and in total atmospheric fallout samples collected in Mohammedia city (Morocco).

## MATERIALS AND METHODS

### Chemicals and reagents

Mercury chloride  $\text{HgCl}_2$ , suprapur grade hydrochloric  $\text{HCl}$  37 % and nitric  $\text{HNO}_3$  68 % acids were purchased from Solvachim (Morocco).  $\text{Cd}(\text{NO}_3)_2$  and  $\text{Pb}(\text{NO}_3)_2$  reagents were purchased from Riedel-de Haën AG (D-30926 Seelze - Germany).

### Apparatus and materials

The setup used was a three-electrode cell (25 mL) consisting of a glassy carbon electrode GCE (3 mm diameter, BASi, USA) coated ex-situ with a mercury film as the working electrode, saturated calomel electrode (SCE) as the reference electrode, and platinum wire as the auxiliary electrode. All the analytical experiments were carried out using a portable potentiostat (PalmSens Ecochemie, Utrecht, Netherlands) operated by means of the PsTrace 3.0 software.

The automatic digestion unit (VELP SCIENTIFICA) equipped with Pyrex tubes was used for PM10 samples digestion. The pH values were measured by OHAUS Starter2100 pH-meter (7 Campus Drive, Suite 310 Parsippany, NJ 07054 USA). The RADWAG AS160.R2 (Torunska 526-600 Radom Poland) analytical balance was used to make gravimetric amounts of dusts (PM 10) collected in quartz filters. All the experiments were carried out at ambient temperature.

### Analytical methods

#### *Electrode preparation*

Prior the electro-deposition of mercury film, the surface of the glassy carbon electrode GCE was polished and cleaned to a mirror-like finish with alumina slurries (0.3  $\mu\text{m}$  and 0.05  $\mu\text{m}$ , Buehler, USA) on polishing clothes (Micropolish II, Buehler, USA) and then rinsed with a deionized water and sonicated for 5 min in ethanol and finally 5 min in deionized water. The mercury film was coated from a stirred mercury (II) chloride solution, 80  $\text{mg}\cdot\text{L}^{-1}$ , prepared in hydrochloric acid 0.1  $\text{mol}\cdot\text{L}^{-1}$ , by holding the electrode at -1.1 V for 5 minutes. The modified glassy carbon electrode coated thin mercury film (GCE/TMF) obtained in this way, was ready for trace metals detection.

The electrochemical measurements of the studied analytes were carried out using square-wave anodic stripping voltammetry by scanning the potential from -0.80 V to -0.35 V. The voltammograms were recorded at a frequency of 15 Hz, step increment of 0.003 V and amplitude of 0.028 V. The electrode was conditioned at -0.3 V for 300 s to

remove the residual traces metal of analytes and then the pre-concentration step was done at  $-1.1$  V during 300 s under stirring condition of 300 rpm. The selected equilibrium time was 30 s before performing the voltammograms.

### ***Solutions preparation***

Heavy metals stock solutions ( $1 \text{ g}\cdot\text{L}^{-1}$ ) were prepared by diluting nitrate salts of cadmium and lead in hydrochloric acid  $0.1 \text{ mol}\cdot\text{L}^{-1}$ .  $\text{HNO}_3$  was used to acidify rainwater samples and to dissolve all metallic compounds. All solutions were prepared using deionized water from a Millipore Milli-Q purification system.

### **Sampling and samples digestion**

#### ***Study area***

Mohammedia city was selected due to its urban/industrial and agricultural surrounding. It hosts the most important oil refinery of Morocco “SAMIR” and the principal thermal power plant, which makes it the center of the Moroccan petroleum industry. The annually average of precipitation is around 432 mm. The figure 1 shows the sampling points (S1, S2 and S3) in the study area.



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

### ***Sampling***

#### ***Rainwater***

Rainwater sampling was conducted using a homemade collector fitted with a polyethylene high-density (PEHD) bottle of 5 L capacity and a funnel of 22 cm of internal diameter [7]. The collector was placed on the roof of the pedagogic building of the Faculty of Sciences and Technologies of Mohammedia (FSTM) at about 20 m from ground level. The collector was deposited on a table at about 1 m from the floor (S1) to

avoid resuspension of previously sedimented particles and to be far from local sources of contamination (elevated terraces and trees) [26]. The total atmospheric fallouts samples (wet and dry deposits) were collected monthly, for a period of 4 months (from November 2014 to February 2015).

The faculty site selected is almost in the close suburban part of the Mohammedia city. This site has the peculiarity of being the higher sampling point compared to the two other sites S2 and S3 where the filter dust samples has been collected. In order to avoid the contamination of rainwater samples by the sampler recipient, a decontamination process was performed before the sample collection as described by Garnaud [26].

#### *Particulate matters*

Regarding particulate matters (PM10) samples collection, a number of 24 samples were collected in the dry season (June of 2015). PM10 was sampled in the same location (S1) as rainwater samples and in two other points (S2 and S3) which are located at about 7 m from the ground level and 1 m above the floor. Those sites are characterized with non-fluid heavy road traffic (S2) and industrial activities (S3). During this campaign, PM10 containing heavy metals were collected on Quartz filters (Quartz filter 4.7 cm - Zambelli PR17079) with a cyclone head sampling. The sampling flow rate was approximately  $1 \text{ m}^3 \cdot \text{h}^{-1}$ .

The field blanks and actual samples were weighed before and after sampling. Before weighing, the filters were conditioned at desiccator for 24 h.

#### *Samples digestion*

##### *Rainwater*

After 1 month of rainwater collection, the obtained rainwater samples were transferred to the laboratory. An aliquot of about 15 mL was immediately used to measure *pH*, and the remainder was acidified with  $\text{HNO}_3$  to  $\text{pH} = 1$  during 48h in darkness in order to dissolve all trace metals and to fix the metals ions in the solution [51]. A vacuum filtration through a clean nitrate cellulose filters (previously washed with  $\text{HCl}$  5 %) was performed. These filters have been analyzed by the ICP spectroscopic technique to show a possible contamination of the samples during the treatment of the latter. The results of this analysis showed quantities of metals not detectable.

The samples were stored in high density polyethylene PEHD bottles previously washed with  $\text{HNO}_3$  10 %. The retentate recovered on the cellulose filters was dried at  $110^\circ \text{C}$  for 24 h and then in desiccator for 48 h and weighed in order to determine the monthly flux of total atmospheric fallout (TAF:  $\text{mg} \cdot \text{m}^{-2} \cdot \text{month}^{-1}$ ).

##### *Particulate matters*

Concerning the choice of the method of digestion of the samples, two approaches have been implemented. The first one is the quadriacid attack by the addition of hydrofluoric acid and boric acid in addition to hydrochloric and nitric acids. The second approach is the use of aqua regia (hydrochloric and nitric acids).

According to the analysis of the virgin quartz filters treated by the two approaches, at this moment we have found significant quantities of impurities in the case of treatment with the first approach. This is certainly due to the fact that it was necessary to use glass digestion tubes. Indeed the glass is attacked by hydrofluoric acid and releases some elements.



In the other hand, for PM10 samples, each filter was digested separately with aqua regia (10 mL mixture of hydrochloric and nitric acids 3:1) in Pyrex tubes during 2 h at 110 °C in the automatic digestion unit until total evaporation. The dry depot was solubilized with 50 mL of deionized water.

A vacuum filtration on nitrate cellulose filter 0.45 µm (Sartorius Stedim - Germany) was performed before the analysis of heavy metals content. The obtained solutions were stored in PEHD bottles previously washed with HNO<sub>3</sub> 10 % and rinsed several times with deionized water and stored in a fridge at 4 °C up to the measurements [26].

PM10 was sampled in the same location (S1) as rainwater samples and in two other points (S2 and S3) which are located at about 7 m from the ground level and 1 m above the floor. Those sites are characterized with non-fluid heavy road traffic (S2) and industrial activities (S3). During this campaign, PM10 containing heavy metals were collected on Quartz filters (Quartz filter 4.7 cm-Zambelli PR17079) with a cyclone head sampling. The sampling flow rate was approximately 1 m<sup>3</sup>·h<sup>-1</sup>.

The field blanks and actual samples were weighed before and after sampling. Before weighing, the filters were conditioned at desiccator for 24 h.

## RESULTS AND DISCUSSION

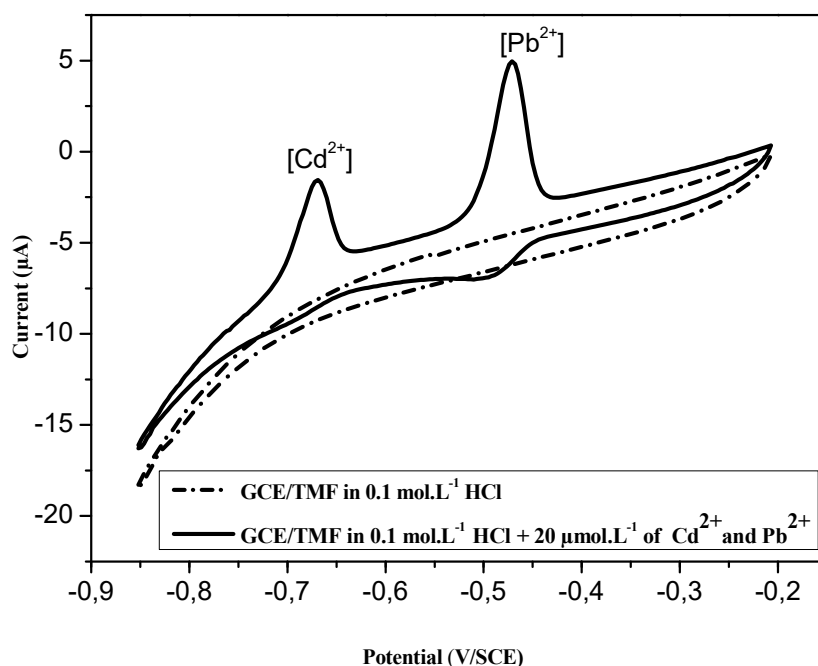
SWASV technique is an analytical method based on current-potential measurements in electrochemical cells. The analytical signal is the current, which flows through the cell during the reaction of the analyte at the interface solution and the working electrode. This technique consist on two steps: a pre-concentration step where the analytes are amalgamate (reduction of analytes on the electrode surface) with mercury film (stirred medium) and a stripping step where the analytes are re-oxidized back in the solution (unstirred medium) [3].

### Electrochemical behavior of Cd<sup>2+</sup> and Pb<sup>2+</sup> at the modified electrode

Figure 2 shows the cyclic voltammograms of HCl 0.1 mol·L<sup>-1</sup> solution in the absence of heavy metals ions (dash dot line) and in the presence of 20 µmol·L<sup>-1</sup> of both Cadmium (Cd<sup>2+</sup>) and Lead (Pb<sup>2+</sup>) at the Glassy carbon electrode modified with thin mercury film GCE/TMF (solid line). The obtained results showed no redox peaks in case of absence of heavy metals ions. However, in presence of 20 µmol·L<sup>-1</sup> of Cd<sup>2+</sup> and Pb<sup>2+</sup>, two oxidation peaks appeared at around -0.672 and -0.471 V respectively. A reduction peak corresponding to lead reduction was observed at around -0.510 V.

According to the voltammograms, the two elements to be quantified have well defined and well separated peaks. The widths of the peaks are 39 mV for Cd<sup>2+</sup> ions, which appears at -0.672V and 42 mV for the Pb<sup>2+</sup> ions, at -0.471 V. These values do not exceed 45 mV, which proves that the electrochemical kinetics of the investigated elements is fast.

It can be concluded from the above results that the use of thin mercury film onto the glassy carbon electrode enhances the electrocatalytic oxidation of both tested heavy metals. Therefore, this electrode was used for all experiments.

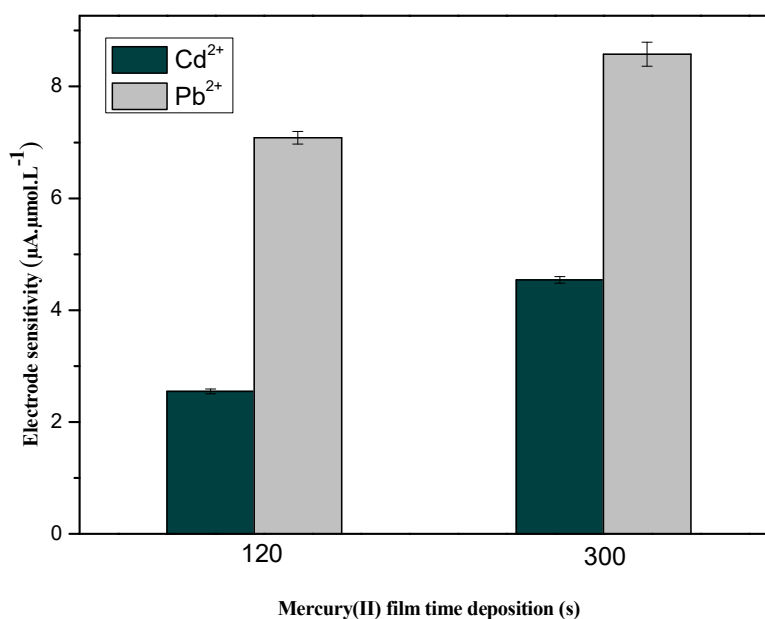


**Figure 2.** Cyclic voltammograms in a solution of  $\text{HCl } 0.1 \text{ mol}\cdot\text{L}^{-1}$  at GCE/TMF (---) and  $\text{HCl } 0.1 \text{ mol}\cdot\text{L}^{-1}$  at GCE/TMF containing  $20 \mu\text{mol}\cdot\text{L}^{-1}$  of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  (—)

### Analytical performance of the modified electrode

#### Effect of Hg film deposition time

The sensitivity of the electrodes prepared by electrodeposition of Hg film onto GCE in 120 s and 300 s was studied. The Figure 3 shows the effect of Hg deposition time onto GCE on the sensitivity of the electrode.

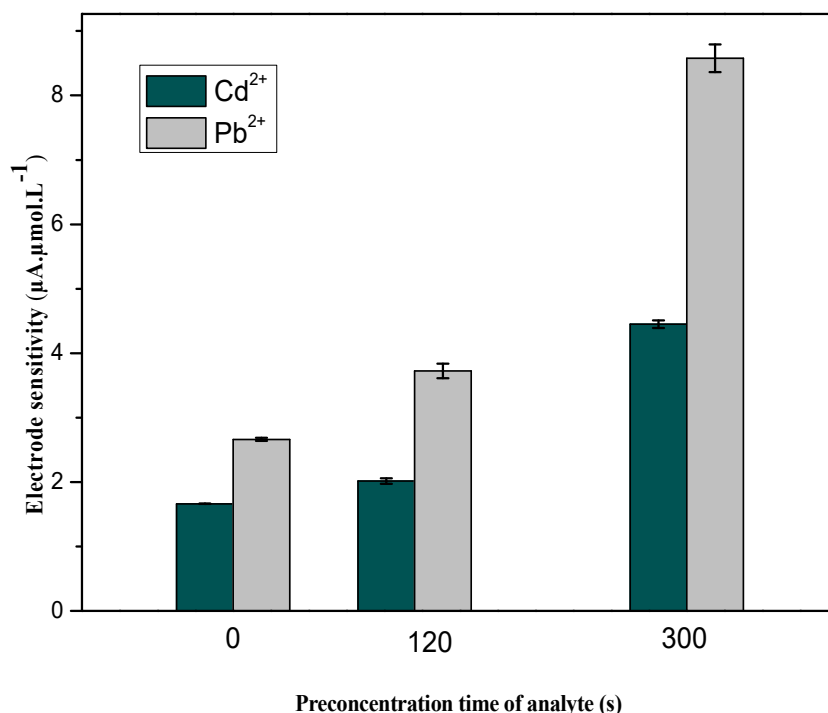


**Figure 3.** Effect of Hg film deposition time on the sensitivity of GCE/TMF towards  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  determination (analytes pre-concentration time: 300 s)

The obtained results showed that the optimum deposition time for the highest electrode performance (GCE/TMF) was 300 s. It can be concluded that the thickness of the Hg film has an effect on the electrocatalytic oxidation of the studied heavy metal ions. Hence, 300 s was selected as value of Hg deposition time for all measurements.

#### **Optimization of pre-concentration time of $\text{Cd}^{2+}$ and $\text{Pb}^{2+}$**

The Figure 4 indicates the pre-concentration time effect of the tested heavy metal ions ( $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ ) on the sensitivity of the GCE/TMF. The obtained results showed that the sensitivity increases with the increasing pre-concentration time and the best analytical performances were found when the samples were pre-concentrated for 300 s. Thus, this value was selected for the further experiments.

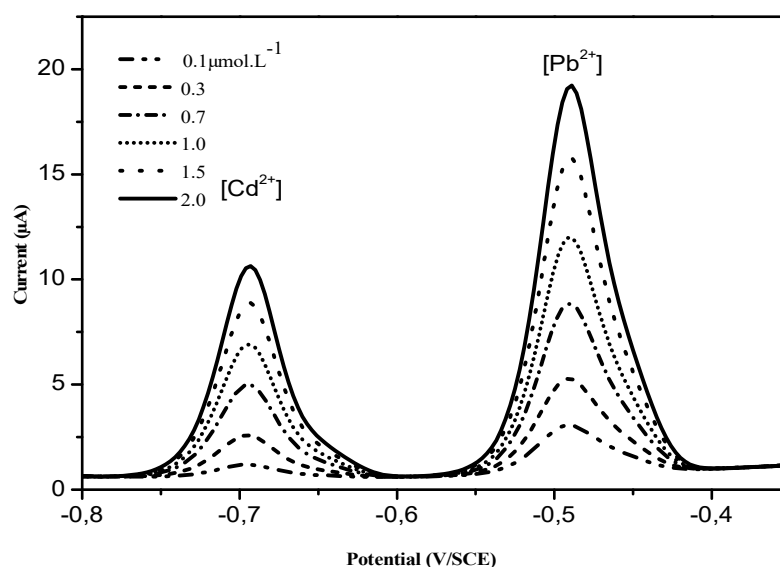


**Figure 4.** Effect of analytes pre-concentration time on the sensitivity of GCE/TMF towards  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  determination (Hg deposition time: 300 s)

#### **Sensitivity of GCE/TMF**

The metal ions of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  were deposited simultaneously at a negative potential of  $-1.1$  V for 300 s onto the GCE/TMF. Square-wave voltammetry (SWV) was applied in the stripping step. As shown in Figure 5, the potential peak ( $E_p$ ) values were  $-0.687$  and  $-0.489$  V versus  $\text{Hg}/\text{Hg}_2\text{Cl}_2$  electrode, for the oxidation of Cd and Pb respectively.





**Figure 5.** Square-wave anodic stripping voltammograms in HCl 0.1 mol·L<sup>-1</sup> at GCE/TMF for a range of concentrations of 0.1-2 µmol·L<sup>-1</sup> for Cd<sup>2+</sup> and Pb<sup>2+</sup>

Under the optimal experimental conditions, a calibration curve for a simultaneous detection of Cd<sup>2+</sup> and Pb<sup>2+</sup> was performed using square-wave anodic stripping voltammetry (SWASV). A linear relationship was obtained in the concentration range comprised between 0.1 and 2 µmol·L<sup>-1</sup> for both Cd<sup>2+</sup> and Pb<sup>2+</sup> in HCl 0.1 mol·L<sup>-1</sup>. The obtained equations of the calibration curves was  $y = 5.2x + 0.0294$  for Cd<sup>2+</sup> and  $y = 11.8x + 1.0405$  for Pb<sup>2+</sup>.

The mean sensitivities were found to be 5.2 and 11.8 µA·µmol<sup>-1</sup>·L for Cd<sup>2+</sup> and Pb<sup>2+</sup> respectively. The limit of detection (LOD) was calculated from the calibration curve according to the following equation:

$$LOD = 3 \cdot Sb/a \quad (1)$$

where  $Sb$  is the standard deviation of the blank [µA] and  $a$  is the slope of the calibration curve [µA·µmol<sup>-1</sup>·L].

The calculated limits of detection (LOD) were 0.012 µmol·L<sup>-1</sup> (3.70 µg·L<sup>-1</sup>) and 0.016 µmol·L<sup>-1</sup> (5.49 µg·L<sup>-1</sup>) for Cd<sup>2+</sup> and Pb<sup>2+</sup> respectively. The characteristics data of the calibration plot are summarized in Table 1.

**Table 1.** Characteristics of Cd<sup>2+</sup> and Pb<sup>2+</sup> calibration curves using square-wave anodic stripping voltammetry in HCl 0.1 mol·L<sup>-1</sup> at GCE/TMF

Analytical parameters Values*	Cd <sup>2+</sup>	Pb <sup>2+</sup>
Linear range [µmol·L <sup>-1</sup> ]	0.1-2.0	
Slope of the calibration plot [µA·µmol <sup>-1</sup> ·L]	5.2	11.8
Standard error of Slope [µA·µmol <sup>-1</sup> ·L]	0.160	0.150
Intercept [µA]	0.0294	1.0405
LOD [µmol·L <sup>-1</sup> ]	0.012	0.016
RSD [%]	3.0	1.3
Coefficient of correlation R <sup>2</sup>	0.995	0.999

\*Average of five determinations

While good peak shapes and linear relations were obtained for the two investigated metals, the sensitivity towards  $\text{Cd}^{2+}$  was lower than that for  $\text{Pb}^{2+}$  (Figure 5). The same results have been also reported in other works; this difference in the sensitivity between  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  may be due to different reasons such as the different diffusivity and the difference on the intermetallic compounds formed among others [52, 53].

In order to test the reproducibility of the used method, all experiments were repeated ( $n = 5$ ) and the current peak responses of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  at GCE/TMF were analyzed. The relative standard deviation (RSD) values were 3.0 % and 1.3 % for  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  respectively. Thus, the obtained results showed that the GCE/TMF displayed a good reproducibility of the measurements.

## Determination of heavy metals ions in real samples

### Application in rainwater samples

The metallic composition of four rainwater samples collected in Mohammedia city were studied in order to determine simultaneously the concentrations of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  eventually present in the samples. Rainwater was investigated during 4 months in the rainy season from November 2014 to February 2015 using the proposed method. All samples were analyzed using the standard addition method. The highest intensity of rain was registered in November 2014 (223 mm) and decreases as indicated in Table 2. The mean pH value of rainwater was slightly acid or neutral. Since the analysis condition requires an acidic pH the rainwater solutions were acidified in order to avoid any modification to the samples and to dissolve all trace metals [51].

**Table 2.** Summary of analytical data obtained for various collected rainwater samples

Samples	Rain volume collected [L]	pH	Flux TAF [ $\text{mg} \cdot \text{m}^{-2} \cdot \text{month}^{-1}$ ]	$\text{Cd}^{2+}$ [ $\mu\text{g} \cdot \text{L}^{-1}$ ]	$\text{Pb}^{2+}$ [ $\mu\text{g} \cdot \text{L}^{-1}$ ]	Flux $\text{Cd}^{2+}$ [ $\mu\text{g} \cdot \text{m}^{-2} \cdot \text{month}^{-1}$ ]	Flux $\text{Pb}^{2+}$ [ $\mu\text{g} \cdot \text{m}^{-2} \cdot \text{month}^{-1}$ ]
Nov 2014	5.00	6.07	910.00	0.90	22.50	3.94	98.68
Dec 2014	0.60	6.60	415.80	0.70	11.30	0.37	5.94
Jan 2015	2.00	6.83	529.00	0.80	7.20	1.40	12.63
Feb 2015	0.75	6.44	339.50	0.30	6.80	0.20	4.49

The monthly-determined fluxes of total atmospheric fallouts range between 339.5 and 910  $\text{mg} \cdot \text{m}^{-2}$ . The optimized described electrochemical technique applied to the analysis of the total dissolved trace metals studied in the rainy period showed an amount of  $\text{Pb}^{2+}$  higher than  $\text{Cd}^{2+}$ . The fluxes of these total dissolved trace metals were calculated using the following equation [26]:

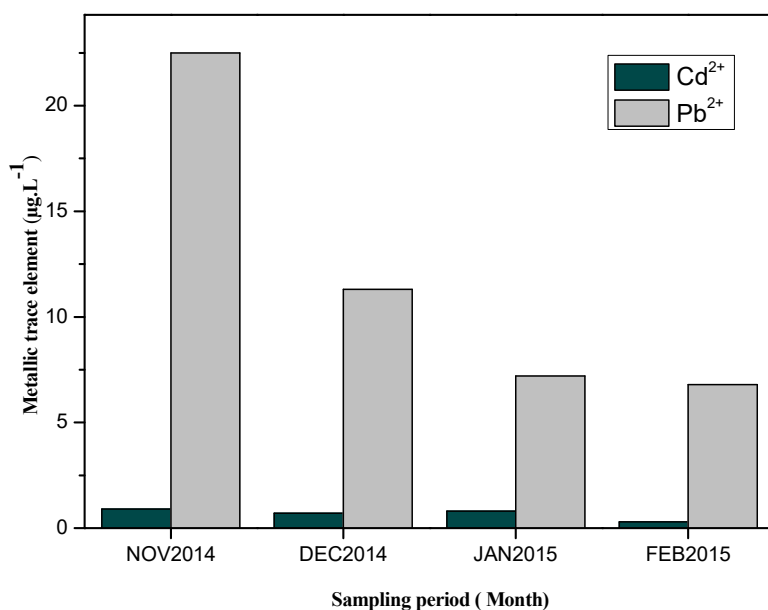
$$\text{Wet flux} = [C_{\text{rain}}] \cdot V/S \cdot t \quad (2)$$

where  $C_{\text{rain}}$  is the concentration of metal ion in rainwater sample [ $\mu\text{g} \cdot \text{L}^{-1}$ ],  $V$  is the collected volume of rainwater [L],  $S$  is the collection surface [ $\text{m}^2$ ] ( $0.038 \text{ m}^2$ ) and  $t$  is the collection time [d] ( $30 \pm 1 \text{ d}$ ).

It can be noticed that the maximum values of metallic fluxes were registered in the first month of sampling. This could be related to the high concentrations of heavy metals in the atmosphere.

The variation of concentration of these elements may be explained by the scavenging of pollutants [23, 54, 55].

This variation between months is probably due to the sources of pollutants emissions and meteorological condition such as wind direction amount of rainfall and evaporation. In comparison with the Moroccan normal value preconized for irrigation (Cd:  $0.01 \text{ mg} \cdot \text{L}^{-1}$  and Pb:  $5 \text{ mg} \cdot \text{L}^{-1}$ ), the obtained results of analytes in rainwater samples are in compliance.

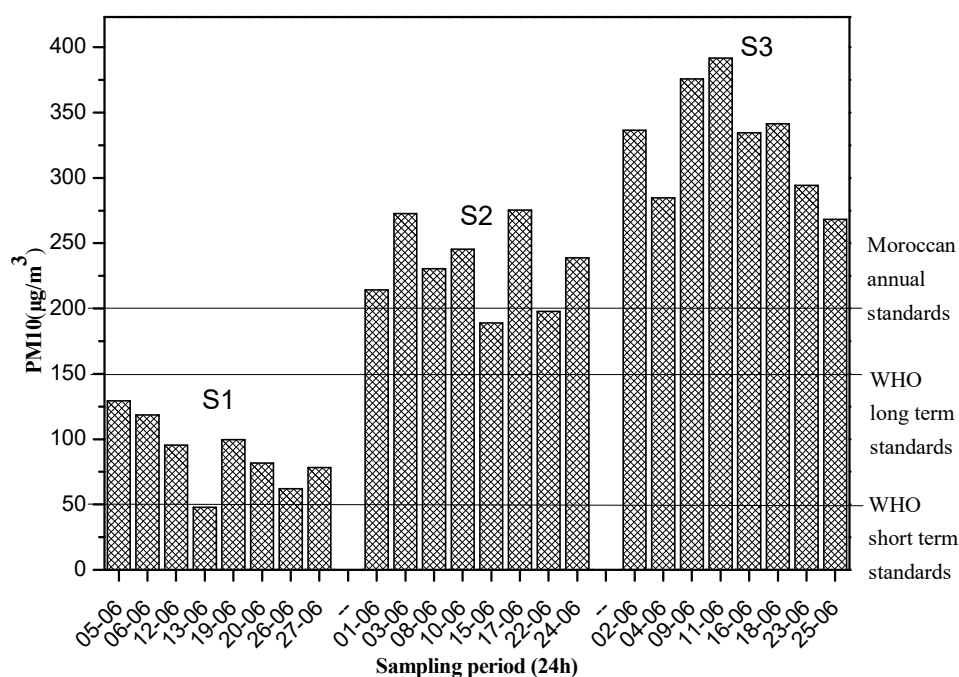


**Figure 6.** Temporal variation of the concentrations of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  during sampling period

It can be observed from the Figure 6 that the concentration of the tested heavy metals during the four months of sampling witnessed a fluctuation for  $\text{Pb}^{2+}$ , while the  $\text{Cd}^{2+}$  remains practically constant. The first sample presents a high amount of  $\text{Pb}^{2+}$  in comparison with  $\text{Cd}^{2+}$ . However, in the second month, the amount of  $\text{Pb}^{2+}$  decreased significantly (moiety). This might be due to the wash out phenomena. Starting from the third month, the amount of dissolved Pb decreased in comparison with the previous two months and remains practically constant, which can be explained by dynamic atmospheric and the cleaning of atmosphere. It can be concluded from the above results that the presented method can be very useful for total dissolved traces metallic elements detection present in the air.

#### ***Application in particulate matters samples***

Particulate matter PM10 was sampled daily in the three different locations named S1, S2 and S3 in Mohammedia city in the dry season (June 2015). Each site has the particularity to be influenced with a type of pollution.

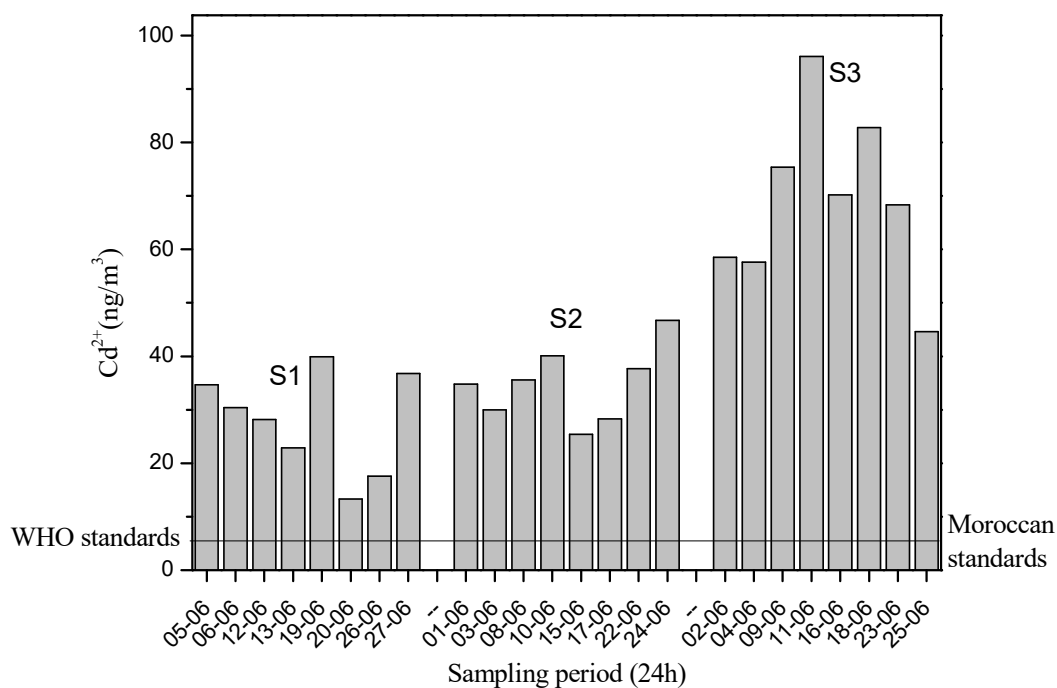


**Figure 7.** Amounts of PM10 samples in the study area

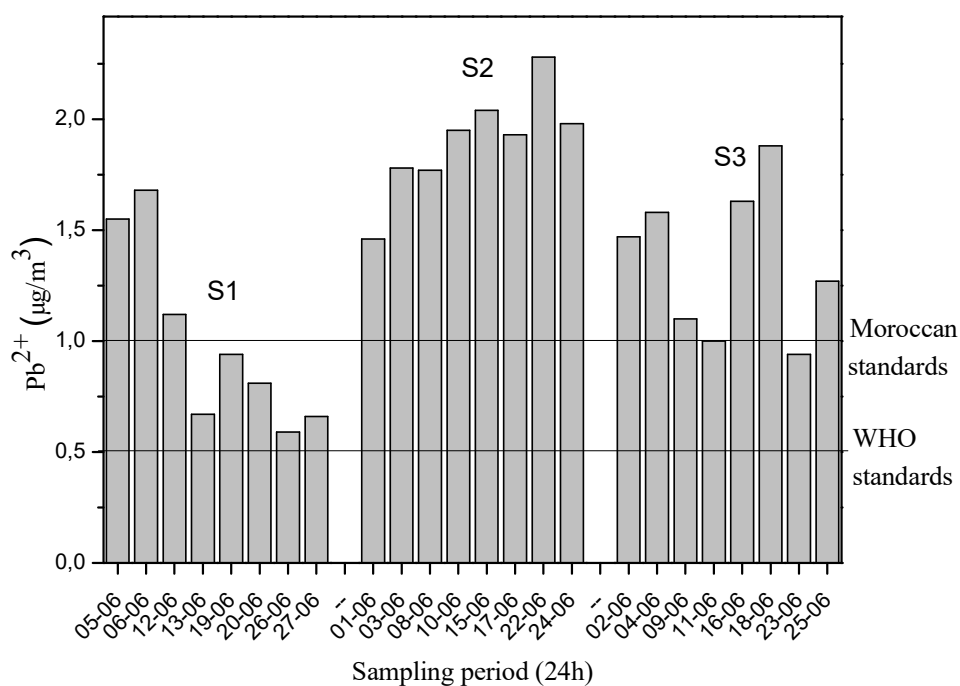
As indicated in Figure 7 the concentrations are variable from a site to another and in time. The obtained results showed a variation of PM10 in the different selected sites and the concentrations of PM10 in S3 were found to be higher than S2 and S1 respectively. The obtained amounts of PM10 registered in S1 are conform with World Health Organization (WHO) standard limits which preconize  $150 \mu\text{g}\cdot\text{m}^{-3}$  at a short time, but S2 and S3 are far out of this standards [56]. In term of particulate matters, the air quality at S2 and S3 of the study area are highly contaminated. The distribution of PM10 in spatial and temporal presents a fluctuation since S2 is characterized with a very Non-Fluid heavy traffic, which causes enormous emissions of diesel particulate, while S3 is influenced with industrial activities such as metallurgical factories.

In term of metallic trace elements as indicated in Figure 8 and Figure 9, all the collected samples exceed so far the WHO guide values for Cd and Pb in particulate matters PM10 ( $10$  to  $20 \text{ ng}\cdot\text{m}^{-3}$  for Cadmium and  $500 \text{ ng}\cdot\text{m}^{-3}$  for Lead).

The concentration levels of trace metals of Cd and Pb in PM10 samples from the three locations of Mohammedia city are presented in figures 8 and 9. The contents of PM10 are higher as followed  $\text{S3} > \text{S2} > \text{S1}$ . The metallic concentrations in S1 range between  $13.3$  and  $36.8 \text{ ng}\cdot\text{m}^{-3}$  for Cd and between  $0.59$  and  $1.68 \mu\text{g}\cdot\text{m}^{-3}$  for Pb. In S2, the concentrations appear more interesting, in comparison to S1 for both elements with a minimum of  $25.4$  and a maximum  $46.7 \text{ ng}\cdot\text{m}^{-3}$  for Cd and a minimum of  $1.46$  and a maximum of  $2.28 \mu\text{g}\cdot\text{m}^{-3}$  for Pb. The concentrations in S3 range between  $44.6$  and  $96.1 \text{ ng}\cdot\text{m}^{-3}$  for Cd and between  $0.94$  and  $1.88 \mu\text{g}\cdot\text{m}^{-3}$  for Pb.



**Figure 8.** Concentration of  $\text{Cd}^{2+}$  in  $\text{PM}_{10}$  samples in the study area



**Figure 9.** Concentration of  $\text{Pb}^{2+}$  in  $\text{PM}_{10}$  samples in the study area

Comparison of the amounts of particulate matters and their metallic component obtained with the developed method and others reported in the literature.

The Table 3 presents a summarize study of the general characteristics of various studies performed in Moroccan sites towards particulate matter monitoring.

**Table 3.** Overview on some reported studies related to the composition and amounts of heavy metals in particulate matter collected in some Moroccan cities

[Study reference]/ City/(Year)	[32] SALE (2003)	[33] MEKNES (2010)	[30] KENITRA (2009)	[14] KENITRA (2013)	[PRESENT WORK] MOHAMMEDIA (2018)
Vocation Site	2 sites • Oulja:pottery <sup>I</sup> • Liège: cork <sup>I</sup>	3 sites • FAR <sup>T</sup> • BAB MANSOUR 65RIAD <sup>R</sup>	4 sites • BAB FES • BUS STATION <sup>T</sup> • PORT <sup>T</sup> MELLAH <sup>R</sup>	BUS STATION <sup>T</sup>	3 sites • S1: FSTM <sup>f</sup> • S2: Traffic • S3: Industry
Aerosol [ $\mu\text{g}\cdot\text{m}^{-3}$ ] Range Or Mean $\pm$ Sd	PM10 50-95 • 99-135	PM10 275 $\pm$ 21.12 272 $\pm$ 57.06 237 $\pm$ 57.06	PM10 11.83-95.21 15.12-127.72 40.83-122.53 6.13-43.42	PM10 34-196	PM10 47.8-129.3 189.1-275.4 268.3-391.8
Cd <sup>2+</sup> Range [ $\mu\text{g}\cdot\text{m}^{-3}$ ]	0.03-0.035 • 0.05-0.085	0.002-0.038 0.003-0.025 0.002-0.019	0.03-0.08 0.00-2.22 0.01-0.06 0.02-0.06	0.002 $\pm$ 0.025	0.013-0.037 0.025-0.047 0.045-0.096
Pb <sup>2+</sup> Range [ $\mu\text{g}\cdot\text{m}^{-3}$ ]	0.85-1.25 • 1.1-1.4	0.133-0.302 0.020-0.301 0.008-0.101	1.09-1.65 0.84-2.82 0.6-2.06 0.27-1.05	0.196 $\pm$ 0.029	0.59-1.68 1.46-2.28 0.94-1.88
Number Of Sample	• 3 per site	6 per site	3 per site	1 a week for 1 year 63	8 per site
Analysis Technique/ Digestion Samples	XRf (Pb) AAS (Cd) Non destructive • nature	AAS Mixture HCL HNO <sub>3</sub> HF At $\mu$ wave 25min	AAS-GF HNO <sub>3</sub> 10ml at hot plat a 100°C 8cycle	TXRF 10mL HNO <sub>3</sub> $\mu$ wav e oven 30min	SWASV 10mL aqua regia 120min 120°C
Sampling Characteristics	<b>Sampler:</b> Dichotomous • <b>Filter</b> <b>substrate:</b> Cellulose acetate 47mm 0.45 $\mu$ m	<b>Sampler:</b> Gent sampler <b>Flow:</b> 17 L $\cdot$ min <sup>-1</sup> Polycarbonate 8 $\mu$ m	<b>Sampler:</b> Dichotomous <b>Flow:</b> 16.7 L $\cdot$ min <sup>-1</sup> <b>Filter</b> <b>substrate:</b> nitrocellulose 37 mm 0.45 $\mu$ m	<b>Sampler:</b> Gent sampler <b>Flow:</b> 16 L $\cdot$ min <sup>-1</sup> <b>Filter</b> <b>substrate:</b> Nuclepore filter 47mm 8 $\mu$ m	<b>Sampler:</b> Zambelli Easy plus <b>Flow:</b> 16.6 L $\cdot$ min <sup>-1</sup> <b>Filter substrate:</b> Quartz filter 47mm

T: Traffic, I: Industry, R: Residence and r: Remote

It can be concluded from the above results that the study area is in exceedance of the limit standards preconized for cadmium and lead elements. Also in comparison of the obtained data to others cited works, Mohammedia city presents higher values than the other Moroccan cities.

The peculiarity of the presented method is the low-cost, availability, simultaneity and suitability of heavy metals detection in the air.



## CONCLUSIONS

Atmospheric fallouts are very interesting to study in rainwater since they reflect the air quality and more convenient to take samples in liquid phase. In this work, we have reported the suitability of using SWASV technique for the detection of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  in both rainwater and particulate matters samples. To this effect, the reported results during the sampling period showed that there is a high contamination level in term of PM10 amounts and in term of the metallic composition (Cd and Pb) in the study area compared to the standards in force. The proposed method constitutes a powerful tool to overcome the information deficit concerning the metal composition of this particulate matter in Morocco especially in Mohammedia city. The presented method is a simple, sensitive and low-cost for trace dissolved toxic heavy metals cadmium and lead and can be used as an alternative analytical technique in air quality monitoring.

## REFERENCES

1. Nejari, C., Filleul, L., Zidouni, N., Laid, Y., Atek, M., El Meziane, A., Tessier, J.F.: La pollution atmosphérique un nouveau risque respiratoire pour les villes du sud, *The International Journal of Tuberculosis and Lung Disease*, **2003**, 7 (3), 223-231;
2. Birmili, W., Allen, A.G., Bary, F., Harrison, R.M.: Trace Metal Concentrations and Water Solubility in Size-Fractionated Atmospheric Particles and Influence of Road Traffic, *Environmental Science & Technology*, **2006**, 40 (4), 1144-1153;
3. Farghaly, O.A., Ghandour, M.A.: Square-wave stripping voltammetry for direct determination of eight heavy metals in soil and indoor-airborne particulate matter, *Environmental Research*, **2005**, 97 (3), 229-235;
4. Hieu, N.T., Lee, B.-K.: Characteristics of particulate matter and metals in the ambient air from a residential area in the largest industrial city in Korea, *Atmospheric Research*, **2010**, 98 (2-4), 526-537;
5. Morselli, L., Olivieri, P., Brusori, B., Passarini, F.: Soluble and insoluble fractions of heavy metals in wet and dry atmospheric depositions in Bologna, Italy, *Environmental Pollution*, **2003**, 124 (3), 457-469;
6. Zereini, F., Alt, F., Messerschmidt, J., Wiseman, C., Feldmann, I., von Bohlen, A., Müller, J., Liebl, K., Püttmann, W.: Concentration and Distribution of Heavy Metals in Urban Airborne Particulate Matter in Frankfurt am Main, Germany, *Environmental Science & Technology*, **2005**, 39 (9), 2983-2989;
7. Farahmandkia, Z., Mehrasbi, M.R., Sekhavatjou, M.S.: Relationship Between Concentrations of Heavy Metals in Wet Precipitation and Atmospheric Pm 10 Particles in Zanjan, Iran, *Iranian Journal of Environmental Health, Science and Engineering*, **2011**, 8 (1), 49-56;
8. Montoya-Mayor, R., Fernández-Espinosa, A.J., Seijo-Delgado, I., Ternero-Rodríguez, M.: Determination of soluble ultra-trace metals and metalloids in rainwater and atmospheric deposition fluxes: A 2-year survey and assessment, *Chemosphere*, **2013**, 92 (8), 882-891;
9. Cerqueira, M.R.F., Matos, M.A.C.: Optimization and determination of dissolved trace metals (Cu, Cd, Zn and Pb) in rainwater by potentiometric stripping at a southeaster site of Brazil, *Sustainable Environment Research*, **2014**, 24 (1), 13-21;
10. Taffere, G.R., Beyene, A., Vuai, S.A.H., Gasana, J., Seleshi, Y.: Characterization of Atmospheric Bulk Deposition: Implications on the Quality of Rainwater Harvesting Systems in the Semi-Arid City of Mekelle, Northern Ethiopia, *Environmental Processes*, **2016**, 3 (1), 247-261;
11. Croitoru, L., Sarraf, M.: Estimating the Health Cost of Air Pollution: The Case of Morocco, *Journal of Environmental Protection*, **2017**, 8 (10), 1087-1099;
12. Benzha, F., Tahiri, M., Souabi, S., Darif, A., Khatami, A.: [Application de la méthode 'CORINAIR' pour l'évaluation de la pollution atmosphérique due au centrales thermiques du parc ONE du Maroc] / Application of the 'CORINAIR' method for the estimation of atmospheric pollution due to the Park ONE thermal power plants in Morocco, *Environmental Technology*, **2009**, 30 (11), 1195-1203;

13. Talbi, A., Kerchich, Y., Kerbach, R., Boughedaoui, M.: Assessment of annual air pollution levels with PM<sub>1</sub>, PM<sub>2.5</sub>, PM<sub>10</sub> and associated heavy metals in Algiers, Algeria, *Environmental Pollution*, **2018**, 232, 252-263;
14. Tahri, M., Bounakhla, M., Zghaid, M., Benchrif, A., Zahry, F., Noack, Y., Benyaich, F.: TXRF characterization and source identification by positive matrix factorization of airborne particulate matter sampled in Kenitra City (Morocco), *X-Ray Spectrometry*, **2013**, 42 (4), 284-289;
15. Tan, J.-H., Duan, J.-C., Ma, Y.-L., Yang, F.-M., Cheng, Y., He, K.-B., Yu, Y.-C., Wang, J.-W.: Source of atmospheric heavy metals in winter in Foshan, China, *Science of The Total Environment*, **2014**, 493, 262-270;
16. Ichikawa, Y., Sada, K.: An atmospheric dispersion model for the environmental impact assessment of thermal power plants in Japan - a method for evaluating topographical effects, *Journal of the Air & Waste Management Association*, **2002**, 52 (3), 313-323;
17. Azimi, S., Rocher, V., Muller, M., Moilleron, R., Thevenot, D.R.: Sources, distribution and variability of hydrocarbons and metals in atmospheric deposition in an urban area (Paris, France), *Science of The Total Environment*, **2005**, 337 (1-3), 223-239;
18. Abdeldjoud, M.: Impact de la morphologie du bâtiment sur la dispersion des polluants atmosphériques Cas d'étude : ville d'Annaba, thèse, Université Mohamed Khider Biskra, **2014**;
19. Sasco, A.J., Merrill, R.M., Dari, I., Benhaïm-Luzon, V., Carriot, F., Cann, C.I., Bartal, M.: A case-control study of lung cancer in Casablanca, Morocco, *Cancer Causes & Control*, **2002**, 13 (7), 609-616;
20. Squalli Houssaini, A.S., Messaouri, H., Nasri, I., Roth, M.P., Nejari, C., Bencheikroun, M.N.: Air pollution as a determinant of asthma among schoolchildren in Mohammedia, Morocco, *International Journal of Environmental Health Research*, **2007**, 17 (4), 243-257;
21. Boularab, I., Elghazi, I., Mouhaddach, O., Kestemont, M.-P., El Jaafari, S.: [Analyse Spatiale de la Pollution Particulaire au niveau de la Ville de Meknès (Maroc)] / Spatial Analysis of Particulate Air Pollution in Meknes City (Morocco), *International Journal of Innovation and Applied Studies*, **2015**, 13 (4), 781-788;
22. Rahali, M.: [Cartographie de la pollution plombique dans la région d'Alger en utilisant un lichen (*Xanthoria parietina*) comme bioaccumulateur] / Mapping of lead pollution in Algiers area with a lichen (*Xanthoria parietina*) as indicator, *Pollution Atmosphérique*, **2002**, 175, 421-432;
23. Türküm, A., Pekey, H., Pekey, B., Tuncel, G.: Investigating relationships between aerosol and rainwater compositions at different locations in Turkey, *Atmospheric Research*, **2008**, 89 (4), 315-323;
24. Grömping, A.H.J., Ostapczuk, P., Emons, H.: Wet deposition in Germany: long-term trends and the contribution of heavy metals, *Chemosphere*, **1997**, 34 (9-10), 2227-2236;
25. Schroeder, W.H., Dobson, M., Kane, D.M., Johnson, N.D.: Toxic trace elements associated with airborne particulate matter: a review, *Journal of Air Pollution Control Association*, **1987**, 37 (11), 1267-1285;
26. Garnaud S.: Transfert et évolution géochimique de la pollution métallique en bassin versant urbain, *Thèse de doctorat*, ENPC, **1999**;
27. Bouh, H.A., Benyaich, F., Bounakhla, M., Noack, Y., Tahri, M., Zahry, F.: [Variations Saisonnières des particules atmosphériques et ses composants chimiques dans la Ville de Meknès-Maroc] / Seasonal variations of the atmospheric particles and its chemical components in Meknes city-Morocco, *Journal of Materials and Environmental Sciences*, **2013**, 4 (1), 49-62;
28. Bounakhla, M., Zghaid, M., Zahry, F., Tahri, M., Benyaich, F., Noack, Y., Benkirane, O., Saidi, N.: [Evaluation de la pollution atmosphérique de la ville de Kénitra] / Assessment of air pollution in the city of Kenitra, *Physical and Chemical News*, **2009**, 45, 22-29;
29. Bounakhla, M., Azami, R.: Heavy Metals And Gas Emissions Assessment In Safi's City (Morocco) in : *la 2<sup>ème</sup> Conférence internationale : La valorisation des phosphates et dérivés COVAPHOS II-2006 RECHERPHOS*, **2006**, 4, 252-261;
30. Zghaid, M., Noack, Y., Bounakhla, M., Benyaich, F.: Pollution atmosphérique particulaire dans la ville de Kenitra (Maroc), *Pollution Atmosphérique*, **2009**, 203, 313-324;
31. Bouh, H., Bounakhla, M., Noack, Y., Benyaich, F.: [Caractérisation des particules en suspension totale (PST) dans la ville de Meknès au Maroc], cas des anions et des alcalins, *Les Technologies de Laboratoire*, **2015**, 2 (38), 34-44;

32. Bounakhla, M., Fatah, A., Embarch, K., Majah, M. I., Azami, R., Sabir, A. & Gaudry, A.: Air pollution assessment of Salé's city (Morocco), *Journal de Physique IV* (Proceedings May, **2003**), EDP sciences, **107**, 211-213;
33. Bouh, H.A., Benyaich, F., Bounakhla, M., Noack, Y., Zahry, F., Tahri, M.: [Caractérisations de la matière particulaire atmosphérique dans la ville de meknès] / Atmospheric particulate matter characterisation in meknès city, *Physical and Chemical News*, **2010**, **54**, 47-54;
34. El Abidi, A., Barcha, S.E., Fekhaoui, M., El alaoui-Faris, F.Z., Yahyaoui, A., Ayrault, S.: Biomonitoring of atmospheric lead, cadmium and zinc using Eucalyptus leaves in Rabat Salé City, Morocco, *Arabian Journal of Chemistry and Environmental Research*, **2015**, **2** (2), 72-83;
35. Bounaga, M., Bellaouchou, A., Benabbou, A., El abidi, A., Ben-aakam, R., Fekhaoui, M.: Using blood's Passer domesticus as a possible bio-indicator of urban heavy metals pollution in Rabat- Salé (Morocco), *Journal of Materials and Environmental Science*, **2014**, **5** (3), 937-944.
36. Garnaud, S., Mouchel, J.-M., Chebbo, G., Thévenot, D.R.: Heavy metal concentrations in dry and wet atmospheric deposits in Paris district: comparison with urban runoff, *Science of The Total Environment*, **1999**, **235** (1-3), 235-245;
37. Dean, J.R.: Instrumental Techniques for Trace Analysis, in: *Analytical Techniques in the Sciences*, (Editors: John Wiley & Sons, Ltd), Chichester, UK, **2003**, 183-205;
38. Azimi, S., Ludwig, A., Thévenot, D.R., Colin, J.-L.: Trace metal determination in total atmospheric deposition in rural and urban areas, *Science of The Total Environment*, **2003**, **308** (1-3), 247-256;
39. Buzica, D., Gerboles, M., Borowiak, A., Trincherini, P., Passarella, R., Pedroni, V.: Comparison of voltammetry and inductively coupled plasma-mass spectrometry for the determination of heavy metals in PM10 airborne particulate matter, *Atmospheric Environment*, **2006**, **40** (25), 4703-4710;
40. Barón-Jaimez, J., Joya, M.R., Barba-Ortega, J.: Anodic stripping voltammetry – ASV for determination of heavy metals in: *Journal of Physics: Conference Series*, 2013, 2<sup>nd</sup> International Meeting for Researchers in Materials and Plasma Technology, **2013**, **466** (1), 12-23;
41. Kefala, G.: A study of bismuth-film electrodes for the detection of trace metals by anodic stripping voltammetry and their application to the determination of Pb and Zn in tap water and human hair, *Talanta*, **2003**, **61** (5), 603-610;
42. Wang, S.-J., Zheng, H., Ye, B.-X.: Simultaneous Determination of Cd (II), Cu (II), Pb (II) and Zn (II) in Human Plasma by Potentiometric Stripping Analysis, *Journal of the Chinese Chemical Society*, **2008**, **55** (5), 1080-1085;
43. Abdelsalam, M.E., Denuault, G., Daniele, S.: Calibrationless determination of cadmium, lead and copper in rain samples by stripping voltammetry at mercury microelectrodes: Effect of natural convection on the deposition step, *Analytica Chimica Acta*, **2002**, **452** (1), 65-75;
44. Colovos, G., Wilson, G.S., Moyers, J.: The determination of trace amounts of zinc, cadmium, lead and copper in airborne particulate matter by anodic stripping voltammetry, *Analytica Chimica Acta*, **1973**, **64** (3), 457-464;
45. Cooper, J., Bolbot, J.A., Saini, S., Setford, S.J.: Electrochemical Method for the Rapid on Site Screening of Cadmium and Lead in Soil and Water Samples, *Water Air Soil Pollution*, **2007**, **179** (1-4), 183-195;
46. Green, D.G., Green, L.W., Page, J.A., Poland, J.S., Loon, G. van.: The determination of copper, cadmium, and lead in sea water by anodic stripping voltammetry with a thin film mercury electrode, *Canadian Journal of Chemistry*, **1981**, **59** (10), 1476-1486;
47. Kroukamp, E.M., Wondimu, T., Forbes, P.B.C.: Metal and metalloid speciation in plants: Overview, instrumentation, approaches and commonly assessed elements, *Trends in Analytical Chemistry*, **2016**, **77**, 87-99;
48. Brett, C.M., Alves, V.A., Fungaro, D.A.: Nafion-coated mercury thin film and glassy carbon electrodes for electroanalysis: Characterization by electrochemical impedance, *Electroanalysis*, **2001**, **13** (3), 212-218;
49. de Oliveira, M.F., Saczk, A.A., Okumura, L.L., Fernandes, A.P., de Moraes, M., Stradiotto, N.R.: Simultaneous determination of zinc, copper, lead, and cadmium in fuel ethanol by anodic stripping voltammetry using a glassy carbon-mercury-film electrode, *Analytical and bioanalytical chemistry*, **2004**, **380** (1), 135-140;
50. Serafim, D.M., Stradiotto, N.R.: Determination of sulfur compounds in gasoline using mercury film electrode by square wave voltammetry, *Fuel*, **2008**, **87** (7), 1007-1013;

51. Garnaud, S., Mouchel, J.M., Chebbo, G., Thévenot, D. R.: Heavy metal concentrations in dry and wet atmospheric deposits in Paris district: Comparison with urban runoff, *Science of The Total Environment*, **1999**, **235** (1-3), 235-245;
52. Palchetti, I., Mascini, M., Minunni, M., Bilia, A.R., Vincieri, F.F.: Disposable electrochemical sensor for rapid determination of heavy metals in herbal drugs, *Journal of pharmaceutical and biomedical analysis*, **2003**, **32** (2), 251-256;
53. Aragay, G., Puig-Font, A., Cadevall, M., Merkoçi, A.: Surface Characterizations of Mercury-Based Electrodes with the Resulting Micro and Nano Amalgam Wires and Spheres Formations May Reveal Both Gained Sensitivity and Faced Nonstability in Heavy Metal Detection, *The Journal of Physical Chemistry C*, **2010**, **114** (19), 9049-9055;
54. Al-Khashman, O.A.: Heavy metal distribution in dust, street dust and soils from the work place in Karak Industrial Estate, Jordan, *Atmospheric environment*, **2004**, **38** (39), 6803-6812;
55. Al-Khashman, O.A.: Chemical characteristics of rainwater collected at a western site of Jordan, *Atmospheric Research*, **2009**, **91** (1), 53-61;
56. \*\*\* Lignes directrices OMS relatives à la qualité de l'air : particules, ozone, dioxyde d'azote et dioxyde de soufre. Mise à jour mondiale 2005. Synthèse de l'évaluation des risques. Organisation Mondiale de la Santé (OMS), **2005**.