Asian Journal of Chemistry Vol. 13, No. 1 (2001), 78–88

Assessment of Atmospheric Pollution from Particulate Matter and Heavy Metals in Urban Environment of Tirana (Albania)

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The content of PM_{10} (particles smaller than about 10 μm in diameter) in the air and the concentration of seven heavy metals in the aerosol samples collected in three sites in Tirana city during the two year period (1997–1998) are presented. High particulate matter values, that exceeded in 82% of cases the WHO-AQG limit for TSP (100 μg/m^3) are found. Heavy metal concentrations in particulate matter (PM), especially lead and cadmium, are much lower compared to the respective levels in Europe and USA urban areas. A discussion of possible sources of particulate matter and heavy metals content is presented, based on obtained data and their statistical analysis using multi-variate techniques.

INTRODUCTION

Clean air is essential to urban life. Among the air pollutants considered, particulate matter (PM) is estimated to pose the greatest potential burden to health leading to various respiratory diseases and cancer[1]. Airborne particulate matter is recognized also as a significant source of many trace metals in the urban environment. Recent time-series analysis had shown that particles less than 10 μm in size (PM_{10}) were more relevant to health, because these particles may reach deep into the lungs and may be absorbed into the blood stream or cause lung or other health problems[3]. Amount of particulate matter is expressed usually as TSP or PM_{10} and its pollutant contents are fundamental measurements in the studies of environmental quality of urban air[2].

Important changes could be expected in the level and composition of urban air pollutants in Tirana, capital of Albania, during the last 10 years. As in many Central and Eastern European cities, particulate matter concentrations in Tirana air show upward trends, contrary to the downward trend observed in the majority of Western European cities during previous years[1, 4–6, 8].

High particulate matter levels originate from the combined effects of various emissions, generally from natural sources and from the combustion of fossil fuels. Road traffic could have a significant contribution to particulate matter emissions. Air quality in Tirana suffers the consequences caused by very rapid urbanization during the transition period. Urban population grew exponentially from 250000

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in 1990 to nearly 1 million in 2000. At the same period, the number of autos in Albania[6] grew from 6000 to more than 250 000. It can be expected that atmospheric particulate matter in Tirana environment is mainly composed of wind-blown dust originated from intensive traffic on the heavily damaged streets and from construction activities[7]. Local weather conditions prevailing are also relevant factors for the aggravation of the situation.[9]

This trend in Tirana air pollution is expected to continue and the share of traffic as an important cause of urban air pollution is also expected to increase. Great percentage of autos are old diesel engines, and particulate matter is associated primarily with diesel engines, with emissions 30–70 times greater than for petrol engines.[1] As a consequence the proportion of cases of acute or chronic respiratory system diseases attributable to prolonged exposure to high concentrations of particulate matter will be expected to be greater.

This is the first complete monitoring survey for the chemical characterization of atmospheric particulate matter in urban environment of Tirana providing useful information about the air quality in urban area of capital of Albania. The aim of this study is an assessment of PM_{10} levels and heavy metal concentrations in PM_{10} samples in urban air of Tirana city and evaluation of possible sources.

EXPERIMENTAL

Sampling: Samples of atmospheric particulate matter were collected during the two year period (1997–1998) in three urban sites situated in different areas of Tirana city. Some of the discernible characteristics of sampling stations are:

Station S1 ("21 Dhjetori") is situated in the western part of the city centre, in a very high traffic density zone;

Station S2 ("Baskhia") is situated at the city centre

Station S3 ("Spitali no. 3") is situated in a peripheral zone, east of the city centre with relatively low traffic density.

Sampling was performed using air sampler equipped with a modified filter head for PM_{10} collection. A sample of air whose volume is measured by a calibrated rotameter is drawn through a filter vacuum pump at a rate of 4 L/min for 3 days period. Four samplings in a month are performed, with a 3–4 days interval from one sampling to another. The sampling device is equipped with a timer which measures automatically the sampling time period. The sampling system employed Whatman membrane filters (37 mm diameter) with a pore size of 1.0 μm. Sampling and determination of particulate matter is carried out by specialists of Air Section in Institute of Public Health at Tirana.

PM_{10} measurement: The amount of PM_{10} in the air is measured by weighing the filter before and after sampling. A Varian Spectr. AA-200 flame AAS equipped with deuterium background correction facility is used for heavy metals analysis. The parameter optimization for each element determined is carried out according to the operating manual of instrument. Analytical reagents grade chemicals and double de-ionized water are used.

Digestion of samples for chemical analysis: Acid digestion procedure was used for air filters analyses by AA. The filter was kept overnight in 5 mL aqua regia in a closed teflon beaker, then evaporated to dryness at ~100°C. 2 mL of 2 M HNO_3 solution were added and the solution was allowed to stand for 1 h at room temperature. The filter was then removed and the remaining solution was then quantitatively transferred to a 10 mL volumetric flask and diluted to the mark with double de-ionized water. A filter blank was digested in the same way as the sampling filter.

Quality control of chemical analysis: A soil CRM prepared by Joint Research Center ISPRA is used as a reference material for analyses of filter samples, in absence of a certified filter medium.

RESULTS AND DISCUSSION

Descriptive statistics of the data: PM_{10} levels during 1997–1998 in three sampling stations are shown in Tables 1 and 2, whereas heavy metal concentrations in the aerosol samples are shown in Table-3.

TABLE-1
OVERALL STATISTICS OF PM_{10} VALUES (IN μg/m^3) DURING 1997–1998 IN URBAN AREA OF TIRANA

Parameters	All samples	Year		Season			
		1997	1998	Spring	Summer	Autumn	Winter
Number of samples	137	103	34	32	31	30	44
Geometric mean	149.08	147.5	153.97	147.24	126.47	133.3	182.29
Volume weighted mean	154.5	152.41	160.49	146.01	132.49	143.28	187.79
Standard deviation	96.914	100.46	86.641	78.015	54.782	67.985	130.21
Percentiles 10%	83	83	93.8	100.5	76.8	81.3	101.5
90%	283.5	281.5	294.6	256.4	202.8	220.3	388.1

Geometric mean values (GM) and volume weighted means (VWM) are given in both Tables 1 and 2, because they represent our data. It can be seen from frequency histogram of particulate*matter*$_{10}$ data (not presented) that distribution curve is very close to a log-normal (Chi-Square value is 5.847 with 6 d.f. and Kolgomarov-Smirnov test has a significant level 0.8772). All GM values are smaller than respective arithmetic means but very close to VWM and median values. In fact, VWM characterize better average values of particulate*matter*$_{10}$ in air in the case when different air volumes are sampled, because using the formula

$$c = \sum_i (c_i V_i) / \sum_i V_i$$

For calculating the VWM values, the effect of air volume is eliminated.

TABLE-2

PM_{10} LEVELS (IN μg/m^3) MEASURED DURING 1997–1998 IN THREE URBAN SITES OF TIRANA

Sampling site	Parameter	All samples	Year		Season			
			1997	1998	Spring	Summer	Autumn	Winter
S1 (21 Dhjetori)	n	48	37	11	10	11	11	16
	GM	196.63	196.03	198.66	183.96	167.95	166.91	255.69
	VWM	197.33	196.24	200.11	181.97	167.19	184.16	255.99
S2 (Bashkia)	n	48	34	14	13	10	9	16
	GM	141.81	140.29	145.57	132.50	101.28	129.48	194.64
	VWM	146.21	144.1	151.78	134.02	104.29	128.84	196.66
S3 (Spitali 3)	n	41	32	9	9	10	10	12
	GM	114.31	111.97	123.04	133.89	115.6	106.86	106.39
	VWM	115.19	113.83	117.01	117.49	122.2	110.93	115.85

Table-3 shows arithmetic mean values of heavy metal concentrations in atmospheric particulates.

TABLE-3

AVERAGE VALUES OF HEAVY METAL CONTENTS IN ng/m^3 IN ATMOSPHERIC PARTICULATE MATTER OF TIRANA AND RESPECTIVE LEVELS IN SOME OF URBAN AREAS IN EUROPE AND USA

Metal	Overall mean	Year		Sampling station			Period		Levels[2] in areas of	
		1997	1998	S1	S2	S3	Summer	Winter	Europe	USA
Cu	27.6	28.9	25.4	40.2	21.4	17.9	19.3	35.1	13–2760	3–5140
Zn	94.6	92.0	99.1	130.1	79.9	62.1	69.2	117.5	160–8340	15–8328
Pb	103.9	100.9	108.8	123.3	106.3	64.9	80.6	128.1	10–9000	30–96270
Cd	2.90	2.79	3.19	1.73	4.54	1.78	2.77	2.99	0.4–260	0.2–7000
Cr	21.7	22.3	20.1	36.9	17.0	10.3	17.4	26.5	3.7–2777	2.2–124
Ni	21.7	24.8	19.7	35.9	17.6	18.8	18.8	28.4	0.3–1400	1–328
Fe	3574	3213	4192	5020	2502	3187	3032	4061	294–13000	130–13800

Discussion about PM_{10} data (Tables 1 and 2)

(a) PM_{10} levels in the air of urban areas of Tirana present relatively high values. Annual mean PM_{10} concentration results in about 150 μg/m^3, exceeding 3 times US Air Quality Standards (50 μg/m^3). More than 82% of our data[1] exceed the TSP WHO-AQG limit of 100 μg/m^3.[1] Taking into consideration that often

PM_{10} represents between 0.4–0.6 of TSP[4, 5] (no data exist about particle size distribution in our samples), the above percentage of TSP limit exceeding must be much higher. Tirana can be considered one of the highest particulate-contaminated capital in Europe. It has to be noted that because of the different monitoring methods the data are not directly comparable but however we can see that particulate matter concentrations for Tirana are comparable with those of Athens centre (reported for 1991–1992)[1], but much higher than those of majority of European capitals, typically 50–100 $\mu g/m^3$ (ranging from 30 $\mu g/m^3$ for London to 100 $\mu g/m^3$ for Moscow).[1]

(b) Atmospheric pollution concerning PM_{10} concentrations in Tirana is more critical for some urban areas and during winter season. From the data presented in Tables 1 and 2, and from the histograms shown in Figure 1 could be observed

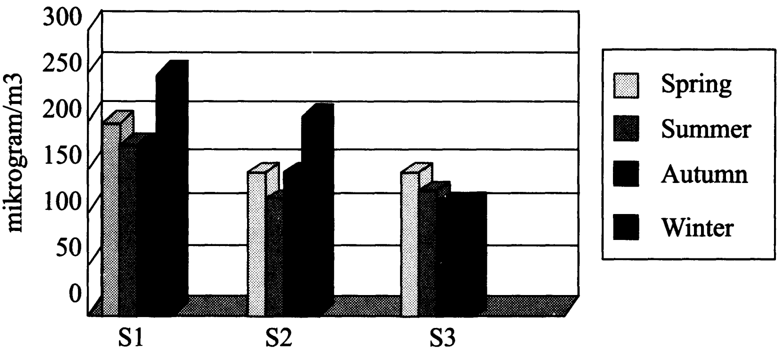

Fig. 1. Levels of PM_{10} in three sampling sites for each of the seasons

a significant distinction between three sampling stations: the most contaminated station was station S1, situated in the highest traffic density area, whereas the least contaminated station was S3 situated in the outskirts of the city. From one-way ANOVA results a significant spatial differentiation between three sites: F value for 95% is 13.53 with significance level = 0.0000 for d.f. = 136.

There is no apparent distinction between yearly averages of 1997 and 1998 (F = 0.016, d.f. = 136 and sign. level = 0.902). But PM_{10} levels belonging to winter period are higher than those belonging to the other seasons. ANOVA results for four seasons are: F = 5.263, with 136 d.f. and sign. level 0.0018. From Fig. 1 could be seen that this statement is valid for all data and for each station separately. It is interesting to compare the results of ANOVA for three sites in different seasons, presented in Table-4. From Table-4 it is clear that distinction between sampling stations becomes more evident in the direction from spring to winter. This indicates that besides the influence of traffic density, meteorological factors should have also some impact on PM_{10} content in air. Such factors can be wind intensity and direction, temperature inversion and precipitation.

Particularly very high PM_{10} levels result in the sites S1 and S2 during winter period, reaching 200–255 $\mu g/m^3$, exceeding the WHO limits by more than two times.

TABLE-4
ONE-WAY ANOVA FOR THREE SAMPLING STATIONS IN EACH SEASON

Season	$F_{(0.95)}$-value	Significance level	Degree of freedom
Spring	1.544	0.2305	31
Summer	4.613	0.0186	30
Autumn	5.341	0.0111	29
Winter	9.167	0.0005	43

(c) No doubt that high PM_{10} levels in Tirana air present a great health risk to the inhabitants. Among the air pollutants PM is estimated to pose the greatest potential burden to health. It is reported that in cities with high dust concentration, the proportion of cases attributable to pollution reaches 23% of asthma and 11% of obstructive airways diseases (OAD)[1]. Besides acute or chronic respiratory system diseases, which are the most common health effects of air pollution, some components of air pollution may increase the risk of cancers[1]. Some studies conducted in the United States have shown that long-term exposure to particulate matter are associated with reduced survival[3, 4].

Unfortunately there are no reliable data concerning the respiratory diseases related to particulate matter level in Tirana air.

Discussion about heavy metals concentration data (Table 3)

(a) Heavy metal content values in particulate matter samples are much lower compared with the average values of heavy metals in urban atmosphere of Europe and USA (Table-3). The only exception is iron showing higher level in all our samples. Two principal causes can explain the relatively low heavy metal concentrations in particulate matter of Tirana: (i) scarce emissions of heavy metals in air from anthropogenic sources, mainly from car engines, and (ii) "dilution" of contaminated atmospheric dust from natural dust, wind-blown and originated from land erosion.

(b) From all toxic metals in air, lead is considered the most important pollutant, and its contents characterize the heavy metal pollution of urban atmosphere. Norms and limits have been established for lead concentration in urban air. WHO-AQG (1987) for Pb is 0.5–1.0 $\mu g/m^3$, and Quality Standard of European Community specifies the limit of 2 $\mu g/m^3$. Average values of lead concentration in Tirana urban air are much lower than above mentioned limits, and they are comparable to the lead content reported for rural areas of Europe. This is explained mainly because of limited use of leaded petrol and the lack of other anthropogenic sources of lead emission.

(c) There is an apparent distinction between three studied sites related to the concentrations of heavy metals in the particulate matter samples. The conclusions are the same as for the PM_{10} data. The level of metal concentration for most metals in samples taken from S1 are about two times higher than the level of respective metal concentration in the samples from S3 (Fig. 2). There are no significant differences between the yearly average results for 1997 and 1998, but the levels of heavy metals are apparently higher during the winter period in comparison with other seasons. ANOVA calculations support the above-mentioned conclusions.

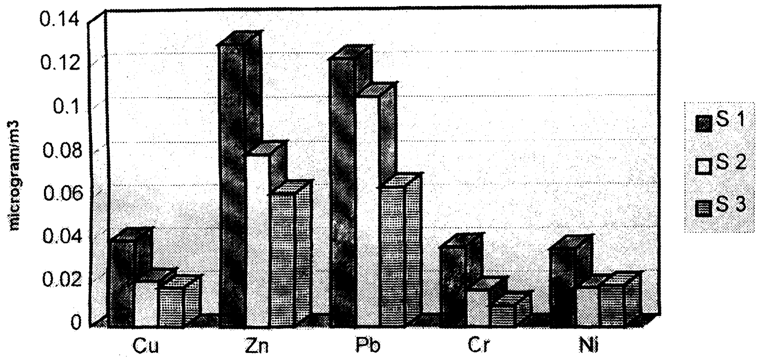

Fig. 2. The levels of heavy metals in the PM samples taken for three sampling sites

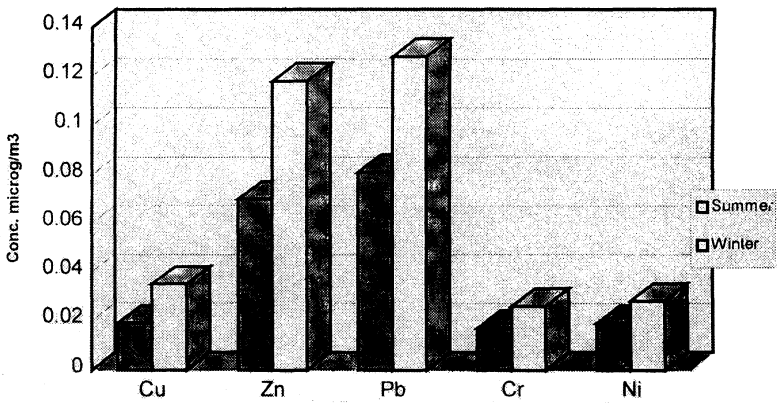

Fig. 3. The levels of heavy metals in the PM samples of two seasons

Statistical analysis

(a) Correlation between analytical data: Specially very good linear correlations exist between metals Cu-Zn-Ni-Fe, showing coefficients of correlation $r > 0.7$ and sign. level < 0.001. Lead correlates only with zinc ($r = 0.76$, sign. level = 0.0002), whereas cadmium does not present any significant correlation with other metals studied.

The high correlation coefficient values for Cu, Zn, Ni and Fe suggest common sources for respective elements, perhaps from wind-blown street dust.

It is interesting that very strong linear correlation exists between mass of PM_{10} and metal concentration in air for each of the metals Cu, Zn, Ni and Fe ($r \geq 0.78$, sign. level = 0.0000). This indicates that the sources of those elements make a main contribution to the particle concentration in air. Lead and cadmium do not show any significant correlation with particulate matter mass, indicating that they originated mainly from anthropogenic sources.

(b) Multivariate analysis: Multivariate statistical techniques, principal component analysis (PCA), factor analysis and discriminant analysis were used for two main purposes: (i) to identify those components (elements) which are of common origin (natural or anthropogenic), and (ii) to form subgroups of elements which would lead to source attributions for those groups.

Principal component analysis is used to obtain an overview of the data and to detect clustering. The results indicate that the sum of the first two principal components is 82.6%. That means that the other components explain little of the data and they contain most of the random errors. Table-5 presents factor matrix

TABLE-5
FACTOR MATRIX

Variable	Factor	
	1	2
Copper	0.90405	–0.00301
Zinc	0.85974	0.11690
Lead	0.77597	0.40938
Cadmium	–0.17920	0.94437
Chromium	0.87856	–0.08707
Nickel	0.96061	–0.09618
Iron	0.89237	–0.08660

for each of the elements using the first two discriminant factors. Plots of the first two factor weights are shown in Fig. 4. Elements Cu, Zn, Fe, Ni and Cr form a

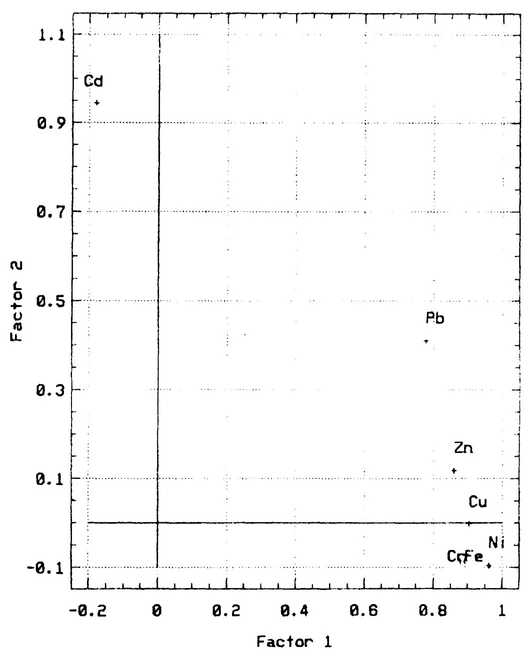

Fig. 4. Plots of first two tactors weights

separate group having similar values of factors 1 and 2, whereas cadmium and lead show very different factor values 1 and 2 from the other elements.

Discriminant analysis is used to establish group differences. Table-6 shows standardized discriminant function coefficients using sampling sites as discriminant factor. Fig. 5 shows a plot of the discriminant scores for each of the samples using the first two discriminant functions. The plot shows that the groups are clearly separated and that means that there is no overlap between sampling sites studied.

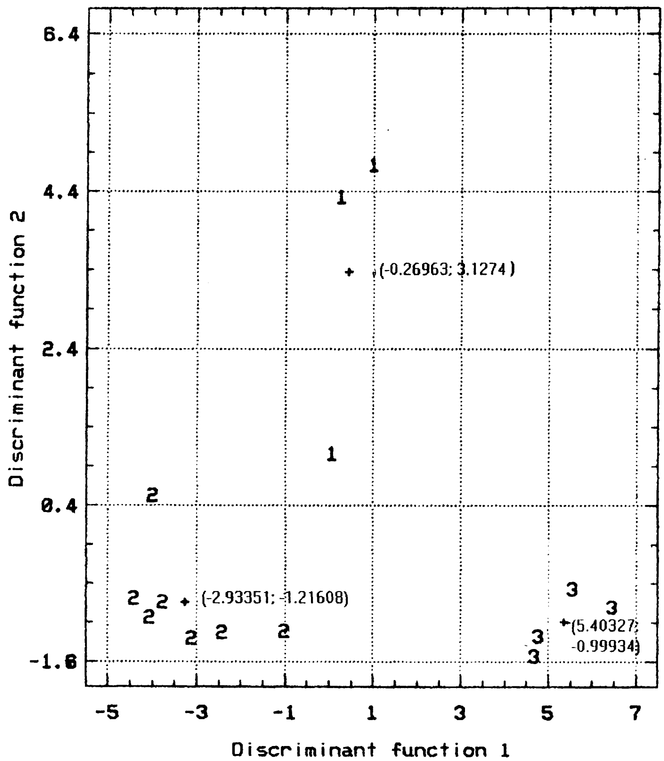

Fig. 5. Discriminant analysis. Discriminant factor: sampling sites

TABLE-6
STANDARDIZED DISCRIMINANT FUNCTION COEFFICIENTS

Element	Function coefficients	
	1	2
Copper	–6.86907	–0.74278
Zinc	–0.07726	0.76100
Lead	–0.19482	–0.27119
Cadmium	–0.98611	–0.34464
Chromium	–3.87490	0.75918
Nickel	6.36060	0.62277
Iron	3.76479	–0.14691

Three group means (centroids) determined by averaging the scores are marked by respective crosses in Fig. 5.

The results from the statistical analysis mainly support the conclusions mentioned.

Conclusions

1. Tirana can be considered one of the highest particulate-contaminated capital in Europe. More than 82% of PM_{10} measurements exceed the TSP WHO-AQG limit of 100 $\mu g/m^3$. Atmospheric pollution concerning particulate matter in air is more critical for some urban areas presenting high traffic density, and particularly during winter period, reaching up to 200–250 $\mu g/m^3$.
2. Concentration of heavy metals in particulate matter samples was much lower than those reported for urban air in Europe and USA. In particular, very low lead level resulted, showing the lack of important anthropogenic sources. Significant differences exist between heavy metal content in the samples from various sampling sites and between summer and winter periods, similar to those resulted for PM_{10} levels.
3. The main source of particulate matter in Tirana air is wind-blown dust and sand, originating from the damaged streets, building activities, road transport and lack of appropriate management of solid wastes. Lack of other important anthropogenic sources such as industrial emissions is the main factor explaining the very low heavy metal levels. Statistical multivariate results support these conclusions.
4. At present further information about pollution sources and their contribution cannot be extrapolated from our data. For this purpose, a more complete study, taking into consideration also meteorological data, should be taken into account.
5. Air pollution from particulate matter could pose some health hazard to inhabitants directly through inhalation and indirectly when they are deposited and taken up by vegetation and in such a way they may enter into the food chain, resulting in exposure to humans and animals. This is a real risk for inhabitants in Tirana, because certain trace metal compounds can be associated with road dust and these associations influence the relative mobility and bio-availability of trace metals in environment.

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(*Received*: 8 July 2000; *Accepted*: 13 September 2000) AJC-2132