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ULTRASONIC LEACHING OF BIO-COLLECTORS FOR HEAVY METAL ANALYSIS

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A Bio Collector – Ultrasonic Leaching Method (BC-ULM) was developed for the analysis of heavy metals (Pb, Cd, Cr, Ni, Cu, Fe and Al) on plant sprouts for the assessment of environmental pollution. *Fabaceae Rabinia Pseudoacacia L.* and *Pinaceae Pinus Sylvertris L.* sprouts were chosen as bio-collectors. The bio-collector sprouts were leached using 1% HNO₃ solution under ultrasonic effect and the obtained leachate samples were analysed by atomic absorption spectrometry (AAS).

The accuracy of BC-ULM was tested by comparing obtained results with those of deposition plate (DPM) and ashing (AM) methods which both are of practical use. Our findings show that BC-ULM and AM results are in agreement. Average heavy metal pollution factors of BC-ULM and DPM are well comparable with each other. Maximum and minimum heavy metal polluted stations were determined with no difference at all for all three methods. The average RSD % of BC-ULM varied between 5.5–8.4 % for n=13, depending on the analyte and the nature of the sample. Again, average RSD % was obtained between 1.7–8.0 % (n=9) and 3.4–9.8 % (n=11) for AM and DPM, respectively. The precision variance between BC-ULM and AM was not significant at 0.05 probability for all metals except copper.

Keywords: Ultrasonic metal leaching; sample preparation; bio-collectors; heavy metal pollution; AAS

INTRODUCTION

Since the industrial revolution, atmospheric pollutants which arise from power supplies, transportation and industrial plants may threaten human welfare, and cause serious problems to the population^[1,2]. Some of the metals found predominantly as particulate matter in polluted atmosphere are known to be hazardous to human health, especially heavy metal consisting particles, the main carcinogens^[1–7]. Determination of pollution sources and their possible effects has, therefore, gained in importance and different monitoring systems have been proposed.

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Heavy metals may be taken directly by inhalation or indirectly via deposited on food or plants^[8-13]. It is known that atmospheric pollution in urban areas is characterized by relatively high concentrations of Pb and Cd^[6,14], two metals which are not present in significant amounts in plants^[15]. The collection of these, and other metals, in plant leaves or sprouts may be used for monitoring atmospheric pollution. Deposition is, however, a complex processes and this will lead to sampling problems.

In conventional ashing techniques for metals determination, the plant material is totally decomposed and the measured metal concentrations reflect the total metal constituent both in inner tissue and surface of the plant. But, a suitable monitoring technique may allow to distinguish whether the metal load is earth crustal (metals coming through the root) or atmospherically deposited (directly on the plant or indirectly in the soil). It is clear that the plant is exposed to soil deposition which is defined as natural pollution, which occurred by natural and seasonal dust circulation. This deposition might be considered as base level pollution. Any pollution over this level on the surface of the considered plant material can be called as anthropogenic pollution.

Ultrasonic leaching method (ULM) was thought to be an alternative method to conventional extraction. It has been reported that this method gives high recoveries of organics from granular activated carbon^[16], sediment^[17], fly ash^[18], biological materials^[19] and elements from atmospheric particulate^[20] in a much shorter time than is required for other extraction procedures. Besides, the ultrasonic leaching is known to be faster and more effective than the conventional extraction methods to extract the adsorbed and remaining metals out of the sediments^[21,22]. Similar results may also be expected for labile (physical bound) metal fractions in atmospheric particulate and on the bio-collector sprouts, from a study of the physical and chemical effects of ultrasonication.^[23,24]

As anthropogenically produced metals are normally found in the labile fractions^[25] rather than in the residual fractions of the aerosol particulates and sediments, the labile fractions are important from the point of view of environmental pollution. It was envisaged that if the ULM technique was applicable to the dissolution of very weakly bound (labile) metals on bio-collectors, then ULM could also be used to promote their rapid release. To prove this hypothesis a series of experiments were designed and their recoveries were compared with those of the AM procedures.

In this study, the usability of bio-collector sprouts with ULM as monitor has been investigated. The contaminant metals which deposited on the sprout surface may be extracted into weak acid solution by ultrasonic leaching without destruction of the inner structure of the biologic sample. Because of ultrasonic leaching in concentrated acid destruct the whole structure of the sprouts^[26], the proposed

process was carried out in a weak acid solution (1 % HNO₃) in order to leach only physical bound metal fractions on the plant surface. Additionally, this type of leaching, which involves the maintain the whole structure of the bio sample (pretreatment steps such as crushing or grinding is avoided), is thought to reflect only the surface contamination.

Populus Nigra Subs. Nigra. L. sprout is one of bio materials that has been used as bio-collector in the literature for monitoring the pollution^[27]. *Pinaceae Pinus Sylvertris L.* and *Fabaceae Rabinia Pseudoacacia L.* sprouts were chosen as bio-collectors in our study because of their abundance in the studied area, fast growing, large surface area and adsorption capacity of the sprouts.

Heavy metal and particulate pollution are expressed as pollution factor (PF)^[7], which can be described as the ratio of the determined contamination to the base level contamination:

$$PF = \frac{C_{\text{determined contamination}}}{C_{\text{base level contamination}}}$$

and

$$\text{Average PF} = \frac{\sum_{i=1}^N (PF)_i}{N}$$

where C is the heavy metal or particle concentration and N the sampling site number. PF value is a degree of pollution of investigated area. Average PF is also a degree of the general pollution of the city for particle or each metal. In this study, the pollution of station 7 which was thought to be unaffected by anthropogenic sources has been chosen as the base level. The PF is used for establishing a criteria which will exhibit the contaminated areas and their possible pollutant sources.

A combined sample preparation technique for monitoring of environmental pollution, bio collector-ultrasonic leaching method (BC-ULM), has been investigated. The results obtained from BC-ULM were compared with the results from AM and DPM^[28-30] for the same stations. Unfortunately, a suitable reference material to test the accuracy of this method couldn't be obtained.

EXPERIMENTAL

Sampling stations

In the city centre of Sivas and its surroundings, seven sample stations with the main characteristics of the city are shown in Figure 1. Station 1 is open to the

effect of the cement factory emissions; station 2 is a residential area with a medium level traffic density; station 3 is the city centre exposed to heavy traffic and with dense population; station 4 is an area where open to emissions of the automotive industry and some other industrial production sites; station 5 is also a residential area where a bus station is located; station 6 is a residence site surrounded with groves; station 7 is a nonresidential area out of the city, chosen as the background site.

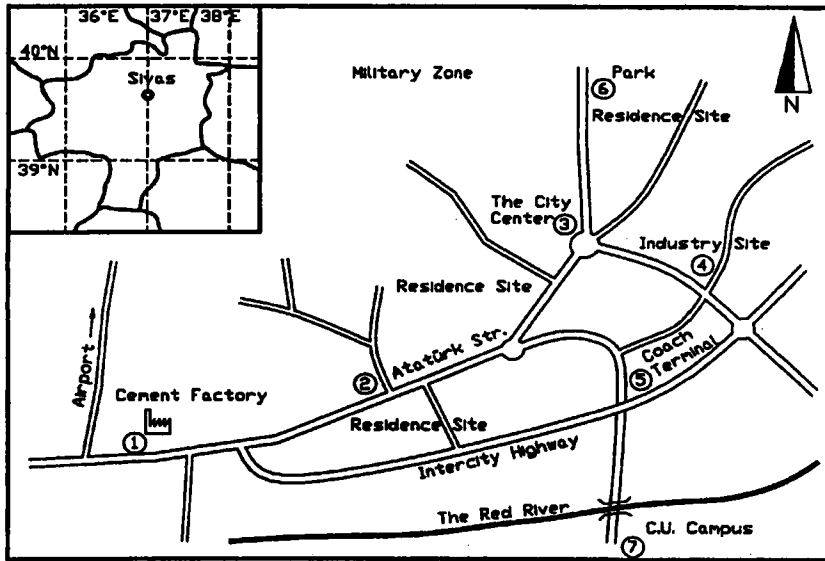


FIGURE 1 The sampling stations for the Sivas city

Samples

Bio-collector samples

Bio-collector sprouts were collected during the first two weeks of October 1992, 1993 and 1994 and wet-weighted. The tips of the sprouts (10 ± 2 g) of *Fabaceae Rabinia Pseudoacacia L.* (acacia) and *Pinaceae Pinus Sylvertris L.* (pine) at 2–3 m high were collected with care from all stations since keeping the particles on the sprouts was important. Reproducibility of the method was tested by taking 5 samples from station 2, 4 samples from station 3, and 4 samples from station 4 for both species.

Deposition plate samples

An aluminium folio (6 cm × 12 cm) was attached on a 10 cm wide 15 cm long cardboard. Kloragrese was spreaded homogenly on (5 cm × 10 cm area) the folio to obtain a deposition plate sticky and thinly. The prepared plates were placed 2–3 meter high at 10° degrees angle vertically where the same locations under investigation. Sampling on deposition plates were carried out between June-October 1994 for 26–30 days period (only dry days). Again, 3 samples from station 1, 4 samples from station 3 and 4 samples from station 6 were collected for testing the reproducibility.

Sample preparation for the analysis

Ultrasonic leaching of the bio-collector samples was carried out in a 1% HNO₃ using a NEY-350 model ultrasonic bath with 50–60 kHz nominal frequency. Extracts were centrifuged at 6000 r.p.m. for 10 minutes using a macro centrifuge with 50 ml tubes volume. Solid particles were successfully separated from the aqueous analyte solution by the way.

The preparation of the bio-collectors by BC-ULM

Fresh sprouts (10±2 g) were dried at 110°C for two hours then weighted and placed in a 250 ml glass beakers. 100 ml of 1% HNO₃ was added and left in ultrasonic bath for 20 minutes. Then, the extracts were filtered off, filtration residues were washed with 1% HNO₃ several times until a clear filtrate was obtained. Combined filtrates were subjected to sonication for another 10 minutes. The extract was evaporated to 20 ml final volume, centrifuged and its volume made up to 25 ml with 2 % HNO₃. Acidic samples were kept in plastic bottles for AAS analyses.

Ultrasonic leaching residues were washed with distilled water and dried at 110°C for two hours, then dry weights were determined. These residue sprout samples were used for the AM. Dry weight difference before and after ultrasonic leaching was considered as total particle contamination.

The blank samples were taken from the station 7 at the beginning of June, when it was assumed there was no pollution. Each sample was washed with distilled water at least 5 times and subjected to the same treatment as described above. The mass loss of dried sprout samples, before and after ultrasonic treatment, was accepted as the blank value. Obtained blank solutions were also used for heavy metal analyses as blank. The same procedure was applied on fresh sprouts of both species, except the drying step.

The preparation of the bio-collectors by AM

In this method, two parallel studies were carried out. In the first study, sprout samples collected from stations 1, 3 and 6 were undergone ashing procedure. The second ashing study was carried out on the residues after the leaching process. Reproducibility of AM was also tested using the 5 sprout samples of both species from station 3 and 6 sprout samples from station 6.

In general, the AM is carried out at approximately 500°C. But, in the case of higher surface depositions, the sprouts couldn't be ashed properly at this temperature. Although there are some drawbacks, e.g. volatile metal losses, the AM was carried out at 700 °C. Dried bio-collector samples (at room temperature) were placed in a porcelain crucible and heated in an ashing oven starting from room temperature to 700°C (4 hours at 700°C). Then, the cooled ash was treated with 20 ml of 2 M HCl and allowed to digest for 1 hour at 160°C. After centrifugation, the total volume was made up to 25 ml using 1% HNO₃ and kept in plastic bottles for AAS analysis.

The preparation of the deposition plates for the analysis, DPM

The greased folio on the each deposition plate was placed in a beaker which was weighted at room temperature then treated with 30 ml of n-hexane for 20 minutes in the beaker in order to dissolve the grease on the aluminium folio. The aluminium plate was removed and the residue was evaporated to dryness. After cooling, the beaker was weighted at room temperature and the mass difference was recorded as total particle contamination.

An aliquot of (10 ml) concentrated HNO₃ was added on each dried, weighted sample and evaporated at 150–200°C until dryness (approximately 2 hours). The residue was finely crushed in a porcelain plate and was dissolved in 20 ml of 1 % HNO₃. After centrifuge the aqueous acidic solution was made up to 25 ml using 1 % HNO₃ and kept in plastic bottles for AAS analysis.

The same procedure was repeated with three blank deposition plates and the obtained average value was subtracted from the contaminated plate measurement.

Element determinations

The leachates were analysed for the heavy metals using a Perkin-Elmer Model 2380 AAS functioning with air acetylene burner for Pb, Cd, Cr, Ni, Cu, Fe and nitrous oxide/acetylene burner for Al. Each result exhibits the average of four readings. The calibration range were set for the analysis in the range of 0.5–5.0 mgL⁻¹ for Pb, Cu, Ni, Cr, Fe, 0.1–2.0 mgL⁻¹ for Cd and 10–100 mgL⁻¹ for Al.

The dynamic range of the heavy metal concentrations required the performing both the concentration and dilution of the sample before the analysis. The higher concentrations were attained by sub-boiling evaporation of the samples in the teflon beakers. Where ever necessary, the samples were diluted with 1% HNO₃. In stations 6 and 7 concentrations of Pb, Cd and Cr were found to be at the limit values.

The blanks were analysed simultaneously together with the field samples. The concentrations of blanks were subtracted from those of each sample. In most cases, the blanks constituted only a small fraction (<1%) of the metal concentration in the field samples.

RESULTS AND DISCUSSION

Particle pollution, BC-ULM versus DPM

Figure 2 indicates that particle pollution has increased from 1992 to 1994 for both of the used collectors. Additionally, acacia and pine sprouts showed similar contamination for each year for the same stations. But interestingly, particles deposited on acacia sprouts were $25 \pm 11\%$ higher than these deposited in pine sprouts (both species were equal in weight) at the same station. This may be because of; 1) acacia sprouts grow faster during the first few months, therefore have larger collector surface, 2) acacia sprouts have larger surface area than pine or, 3) acacia may have more effective adsorption capacity. Therefore, the evaluation of BC-ULM study depended upon the acacia data and all BC-ULM results respect to this species.

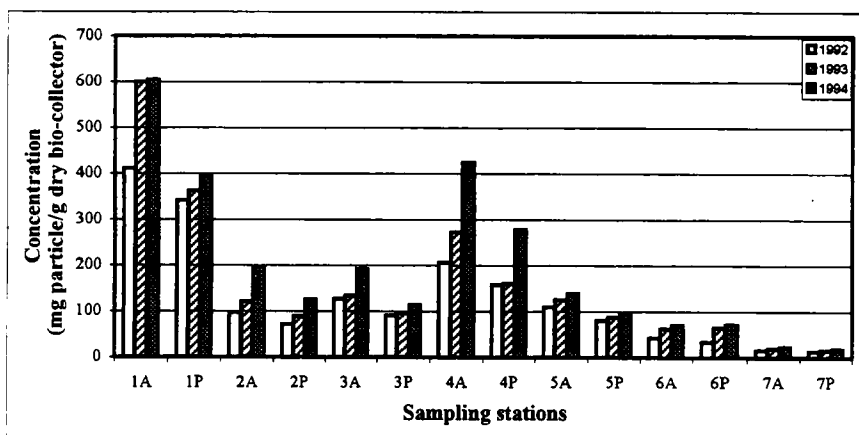


FIGURE 2 BC-ULM particle pollution of Sivas city between 1992–1994. A: Acacia P: Pine

According to Figure 2, while stations 1 and 4 have the highest particulate pollution, 6 and 7 have the lowest. Figure 3 also exhibits similar results. This can be explained as station 1 is affected by the cement factory emissions and station 4 is exposed to local industrial emissions. Station 7 which is far away from city's atmosphere showed the lowest particle pollution.

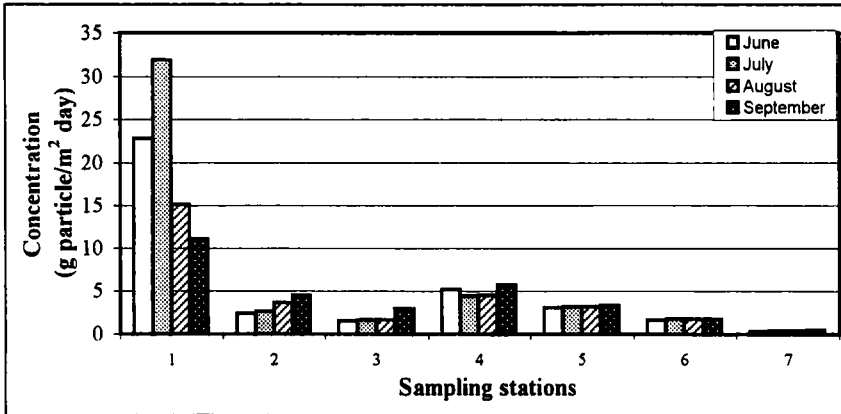


FIGURE 3 DPM particle pollution of Sivas city in 1994

As can be seen in Figures 2 and 3, particle pollution in 1994 can be set out as $1 > 4 > 2 > 3 > 5 > 6 > 7$ for BC-ULM and $1 > 4 > 2 > 5 > 3 > 6 > 7$ for DPM. Here, similar results were obtained except the replacement of stations 3 and 5. In Figure 3, the particle pollution showed a small increase from June to September. However, station 1 showed a significant decrease since the cement factory had a chimney filtration unit by the end of July 1994.

The local and chronologically particle PFs of the stations are given in Figure 4. In accordance with previous results, the PF values of stations 1 and 4 are the highest and stations 6 and 7 are the lowest for BC-ULM. The same PF values were also obtained from DPM. The average PF for BC-ULM in Sivas city increased in the order $7.99 (1992) < 9.07 (1993) < 9.52 (1994)$, which is similar to the average PF obtained from DPM (9.27 for 1994). It is clear that average PFs arisen from anthropogenic resources show a regular increase from 1992 to 1994 which was confirmed with both BC-ULM and DPM.

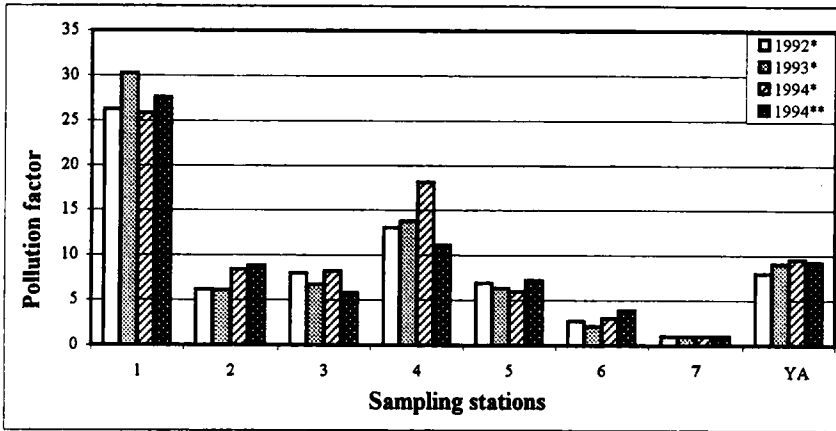


FIGURE 4 Particle PFs of stations in Sivas between 1992–1994. *: BC-ULM, **: DPM, YA: Yearly Average

Heavy metal pollution, BC-ULM versus AM

A previous study already revealed that heavy metal pollution increased from 1992 to 1994 in the Sivas city^[26]. As a result, there is a relation between particle amount and heavy metal pollution. The present heavy metal pollution and average RSD % bound by BC-ULM and AM are given in Table I.

BC-ULM and AM results revealed that there is no significant difference between both methods at 0.05 probability (P), except for copper^[31,32]. The traditional AM was also carried out on the residue from BC-ULM and none of the metals studied could be determined, even though samples were concentrated five times. Therefore, it can be deduced that, the pollution occurs only on the surface of the fresh sprouts not internally. But more important is that we can compare the results of both methods to obtain a reliable physically bound (labile) heavy metal pollution on the surface of the bio-materials. In Table I, the average RSD % of bio-collector samples for all metals are in the range of 5.5–8.4 % (n=13) and 1.7–8.0 % (n=9) for BC-ULM and AM, respectively. Average RSD % of BL-ULM is higher than that of AM but still in the acceptable range. According to these findings, it can be said that BC-ULM is an acceptable and a repeatable method of preparation of externally polluted samples for chemical analysis.

TABLE I Heavy metal concentrations and average RSD % determined by BC-ULM and AM in Sivas city in 1994

Metals	Concentration ($\mu\text{g metal/g dry bio-collector}$)						Average RSD %	
	Station 1		Station 3		Station 6		BC-ULM	AM
	BC-ULM	AM	BC-ULM	AM	BC-ULM	AM		
Pb	19.78	20.69	25.40	24.88	2.88	2.92	5.5	3.6
Cd	1.88	1.96	0.64	0.64	0.33	0.38	5.7	8.0
Cr	34.30	35.70	6.21	6.20	4.00	4.35	7.7	6.5
Ni	92.40	90.80	21.00	21.40	9.28	9.32	7.7	4.9
Cu	19.84	19.43	16.40	16.78	5.92	6.11	8.4	1.7
Fe	5807.00	5782.00	830.00	780.00	642.00	640.00	7.8	5.2
Al	3076.00	3176.00	320.00	306.00	670.00	690.00	6.9	5.3

Heavy metal pollution, BC-ULM versus DPM

The heavy metal pollution determined by BC-ULM and DPM in Sivas samples is shown in Figures 5 and 6. The BC-ULM results were supported by DPM results. Statistical calculations^[31,32] showed that samples collected from stations located in the city and its surroundings are under strong anthropogenic pollution, since results were significantly different at $P = 0,05$, according to the background level station (station 7), except for Pb, Cd, Cu, Ni and Cr concentrations for station 6 and Cr concentration for stations 5. Besides, PFs of both methods provided comparable results.

TABLE II Average heavy metal PFs and average RSD % determined by BC-ULM and DPM in Sivas city in 1994

Metals	Average heavy metal PF		Average RSD %	
	BC-ULM	DPM	BC-ULM	DPM
Pb	8.43	16.28	5.5	5.4
Cd	6.65	9.04	5.7	6.6
Cr	4.50	6.08	7.7	3.4
Ni	6.08	10.84	7.7	7.7
Cu	3.78	5.09	8.4	5.8
Fe	14.11	16.56	7.8	6.5
Al	20.71	18.78	6.2	7.8

Average heavy metal PFs and average RSD % of BC-ULM and DPM are given in Table II. As it can be seen, the average heavy metal pollution is in the order: Fe>Al>Pb>Cd>Ni>Cr>Cu for BC-ULM and Fe>Al>Pb>Ni>Cd>Cr>Cu for DPM, respectively. In general, DPM have higher PF values than BC-ULM except for Fe. It appears that the city is under heavy Fe, Al, Pb pollution while Cr and Cu pollution is lower.

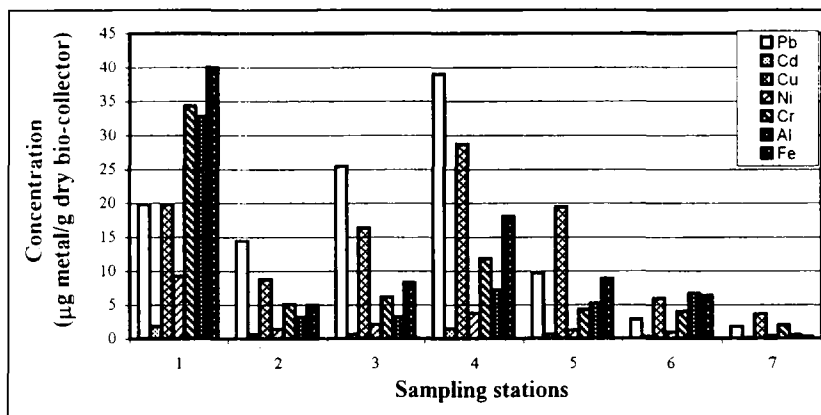


FIGURE 5 Heavy metal pollution determined by BC-ULM in Sivas city in 1994 (Fe and Al= $\times 10^2$; Ni= $\times 10$)

When the average heavy metal PF values were compared using a significance statistical test^[31] it was concluded that there is no difference for the two methods at $P=0.05$, except for Pb and Ni. In the precision test, the average RSD % values for all metals varied in the range of 5.5-8.4 % ($n=13$) and 3.4-7.8 % ($n=11$) for BC-ULM and DPM, respectively (see Table II). Geometric RSD % values in the range of $3.5 (\pm 1.9) - 5.7 (\pm 2.5)$ were obtained in a previous DPM study^[30] The difference in the precision of the two methods was tested using F-test method^[31] but each method use different concentration units, therefore the RSD % were used as relative values for comparison. It was found that the two methods did not significantly differ from each other, at $P= 0.05$, except for Cr. BC-ULM and reference DPM values are in good agreement so it can be concluded that, BC-ULM is an acceptable and easily applicable method for monitoring the local and time dependent heavy metal pollution.

Additionally, BC-ULM was applied on wet (fresh) and dried bio-collectors. When the procedure was carried out with wet samples, Pb, Cd, Cr, Cu and Ni concentrations were 3.7 ± 2.4 % higher; Fe and Al concentrations were $3.4 \pm$

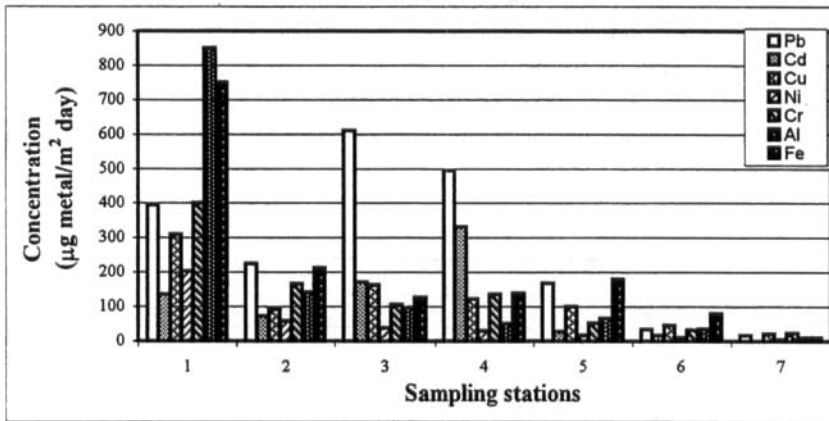


FIGURE 6 Heavy metal pollution determined by DPM in Sivas city in 1994 (Fe and Al = $\times 10^2$; Ni = $\times 10$; Cd = $\times 1/10$)

3.1 % lower than those observed with dried samples ($P = 0.05$). Therefore, wet bio-collector leaching seems to be providing better results for minor metals, it is easier and less time consuming. But, dry bio-collector leaching is preferred for determination of total particles.

A suitable international standard material couldn't be obtained to test the acceptability of the proposed BC-ULM method. But, ultrasonic leaching was previously tested on certificated sediment standard (NIES CRM-2, from the National Institute for Environmental Studies, Japan) for Cu, Pb and Fe^[21]. Ultrasonic leaching provided (+4) – (-11.50) % relative error and 8.7–11.9 % (n=10) RSD %, depending on the analyte and sample, which are acceptable ranges for this kind of studies.

When the sample preparation time is considered, BC-ULM is two times faster than AM. It requires less reactive, energy and analyst is exposed to less toxic gases. It is clear that the BC-ULM is a rapid, inexpensive, easy, reproducible and selective technique for the determination of physically bound (labile) metals on bio-collectors which are important in monitoring environmental pollution.

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