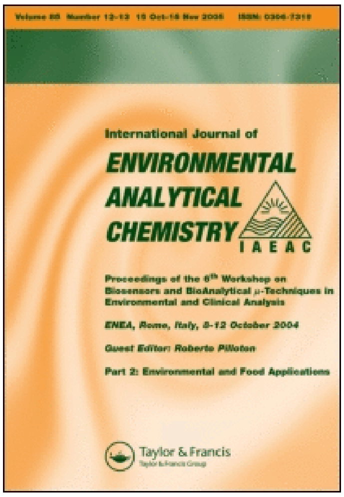

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Determination of Heavy Metals in Bio-Collectors as Indicator of Environmental Pollution

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To cite this Article Çinar, Tuncay and Elık, Adıl(2002) 'Determination of Heavy Metals in Bio-Collectors as Indicator of Environmental Pollution', International Journal of Environmental Analytical Chemistry, 82: 5, 312 — 329
To link to this Article: DOI: 10.1080/03067310290007804
URL: http://dx.doi.org/10.1080/03067310290007804

Intern. J. Environ. Anal. Chem., Vol. 82, No. 5, pp. 321–329

DETERMINATION OF HEAVY METALS IN BIO-COLLECTORS AS INDICATOR OF ENVIRONMENTAL POLLUTION

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(Received 16 August 2001; In final form 31 December 2001)

The heavy metal levels in bio-collector (*Fabaceae Rabinia Pseudoacacia L.* sprouts) samples collected from seven sites, which had the characteristic properties of the Sivas city, Turkey, in year 2000, have been determined by atomic absorption spectrometry (AAS), after the bio-collector sprouts were prepared for analysis by bio-collector–ultrasonic leaching method (BC–ULM).

The results of the analyses were used to determine major sources and magnitude of heavy metal pollution. The mean concentration levels of Pb, Cu, Ni, Zn and Cd were found to be 6.8, 5.5, 6.7, 12.4 and 0.20 μg/g fresh bio-collector, respectively, for September 2000. The highest levels of the heavy metals at the sites affected by industrial emissions and heavy traffic were noted. The heavy metal levels in urban bio-collectors were several times higher than the background levels. After heavy metal pollution factors of each site were determined, their possible major pollutant sources were discussed.

Keywords: Heavy metals; Environmental pollution; Bio-collectors; Ultrasonic leaching method; AAS; Sivas-Turkey

INTRODUCTION

It is known that the increase of industrial activities, power supplies, transportation and urbanization were brought along the environmental heavy metal pollution problems [1]. Heavy metals at trace levels play important roles in human life [2,3] and present in air, soils, sediments, dusts, plants and natural waters enter the human body by inhalation, percutaneous re-sorption and ingestion, etc. when passing through the nutritional chain [4–8]. The heavy metals such as Pb, Cd, Ni, Cr are toxic for the human and animal bodies [9,10]. It is known that heavy metal pollution is common in urban areas rather than rural areas since presence of industrial resources [11–13]. Knowledge of the sources and levels of the toxic heavy metals are an important undertaking due to their effects for humans, especially for children.

There is an increasing use of bio-monitoring of metal concentrations in biological and environmental samples such as foods [14], blood and serum [4,15], autopsy

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ISSN 0306-7319 print: ISSN 1029-0397 online
DOI: 10.1080/03067310290007804

tissues [16], urine [17], water [18], soil and sediment [19–21], street dusts [22–24], mosses and lichen [25–28], etc. Plants are also important environmental materials to follow the levels of heavy metals [29–34]. Elik *et al.* [35] and Martin *et al.* [36] have shown that exposed to atmospheric pollution bio-collectors (oak, acacia, pine, etc.) exhibit the property of accumulating heavy metals such as Cd, Pd, Zn, Ni and Cu. In general heavy metals such as Pb, Ni and Cd are not present in significant amounts in plants [37]. Even trace amounts of these heavy metals indicate possible contamination [35].

Fabaceae Rabinia Pseudoacacia L. sprouts were chosen as bio-collector in our study because of their abundance in the studied area, fast growing, large surface area and adsorption capacity of the sprouts. The contaminant metals deposited on the sprout surface were prepared for analysis by the bio-collector–ultrasonic leaching method (BC–ULM) [35] without destruction of the inner structure of the biologic samples. This is a rapid, easy, reproducible and selective technique for the determination of metals on bio-collectors which are important in monitoring environmental pollution. It has been shown that the ULM gives high recoveries of organics from sediment [38], fly ash [39], biological materials [40] and elements from atmospheric particulate [35,41] and sediment [20,42] in a much shorter time than is required for other extraction procedures.

The aim of this work is to determine major sources and magnitude of heavy metal pollution in Sivas city in 2000 using BC–ULM. Besides, after determination of pollution factors (PF) [35,43], which is an important parameter of anthropogenic pollution, of each site, evaluation of their possible major sources were aimed. PF can be described as the ratio of the determined pollution to base level or background pollution. The pollution of site 7 which was though to be unaffected by anthropogenic sources has been chosen as the base level.

In this paper, the Pb, Zn, Ni, Cu and Cd contents of the bio-collector samples from seven sites in and around urban areas of Sivas city, Turkey, during the summer season, in 2000, were determined by atomic absorption spectrometry (AAS). The results of the analyses were compared with the global values.

EXPERIMENTAL

Sampling Sites

Sivas is a small industrial and agricultural city with a population of about 225,000 inhabitants, in central Anatolia, Turkey. The city of Sivas has the continental climate at which the winters are cold and snowy, the summers are usually drought and hot, having a height of 1250 m from the sea level. During the period under consideration total rainfall is measured for July, August and September as 0.0, 16.2, 12.2 mm, respectively, by the National Meteorology Office, Turkey. The mean traffic density in the streets with heavy, medium, light and low traffic of Sivas city are >700, 500 ± 200, 200 ± 100 and <100 vehicle/h, respectively.

The main characteristics of sites selected for sampling in the Sivas city are the following (see Fig. 1). Site 1 is the city centre exposed to heavy vehicular traffic and with dense population; site 2 is an area open to emissions of the automotive industry and some other industrial production sites, and having medium level vehicular traffic; site 3 is a residence site surrounded with groves, and having low traffic density; site 4 is a

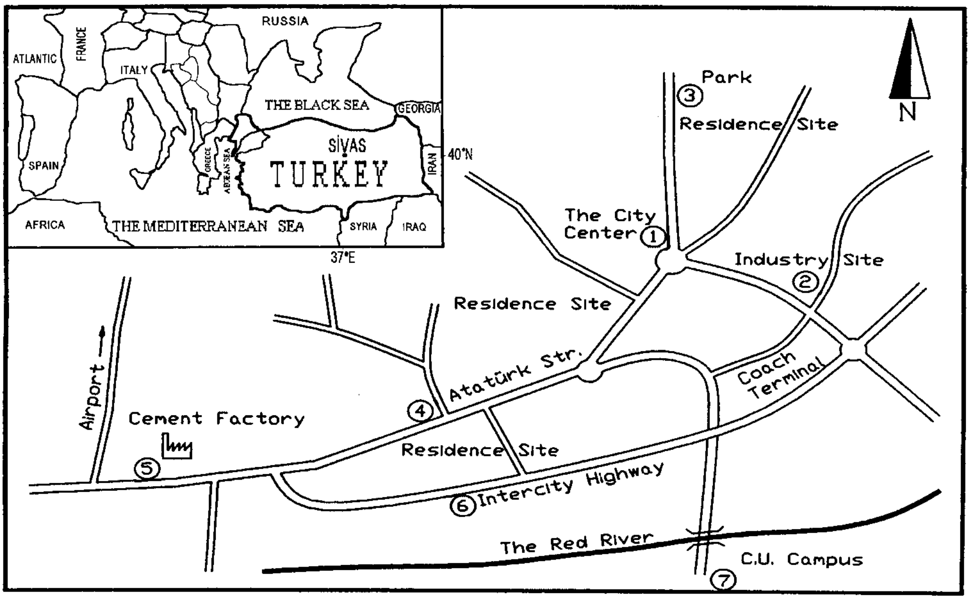

FIGURE 1 Location of the sampling sites for the Sivas city.

residential area with a medium level traffic density; site 5 is open to the effect of the cement factory emissions, and having medium level traffic density; site 6 is also a residential area open to emissions of the intercity highway with a light traffic density, site 7 is a non-residential area out of the city atmosphere, chosen as the background site.

Bio-Collector Samples

Bio-collector (*Fabaceae Rabinia Pseudoacacia L.*) sprouts (three samples) were collected from each site for each month, during the first weeks of July and September 2000 and wet-weighted. The tips of the sprouts (10 ± 2 g) of bio-collectors at 2–3 m high were collected with care from all sites since keeping the particles on the sprouts was important.

The Preparation of Bio-Collectors for the Analysis by the BC–ULM

The details of BC–ULM used for the preparation to analyses of bio-collector samples are described elsewhere [35]. Ultrasonic leaching of the bio-collector samples was carried out in a 1% HNO_3 using a ultrasonic bath with 50–60 kHz nominal frequency. Leachates were filtered by suction through a Whatman-42. Solid particles were successfully separated from the aqueous analyte solution by the way. HNO_3 (Merck–Darmstadt) and other chemicals used were of analytical-reagent grade.

Fresh sprouts (10 ± 2 g) were exactly weighed with ± 1 mg sensitivity then placed in a 250 ml glass beaker. One hundred millilitre of 1% HNO_3 was added and left in ultrasonic bath for 20 min. Then, the leachates were filtered off, filtration residues were washed with 1% HNO_3 several times until a clear filtrate was obtained. Combined filtrates were subjected to sonication for another 10 min. The leachates were evaporated to 20 ml final volume, were filtered by suction through a Whatman-42 and its volume made up to 25 ml with 2% HNO_3. Acidic samples were kept in plastic bottles for AAS analyses. The blank samples were taken from the site 7 at the beginning of June 2000, when it was assumed there was no pollution. Each sample was washed with distilled water at five times and subjected to the same treatment as described above. Obtained blank solutions were used for heavy metal analyses as blank. In addition, ultrasonic leaching residue sprout samples were used for the dry ashing method (AM) [35], three each samples from sites 1, 2 and 4.

Element Determinations

The heavy metals in the leachates were determined by flame AAS using a UNICAM Model 929 spectrometer, functioning with air/acetylene burner. Each result is the average of four readings. The operating parameters for working elements were set as recommended by the manufacturer. The concentrations were obtained directly from calibration graphs after correction of the absorbance for the signal from an appropriate reagent blank. In most cases, the blanks constituted only a small fraction ($<1\%$) of the metal concentration in the field samples.

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. Wherever necessary, the samples were diluted with 0.1 M HNO_3. In sites 3 and 7 concentrations of Pb and Cd were found to be at the limit values.

RESULTS AND DISCUSSION

Heavy Metal Pollution on the Bio-Collectors

The present work provides data on the Pb, Zn, Ni, Cu and Cd concentrations in the bio-collector samples of Sivas city, Turkey. The traditional AM was 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. Wherever necessary, the average mass loss for fresh acacia sprouts after dying were found to be as $50 \pm 6\%$, for the results in term of μg metal/g dry bio-collector unit [32].

The mean concentrations of Pb, Zn, Ni, Cu and Cd in bio-collector samples at different locations in Sivas city, Turkey, are given in Table I. Each value is the mean of three replicate measurements and RSDs (relative standard deviation) were calculated from pooled data for method [44]. The precision obtained from 42 replicate BC–ULM yielded an average relative standard deviation of 3.2, 2.9, 4.2, 4.6 and 5.7% for Pb, Zn, Ni, Cu and Cd, respectively, depending on the analyte and the nature of the sample. The statistical analysis based on these data showed that bio-collector samples collected from sites located in the city and its surroundings are exposed to strong anthropogenic pollution, since results were significantly different at 0.05 probabilities, according to the background level site (site 7). Besides, heavy metal pollution on bio-collectors increased from July to September for all sites in the Sivas city. Therefore, the evaluation of this study depended upon the September data. This

TABLE I Mean concentrations of heavy metals on bio-collector samples in Sivas city in 2000

Sites	*Months*	µg metal/g *Fresh bio-collector, $\bar{x} \pm SD$, $N = 3$*				
		Pb	*Zn*	*Ni*	*Cu*	*Cd*
1	July	7.4 ± 0.2	10.7 ± 0.4	5.8 ± 0.3	5.4 ± 0.2	0.18 ± 0.01
	September	12.8 ± 0.3	16.0 ± 0.2	7.4 ± 0.2	7.2 ± 0.3	0.22 ± 0.02
2	July	7.0 ± 0.2	11.9 ± 0.5	9.2 ± 0.3	8.1 ± 0.5	0.32 ± 0.02
	September	12.1 ± 0.2	17.7 ± 0.4	12.4 ± 0.3	10.7 ± 0.4	0.37 ± 0.03
3	July	1.2 ± 0.1	6.7 ± 0.2	2.1 ± 0.2	2.4 ± 0.1	0.09 ± 0.02
	September	1.7 ± 0.1	9.2 ± 0.2	3.5 ± 0.1	3.2 ± 0.2	0.11 ± 0.01
4	July	5.9 ± 0.3	8.1 ± 0.4	3.6 ± 0.3	3.0 ± 0.3	0.12 ± 0.03
	September	7.4 ± 0.3	11.1 ± 0.4	5.3 ± 0.2	4.5 ± 0.3	0.16 ± 0.02
5	July	5.1 ± 0.2	12.4 ± 0.5	10.3 ± 0.4	6.3 ± 0.2	0.30 ± 0.04
	September	9.3 ± 0.2	18.0 ± 0.4	12.7 ± 0.4	7.9 ± 0.4	0.33 ± 0.04
6	July	2.8 ± 0.1	8.4 ± 0.2	3.2 ± 0.5	2.7 ± 0.3	0.13 ± 0.03
	September	3.8 ± 0.1	12.2 ± 0.2	4.0 ± 0.4	3.6 ± 0.3	0.15 ± 0.04
7	July	0.6 ± 0.2	2.3 ± 0.4	1.4 ± 0.4	1.2 ± 0.3	0.05 ± 0.02
	September	0.8 ± 0.2	2.8 ± 0.5	1.7 ± 0.3	1.4 ± 0.3	0.05 ± 0.02
General	Average (September)	6.8	12.4	6.7	5.5	0.20

SD: Standard deviation.
N: Number of samples.

phenomenon is the result of the accumulation and mixing of the various pollutants. Within the urban area, heavy metal concentrations on the bio-collectors are affected by many factors; for example, winds created by buildings and anthropogenic pollutants, which may be brought in from other areas. It is important to select a variety of contrasting sampling sites if the concentration of heavy metal on bio-collector, is to be used as an indicator of environmental pollution.

As can be seen in Table I, the average heavy metal concentrations in the city based on bio-collector samples were in the order Zn > Pb > Ni > Cu > Cd. The mean concentrations of metals are lower at site 7 compared to the other sites in the city. Concentrations of metals on bio-collectors were measured in industrial areas of the city as compared to residential areas. The mean concentrations of Pb, Zn, Ni, Cu and Cd in industrial areas were 12.1, 17.7, 12.4, 10.7 and 0.37 µg/g fresh bio-collector, respectively, while they were 17, 9.2, 3.5, 3.2 and 0.11 µg/g fresh bio-collector in residential areas.

Site 1 has higher vehicular traffic density. In Table I, the Pb levels are the lowest at site 7 (0.8 µg/g fresh bio-collector) and the highest by a factor of 9–16 at site 1 (12.8 µg/g fresh bio-collector), site 2 (12.1 µg/g fresh bio-collector) and site 4 (7.4 µg/g fresh bio-collector). Similar decreasing trends have also been observed for concentrations of Zn, Ni, Cu and Cd on the bio-collectors.

In general, most of the sites in Sivas showed a significant correlation between airborne Pb and vehicular (gasoline) traffic density indicating that automobiles exhaust emissions could be the prominent source of atmospheric Pb in the city [32], because of the usage of leaded petrol (150–400 mg/L) on the automobiles in Turkey. European threshold value for Pb pollution has been accepted as 8.0 µg/g dry bio-collector (*Populus Nigra*) [29]. The concentrations of Pb on the *Fabaceae Rabinia Pseudoacacia L.* sprouts at site 1 (25.6 µg/g dry bio-collector), site 2 (24.2 µg/g dry bio-collector), site 4 (14.9 µg/g dry bio-collector) and site 5 (18.7 µg/g dry bio-collector) in Sivas city are much higher than the threshold value. Pb levels of site 1 have been found to be three times more than the threshold value. The bio-collector Pb concentrations (3–25 µg/g dry bio-collector) observed in Sivas, Turkey are similar to that from Amman, Jordan [45] (7.3 µg/g dry *Anabasis Articulate*). However, they are lower than those from some larger cities including Hong Kong, China [46] (134 µg/g dry *Anabasis Articulate*) and Auckland, New Zealand [47] (180 µg/g dry *Anabasis Articulate*).

Higher levels of Zn and Cd in high vehicular traffic zones indicate that fragmentation of car tyres is a likely source of these metals [9,48]. Cd is released as a combustion product in the accumulators of motor vehicles or in carburettors. European threshold values for Zn and Cd have been accepted as 200.0 and 20.0 µg/g dry bio-collector (*Populus Nigra*) [29], respectively. Zn and Cd concentrations at all sites did not exceed the European threshold values. The bio-collector Zn concentrations (13–36 µg/g dry bio-collector) observed in Sivas are comparable with those from USA [9] (32–85 µg/g dry *Anabasis Articulate*) and Belgium [49] (37–114 µg/g dry *Anabasis Articulate*). However, they are lower than those from Amman, Jordan [45] (98.7 µg/g dry *Anabasis Articulate*) and Hong Kong, China [46] (124 µg/g dry *Anabasis Articulate*). Ni and Cu comes from corrosion of metallic parts of cars [22]. The bio-collector Cu concentrations (5–21 µg/g dry bio-collector) observed in Sivas are comparable with those from Auckland, New Zealand [47] (17 µg/g dry *Anabasis Articulate*) and Hong Kong, China [46] (17 µg/g dry *Anabasis Articulate*).

Machining and smelting of non-ferrous materials are responsible for enhanced concentrations of metals in the atmosphere of Sivas. We will try to distinguish between pollution, caused by municipal, coal combustion furnace, industrial and traffic in the city.

Background Levels

The concentrations of pollutants in the atmosphere depend on a variety of mechanisms, as well as on the uniqueness of each area, so that the assessment of background levels is problematic. There have been reports on atmospheric precipitation sampling procedure, and chemical properties and chemical composition have been studied in attempts to determine the composition of background aerosol [43,50]. Heavy metal concentrations on bio-collectors can be more reliably related to atmospheric concentrations if they are compared with their background level concentrations on bio-collectors from an urban area.

Because the concentrations of heavy metals in atmosphere depend on a variety of mechanisms, it has always been difficult to assess heavy metal pollution. The pollution factor (PF) was chosen as a general indicator of anthropogenic inputs to the heavy metal budget of the bio-collector samples. The limitations of this approach, caused by variable composition of the crustal components, are well known [51]. Nonetheless, in cases when PFs differ by orders of magnitude for samples collected in this same general area, they can be treated as a reasonably valid measure of the anthropogenic pollution. Any pollution over background levels in the considered bio-collector material can be called as anthropogenic pollution in the city atmosphere.

The PF as a simple and effective method for assessing of city atmosphere pollution is defined as the ratio of heavy metal contents in urban bio-collectors to the heavy metal contents in unpolluted bio-collectors (background level). Values for bio-collectors from site 7 were taken as background levels for Sivas; at this site, the heavy metal concentrations were at their minimum value.

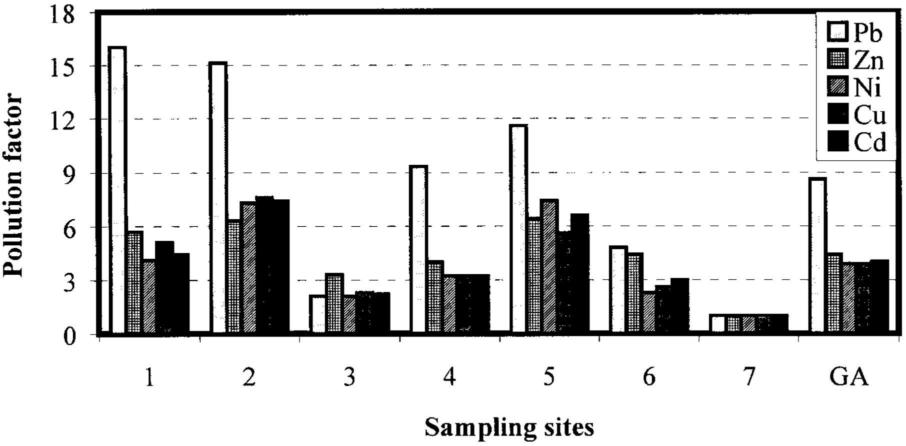

FIGURE 2 Average heavy metal PFs according to sites in Sivas for September-2000, GA: general average for all sites.

Pollutant Sources

Figure 2 shows a comparison of the average heavy metal PFs according to sites. The PF values obtained in our study show that Pb concentrations were about 16.0 times greater than the background levels as site 1, Pb, Zn, Ni, Cu and Cd were about 15.1, 6.3, 7.3, 7.60 and 7.4 times greater at site 2, and Pb, Ni and Cd were about 11.6, 7.4 and 6.6 times greater at site 5, in September, respectively.

As it can be seen in Fig. 2, the average heavy metal PFs are in the order Pb(8.6) > Zn(4.4) > Cd(4.0) $\geq$ Ni(3.9) = Cu(3.9), (general average for all months and sites). In accordance with previous results, the PF values of sites 1, 2 and 5 are the highest and site 3 is the lowest for all metals.

The Pb is highly enriched on bio-collector samples taken from sites 1, 2 and 5. The different level of Pb enrichment at these three sites is paralleled by the particulate material load, and reflects the relative volume of vehicular traffic in these three locations. The high Pb enrichment can be attributed to Pb from the automobile emissions [52] and accumulation of this element in the road dust [53]. High levels of Zn are present on bio-collector samples collected in the downtown. The proximity of the cement plant may be responsible for high levels of Zn at site 5, while its enrichment in the downtown bio-collector samples can be explained by the presence of Zn from tire wear in the re-suspended road way dust [53]. The Cd can come from a variety of local sources. Although Zn, Ni, Cu and Cd concentrations on the bio-collectors are relatively low according to Pb, the PFs indicate a strong anthropogenic input. Oil combustion and automobile emissions can be the main source of Cu and Ni.

It is considered that the PFs of heavy metals at each site are suitable for use as an index of atmosphere pollution. It appears that the city is under heavy Pb pollution while Zn, Cu, Ni and Cd pollution are lower.

These studies do not indicate the individual sources of heavy metal pollution of an environment. Central to all major questions concerning assessment of environmental pollution using trace and minor elements is the availability of a set of natural background values. A background value for any element may undergo extreme variations between different regions and even within a particular region, as a result of factors such as source-rock geology and weathering conditions.

CONCLUSION

The aim of this contribution was to define the essential characteristics of environmental pollution and the source of heavy metal pollution on the bio-collectors. This study demonstrated that bio-collector chemistry in the Sivas city atmosphere successfully reflects the magnitude of the local atmospheric deposition. The heavy metal concentrations on the bio-collectors clearly increased from July to September. In the cities, the heavy metal pollution on bio-collector was influenced more by traffic and industrialization than by population size. The highest heavy metal concentrations were found in the sites (sites 2 and 5) with industrial emissions and in the site 1 with heavy traffic. The lowest levels for the heavy metals on bio-collectors were found in the sites 3 and 7. The mean concentrations of the elements studied were in the order Zn > Pb > Ni > Cu > Cd.

The results found for the bio-collector samples showed that bio-collector samples contained significant levels of the metals studied compared with the background values. The PFs were fairly consistent with heavy metal pollution originating from anthropogenic sources. The PF can be used as simple and effective indicators of urban environment pollution. Although current level of Pb, Zn, Ni, Cu and Cd on the bio-collector samples from the Sivas city are within acceptable limits (except Pb), the trend of increasing industrialization and traffic in the city Sivas indicates the need for pollution control in the environment.

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