Use of STAT-Flame AAS for the Determination of Lead and Cadmium Pollution in Urban Center

Nagihan M. Karaaslan and Mehmet Yaman*
Firat University, Sciences Faculty, Department of Chemistry,
Elazig, Turkey

INTRODUCTION

It has been reported that lead (Pb) and cadmium (Cd) accumulation in the human body can cause health risks and adversely affect physiological functions such as the brain, kidneys, the reproductive system, and intellectual functions (1-3). The World Health Organization (WHO) (4) provides guidelines with regard to tolerable amounts of these elements and established provisional tolerable weekly intake (PTWIs) of Pb and Cd at 0.025 and 0.007 mg kg⁻¹ body weight, respectively. It has been reported that the absorption rates of Pb and Cd by inhalation are significantly higher (50-60%) than by ingestion (3-10%) (5). Thus, the determination of these elements in the air is more important than in other environmental matrices. However, few of these studies are available because it is difficult to obtain air samples, and the concentration of these metals in an aerial matrix is very low. As a result, plant parts such as leaves, shoots, and bark have been used for biomonitoring purposes (6-15) and, therefore, proper selection of plant species plays an important role. These types of samples can establish the source of metal emissions and verify overland transportation of the individual elements (7-10). Kaya et al. (16) reported that the leaves from *Pinus Nigra L.*, growing near a lead battery factory, contained Pb concentrations above 3.000 mg kg⁻¹.

ABSTRACT

Lead (Pb) and cadmium (Cd) concentrations in *Pinus Nigra L.*, *Cedrus Libani*, and *Cupressus Arizonica* plants were determined for biomonitoring of environmental pollution in Elazig, Turkey. For this purpose, leaves from these plant species together with soil samples were collected from various locations during different months of the year.

The samples were digested using the dry ashing method. For the determinations, an on-line method was applied using slotted tube atom trap-flame atomic absorption spectrometry (STAT-FAAS) which is fast, involves low risk of contamination, and low cost. The results obtained were evaluated based on traffic density, industrial factories, population, and seasonal variation.

Lead and Cd concentrations were found to range from 139 to 768 µg kg⁻¹ and <LOD-57 µg kg⁻¹ for *Pinus Nigra L.*, 113 to 908 µg kg⁻¹ and 9 to 55 µg kg⁻¹ for *Cedrus Libani*, and 88 to 813 µg kg⁻¹ and <LOD-50 µg kg⁻¹ for *Cupressus Arizonica*, respectively. The levels observed for Pb and Cd in the soils ranged from 3100-10112 µg kg⁻¹ and 106-505 µg kg⁻¹, respectively.

Kaya and Yaman (9) found Pb concentrations higher than 5.000 mg kg⁻¹ in leaves from *Cupressus Arizonica* also growing near a lead battery plant.

In addition to occupational exposure, humans are exposed to Pb and Cd through food and air. It has been reported that Pb exposure of school-aged children can significantly reduce their IQ and has also

been associated with aggressive behavior, delinquency, and attention disorders (1). Cadmium competes with zinc (Zn) for binding sites and can therefore interfere with some of zinc's essential functions. Thus, it may inhibit enzyme reactions and utilization of nutrients. Cadmium can generate free radical tissue damage because it may be a catalyst to oxidation reactions. Furthermore, excessive Cd exposure can cause renal damage, reproduction problems, cardiovascular diseases, and hypertension. The frequently observed toxic effect of Cd in humans is chronic nephropathy characterized by proximal tubular necrosis and proteinuria (2). The International Agency Research on Cancer (IARC) reported that inhalation of Cd can cause lung cancer in humans and animals (17). Other sources of Cd exposure include employment in primary metal industries, production of certain batteries, electroplating processes, and use of tobacco products. Lead is also used in hundreds of products such as pipes, solder, brass fixtures, crystal, paint, cable, ceramics, and batteries due to its malleability, low melting point, and the ability to form compounds. The population of at least 100 countries is still exposed to considerable Pb levels owing to air pollution caused by leaded gasoline despite its ban.

Due to low concentrations of toxic trace metals such as Pb and Cd, analytical techniques with high sensitivity are required for detection of these metals. These techniques include electrothermal atomic absorption spectrometry (ETAAS), inductively coupled

*Corresponding author:
E-mail: myaman@firat.edu.tr
Tel: 904242370000
Fax: 904242330062

plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS).

It is well known that flameless atomic absorption spectrometry is a more sensitive technique than flame atomic absorption spectrometry (FAAS). However, relative to the latter technique, some of the disadvantages associated with flameless AAS are high cost, slow speed, and being prone to interferences (10). Effective chemical modifiers, background correction systems, improved furnace and platform designs, and careful optimization of temperature programs are used to remove the interferences in flameless AAS analysis. However, FAAS is still considered the preferred method because FAAS is faster, less expensive, and does not require expert operators.

In recent times, Cd, Pb, and Cu concentrations in biological and environmental sample, have been determined by slotted tube atom trap-flame atomic absorption spectrometry (STAT-FAAS) with or without preconcentration methods. In those studies, 7- and 13-fold improvements in the sensitivity of FAAS in conjunction with the appli-

cation of STAT were achieved for Pb and Cd determination.

In this study, we propose the use of STAT-FAAS to determine Cd and Pb in leaf and soil samples from urban areas in Elazig, Turkey. In one of the studied areas, there is a cement factory which has been operating for 50 years. Consideration was also given to regions with heavy traffic and population density. In addition to collecting plant and soil samples from different sites, we also established a control location away from the city center. Three plant species (*Pinus Nigra L.*, *Cedrus Libani*, and *Cupressus Arizonica*), which are evergreen needle conifer trees, were selected to determine the atmospheric pollution of the areas.

EXPERIMENTAL

Sampling

The six sampling sites in the center of Elazig city (population of 322,000), including an urban control area selected for this study, are shown in Figure 1. The results obtained were evaluated based on heavy traffic, type of factory, population density, and seasonal variation. Sampling was conducted during the months of July, November, and December 2008 and

March 2009. The plant species (angiosperm), *Pinus Nigra L.*, *Cedrus Libani*, and *Cupressus Arizonica*, were planted many years ago and are of about the same age. Healthy looking leaves (about 100 g of fresh and new leaves) were taken from the top points (about 2–3 m above the ground) of the three types of trees at each location. The samples were homogenously mixed, put into dry plastic containers, and covered. Azcue and Mudroch (18) suggest that the best cleaning method for studies of multi-element concentrations in vegetation is washing thoroughly with distilled water. In our laboratory, the samples were rinsed with tap water, scrubbed by hand to completely remove the dust, and then rinsed with distilled water. The soil samples were taken from around the sample trees at a depth of 10.0 cm and at a distance of 2.0 m.

INSTRUMENTATION

The Cd and Pb concentrations were determined using a Model ATI UNICAM 929 flame atomic absorption spectrometer (Unicam Ltd., Cambridge, England). The optimum instrumental conditions for Pb and Cd were applied as described in the FAAS handbook and are listed in Table I.

Fig. 1. Map of sampling locations: 1 = Cayda Cira (traffic intersection), 2 = University, 3 = Province (city center), 4 = Ordu Evi (city center), 5 = Cement factory location, 6 = Control area (away from residential areas and factories).

TABLE I
Instrumental Operating Conditions of
ATI UNICAM 929 FAAS

Parameter	Pb	Cd
Wavelength (nm)	217.0	228.8
HCL current (mA)	9.5	4.0
Acetylene flow rate (L/min)	0.6	0.6
Air flow rate (L/min)	4.0	4.0
Slit (nm)	0.5	0.5

A quartz slotted tube atom trap (STAT) (Quarzschnelze Ilmenau GmbH, Ilmenau, Germany) was used to enhance the sensitivity of FAAS analysis. The tube was slightly modified in a local glass workshop (10,19) to the measurements as listed in Table II.

Standard Solutions and Reagents

The standard solutions (1000 mg L⁻¹) of Pb and Cd were prepared from their nitrate salts (Merck, Darmstadt, Germany). Nitric acid (65%, Merck) and hydrogen peroxide (35%, Merck) were used for digestion of the samples. All chemicals used were of analytical reagent grade. Double distilled water obtained with a water purification system (Millipore® Direct-Q, Millipore Corporation, Bedford, MA, USA) was used for all preparations. When not in use, all Pyrex® glassware was kept permanently full of 1 mol/L nitric acid.

Sample Preparation and Pb and Cd Determination in Leaves and Soils

The leave samples (about 100 g of fresh and new leaves) were homogeneously mixed. After drying to constant weight at 70 °C, three separate portions of the sub-sample from the mixed samples described above from each of the plants *Pinus Nigra L.*, *Cedrus Libani*, and *Cupressus Arizonica* were prepared for the ashing procedure. Sample amounts of 0.2–2.0 g (depending on the metal concentrations in the matrix) were transferred into Pyrex® flasks and digested using the dry ashing procedure. As a result, each of the samples was analyzed in triplicate and the average of three values was used as the mean value on a dry-weight basis.

Sample digestion procedures should be safe and simple, use a short digestion time, have minimal risk for contamination during sam-

Table II
Conditions for the Quartz Tube in the Slotted Tube Atom Trap (10,19)

Parameters	Pb	Cd
Diameter of tube	6 mm	6 mm
Length of upper slot	1 cm	1 cm
Length of tube	12 cm	12 cm
Improvement in the sensitivity	7-fold	13-fold
Length of the lower slot	5 cm	5 cm
Tube thickness	1.5 mm	1.5 mm

ple handling, and recover the total amount of the trace elements in plant tissue (16,20,21). Although wet and dry ashing procedures have been used by a number of researchers, each procedure has its shortcomings. For example, some elements such as As, Cr, and Pb may be lost at ashing temperatures of 500–550 °C (20). Thus, lower ashing temperatures of 400–450 °C are advisable, but these often are not sufficient for ashing of some plant tissues and require repetitive sample heating and acid treatment. This in turn increases the risk of sample contamination.

Taking these points into consideration for dry ashing of the leaves, the dried samples were heated gradually in a furnace using the following sequence: at 250 °C for 30 minutes, at 300 °C for 5 minutes, at 350 °C for 5 minutes, at 400 °C for 5 minutes, at 450 °C for about 20 minutes to finish gas formation, and ashed at 480 °C for 4 hours. The mixture (1/1) of concentrated HNO₃/H₂O₂ (3 mL for 1 g of dried sample) was added to the ashed sample and then evaporated to near dryness with occasional stirring. This procedure was repeated once again. After cooling, 3.0 mL of 1.0 M nitric acid was added, and the samples were centrifuged, if necessary. The clear solutions were analyzed by STAT-FAAS for Pb and Cd. In addition, blank samples were prepared and analyzed using the same procedure. The limits of detection (LODs) for the plants were found to

be 0.050 mg kg⁻¹ for Pb and 0.005 mg kg⁻¹ for Cd using 2 g of dried sample and 3 mL of final solution.

The soil samples were dried at 100 °C, then 0.2-g portions were transferred into the flasks, and 2.0 mL of the concentrated (1/1) HNO₃/H₂O₂ mixture was added. This solution was evaporated to near dryness using occasional stirring. This procedure was repeated once again. After cooling, 3.0 mL of 1.0 M HNO₃ was added, mixed and centrifuged to bring the released metals into solution. The clear solution was analyzed using STAT-FAAS for Pb and Cd determination. Blank samples were also prepared and analyzed using the same procedure. The results are given on a dry-weight basis. The LODs for the soils were found to be 0.50 mg kg⁻¹ for Pb and 0.05 mg kg⁻¹ for Cd using 0.2 g of dried sample and 3 mL of final solution. As a result, each of the samples was analyzed in triplicate, and the average of three values of the same sample was used as the mean value.

Calibration Curves

Calibration curves were obtained by using the solutions of the studied elements at different concentrations. The obtained curves (Figures 2-3) were linear in the concentration ranges described below; the equations of the curves were as follows:

$$y = 0.306x - 0.0734 \quad R^2 = 0.9998$$

for Pb by STAT (30–400 ng mL⁻¹)

$$y = 3.1284x + 0.3547 \quad R^2 = 0.9999$$

for Cd by STAT (3.0–40.0 ng mL⁻¹)

One-way Analysis of Variance (ANOVA) was used for the statistical evaluation of the results.

RESULTS

Analytical Performance

It is known that there are three methods to check the reliability of the analytical results obtained: (a) Use of a Standard Reference Material (SRM), (b) comparison of the results with the results obtained by the independent method for the same samples, and (c) the recovery test (16).

In this study, two methods were applied to check the accuracy of the results. Firstly, the accuracy of the method was checked by using Standard Reference Material NCSDC73348 Bush Branches and Leaves (obtained from China National Analysis Center). The recoveries were found to be 96% for Pb and 93% for Cd (see Table III). Secondly, the recoveries of Pb and Cd from the soil and leaves fortified with these metals were also used to test the accuracy. It was found that at least 91% of Pb and Cd added to the leaves was recovered, while recoveries up to 95% and 92% were obtained for the soil samples, respectively. The levels of Pb and Cd in the reagent blanks in the total analytical steps were, respectively, found to be 8.0 and 0.6 ng mL⁻¹ with standard deviations (s) of 2.1 and 0.2 ng mL⁻¹.

Fig. 2. Calibration curve obtained using STAT-FAAS for Pb determination.

Fig. 3. Calibration curve obtained using STAT-FAAS for Cd determination.

TABLE III
Pb and Cd Concentrations in
SRM NCSDC73348 Bush Branches and Leaves,
and Soil and Leaves
(on dry-weight basis) (mg kg⁻¹)

		Pb	Cd
SRM NCSDC73348	Certified Value	7.1 ± 1.1	0.14 ± 0.06
	Found	6.8 ± 0.9	0.13 ± 0.03
	Recovery	96%	93%
Soil 1 (July)	Added Metal	5.0	0.20
	Found	14.38 ± 1.5	0.428 ± 0.05
	Recovery	95%	92%
<i>Pinus Nigra</i> L. 1 (July)	Added Metal	0.2	0.020
	Found	0.518 ± 0.05	0.0418 ± 0.006
	Recovery	91%	91%

Therefore, the limits of detection (LOD), defined as three times of the s values of the blanks, were calculated as 6.3 and 0.6 ng mL⁻¹. The limits of quantitation, defined as 10 times of the s values of blanks, were calculated as 21 and 2.0 ng mL⁻¹. The effects of contamination were eliminated by subtracting the obtained values from the blank. In order to overcome the enhancement or suppression due to the presence of major components such as Ca and Mn in the matrices, calibration solutions were performed within the sample matrix itself. On the other hand, the standard additions method for Pb and Cd was also applied to check for possible matrix interferences. The slopes of the calibration curves were compared with the slopes obtained for the standard additions method. It was found that the slopes of both methods were the same showing that there were no chemical interferences. Therefore, the calibration curves were used to determine the metal concentrations in the samples. The calibration curves were linear and the concentrations ranged from 200–5000 ng mL⁻¹ Pb for FAAS (30–400 ng mL⁻¹ Pb for STAT-FAAS) and 50–500 ng mL⁻¹ Cd for FAAS (3–40 ng mL⁻¹ Cd for STAT-FAAS).

Pb and Cd Concentrations in Leaves and Soil

The concentrations of Pb and Cd in the leaves of the 3 species taken from 6 locations are listed in Table IV. Each of the samples was analyzed in triplicate and the average of three values was given as the mean value plus standard addition.

Lead and Cd concentrations in the studied soil samples were found in the range of 3.1–10.1 and 0.11–0.51 mg kg⁻¹, respectively. The observed Pb and Cd levels in the studied leaves were in the range of 0.14–0.77 and <LOD–0.057 mg kg⁻¹ for *Pinus Nigra L.*, 0.11–0.91 and 0.009–0.055 mg kg⁻¹

for *Cedrus Libani*, and 0.09–0.81 and <LOD–0.05 mg kg⁻¹ for *Cupressus Arizonica*, respectively.

Figures 4–11 show the variation of Pb and Cd concentration in the different months of sampling. Figures 5 and 9 show the changes in Pb and Cd concentrations of *Cedrus Libani* depending on sampling location and sampling time, respectively. It was found that Pb and Cd concentrations in the leaves of *Cedrus Libani* collected in November and December were higher than in July and March almost for all locations ($p < 0.05$). These increases can be attributed to the weather and/or temperature conditions. Following the November and December months is the arid summer season and July and March are followed by the rainy winter and spring seasons. Further, it was found that Cd concentration in leaves from *Cedrus Libani* collected in July were lower than in other months, except for location 4.

Figures 4 and 8 show the changes in Pb and Cd concentration of *Pinus Nigra L.* depending on sampling location and sampling time, respectively. It was found that the Pb concentration in leaves of *Pinus Nigra L.* in March were lower than in July, November, and December. Figures 6 and 10 show the changes in Pb and Cd concentrations of *Cupressus Arizonica* depending on sampling location and sampling time, respectively.

Briefly, Pb and Cd levels in the leaf samples collected in November and December were higher than those in collected in July and March ($p < 0.05$). Interestingly, the Cd levels in the soil samples from location 4 were higher than in the others ($p < 0.05$). Lead and Cd concentrations in all studied plants taken from location 4 were higher than in most other locations ($p < 0.05$). This may be attributed to the fact that location 4 has heavy traffic, although the correlation was not as

strong for other locations. In Turkey, unleaded petrol was introduced about 10 years ago. Yet, high Pb concentrations in heavy traffic areas were still identified because of the long residence time of Pb in urban soils and active dust re-suspension (22). In addition, the source of Pb in the soil from the center of the city may be due to corrosion of the metallic parts in cars, such as engine wear, thrust bearing, and brush wear.

The degree of Pb and Cd concentrations in the leaves was found to be proportional to industrial and human activities. High metal concentrations in plants located around industrial sites and urban and highway roadsides are due to anthropogenic activities in addition to traffic volume. Based on the Pb values obtained at the control and other locations, our study concluded that future biomonitoring studies for Pb contamination would be performed using the leaves of *Cedrus Libani*.

CONCLUSION

The advantages of the proposed on-line slotted tube atom trap-flame atomic absorption spectrometry (STAT-FAAS) method are high speed, less risk of contamination, low cost, and easy construction of the required quartz tube. In comparison to off-line enrichment techniques such as solid phase extraction and solvent extraction (23,24), the STAT method is simple and can be easily applied.

In this study, the STAT-FAAS method was used to determine Pb and Cd in soils and leaves. Sampling was performed in different months of the year and evaluated based on industry (cement factory), as well as traffic and population density. Based on the Pb values obtained for the different plant species in the control area and other locations, it was concluded that future Pb biomonitoring studies should be done

Fig. 4. *Pinus Nigra* L. leaves. Variation in Pb concentration in different months.

Fig. 5. *Cedrus Libani* leaves. Variation in Pb concentration in different months.

Fig. 6. *Cupressus Arizonica* leaves. Variation in Pb concentration in different months.

Fig. 7. Soils. Variation in Pb concentration in different months.

Fig. 8. *Pinus Nigra* L. leaves. Variation in Cd concentration in different months.

Fig. 9. *Cedrus Libani* leaves. Variation in Cd concentration in different months.

Fig. 10. *Cupressus Arizonica* leaves. Variation in Cd concentration in different months.

Fig. 11. Soils. Variation in Cd concentration in different months.

in regions where the *Cedrus Libani* species are growing.

The Pb and Cd concentrations were found to range from 139–768 $\mu\text{g kg}^{-1}$ and <LOD–57 for *Pinus Nigra L.*, 113–908 $\mu\text{g kg}^{-1}$ and 9–55 $\mu\text{g kg}^{-1}$ for *Cedrus Libani*, and 88–813 $\mu\text{g kg}^{-1}$ and <LOD–50 $\mu\text{g kg}^{-1}$ for *Cupressus Arizonica*. The levels observed for Pb and Cd in the soils ranged from 3100–10112 $\mu\text{g kg}^{-1}$ and 106–505 $\mu\text{g kg}^{-1}$, respectively.

The Pb and Cd concentrations in the leaves of these plants growing in Elazig, Turkey, were found to be below the phytotoxic level of 30 mg kg^{-1} for Pb and the permissible level of 3 mg kg^{-1} for Cd.

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TABLE IV
Metal Concentrations in Soil and Leaves From 6 Locations in Elazig, Turkey
Values are ng g⁻¹ for Pb and Cd (on dry-weight basis);
Results are mean values ± standard deviation, n=3

No. in Fig. 1	Sampling Point	Months	Soil (ng g ⁻¹)		<i>Pinus Nigra L.</i> (ng g ⁻¹)		<i>Cedrus Libani</i> (ng g ⁻¹)		<i>Cupressus Arizonica</i> (ng g ⁻¹)	
			Pb	Cd	Pb	Cd	Pb	Cd	Pb	Cd
1	Cayda Cira (Traffic inter section)	July	10112±1214	255±26	358±32	25±0.8	306±43	14±2	345±35	19±2
		November	8466±1016	122±13	448±4	28±0.1	777±132	42±2	514±57	36±4
		December	8144±977	156±19	609±55	31±0.9	508±71	32±4	552±66	28±2
		March	7535±904	141±14	139±13	22±1.0	115±16	25±3	123±12	23±2
2	University	July	6805±953	162±21	458±50	26±2.6	417±54	15±2	380±48	15±2
		November	6317±821	184±24	536±54	39±4.3	567±45	28±2	343±49	16±1
		December	6400±832	192±25	687±82	43±4.3	727±58	38±4	88±10	25±2
		March	5955±596	183±26	143±14	20±2.2	113±9	12±1	217±24	12±1
3	Province (City center)	July	4058±406	118±17	371±41	15±2.0	328±30	9±1	361±36	13±1
		November	6991±699	111±16	593±65	48±5.0	659±56	35±5	607±67	32±3
		December	5995±600	150±21	768±77	36±4.0	908±82	25±3	813±98	30±4
		March	5845±585	130±18	389±47	27±3.0	446±40	21±2	425±43	26±3
4	Ordu Evi (City center)	July	7595±904	164±16	574±80	33±3	617±68	42±5	450±44	20±1
		November	8987±1078	492±49	358±15	43±4	596±75	47±6	673±51	50±3
		December	6950±834	505±51	240±34	57±6	771±85	55±6	807±89	30±2
		March	5935±712	485±49	220±31	40±4	511±56	41±5	770±85	45±3
5	Cement factory location	July	10064±1107	404±49	648±78	19±2	448±45	13±1	497±50	15±2
		November	4857±534	170±20	285±34	31±4	344±35	35±4	315±32	27±3
		December	3550±391	230±23	455±55	45±5	684±69	21±2	547±66	32±4
		March	3400±374	220±24	145±17	56±6	202±20	11±1	181±20	43±5
6	Control area ^a	July	5765±750	122±15	205±21	< LOD	210±25	17±2	193±25	< LOD
		November	5640±733	106±15	183±19	< LOD	186±24	20±2	207±24	< LOD
		December	5100±612	119±17	182±18	< LOD	175±21	18±2	180±22	< LOD
		March	3100±595	121±13	175±18	< LOD	179±18	20±3	174±21	< LOD

LOD: Limit of detection.

^a Away from residential areas and factories.