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Atmospheric Deposition of Pb, Zn, Cu, and Cd in Amman, Jordan

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Atmospheric samples were collected using a low-volume air sampler and dustfall containers during the summer of 1995 at different sites in the city of Amman, Jordan. The heavy metal contents in settleable particles (dustfall) as well as in air particulates (suspended) were analyzed by graphite furnace atomic absorbation spectrophotometry. The atmospheric concentrations of Zn, Cu, Pb, and Cd were 344, 170, 291, and 3.8 ng/m^3, respectively. The levels of these elements in the dustfall deposition were 505, 94, 74 and 3.1 μg/g, respectively. The fluxes and dry deposition velocities of these heavy metals were determined and compared with the findings of other investigtors worldwide. The enrichment coefficients of the heavy metals in the dustfall were found to be significant. The enrichment coefficients were 12.1, 6.1, 11.7, and 1.1 for Zn, Cu, Pb, and Cd, respectively.

Key Words: heavy metals, air particulates, dustfall, atmospheric deposition, Jordan.

Introduction

The anthropogenic impact on the natural environment and especially on atmospheric pollution is well documented in many prats of the world[1−3]. Pollutants can be in many forms and levels of toxicity, and among them are trace elements which are known for their toxicity when they occur above certain levels. These pollutants are emitted into the atmosphere continuously through various human activities, especially in large cities where inhabitants and industrial activities are concentrated. Airborne pollutants are depleted continuously from the atmosphere through two major routes: dry and/or wet deposition. The predominant path depends upon the type of chemical species and upon meteorological factors such as the intensity and distribution of rain fall.

Atmospheric particulates are usually of two types; suspended and settleable particles. However, the settling velocity depends upon the size of the particles. Differences can be expected in the physical and chemical properties of both types of particles. Studying such differences could be helpful in producing information about air quality and sources of pollutants. Heavy metal pollution of the atmosphere can be estimated by determining the concentration of these heavy metals in suspended and settleable particles. This is because the heavy metals are associated with the solid particulate matter in many forms.

Lead is one of the metals of most interest in environmetal samples. Many investigators have concentrated on the determination of lead alone in particulate matter[4,5]. Other heavy metals have also been extensively studied[6−9].

Atmospheric pollution in Amman has received little study, and this has mostly been in the form of internal reports. In previous investigations, we studied the cationic and anionic composition of air particulates in Amman[10,11] The aim of this study was to investigate heavy metal concentrations in settleable and suspended particulate matter as well as deposition rates in the atmosphere of Amman. In fact, this is the first data published in terms of freely available literature on the levels of heavy metals in the atmosphere in Amman, Jordan.

Experimental, Sites, and Methods

Settleable and suspended particulates were collected from the atmosphere at different sites in Greater Amman (Figure 1) during the summer of 1995 in order to show the effects of different activities on the level of Pb, Zn, Cu, and Cd in the atmosphere.

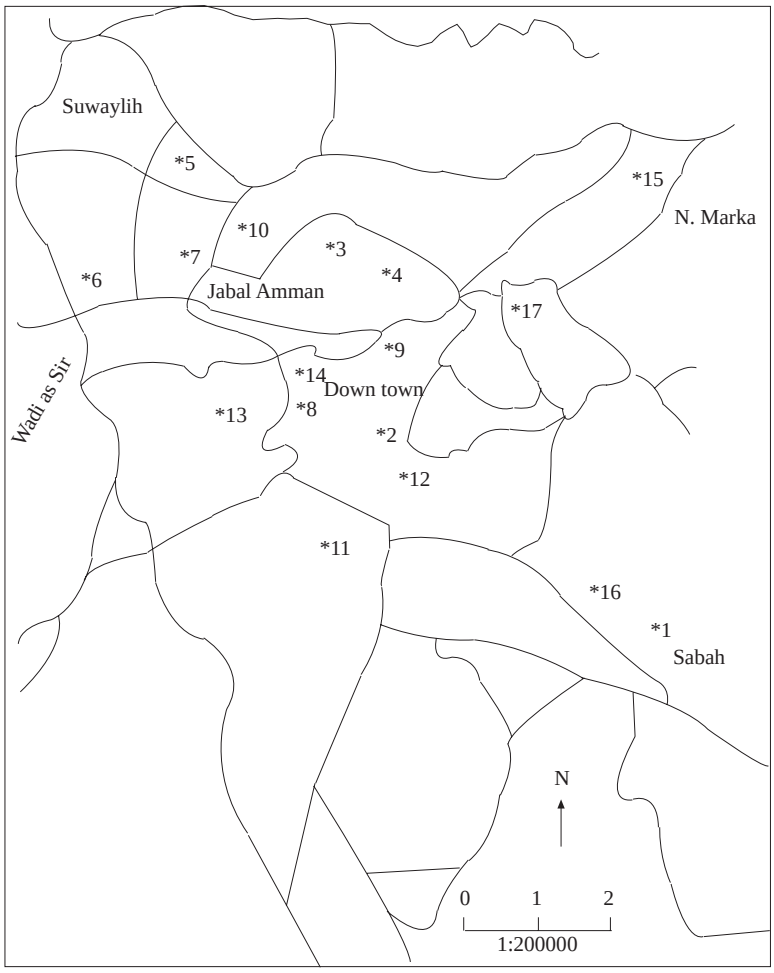

Figure 1. Location map of the sampling sites(*)

Dustfall samples were collected from the same sites as those for suspended matter at a height of 10 m using dry polyethylene cylindrical containers. The dimensions of these containers were 31 cm in heihgt and 15.5 cm in diameter. They were mounted on 1.5 m-high tripods to avoid the collection of dust picked up by wind eddies. There was a bird ring on each holder in order to avoid material from brids. The collectors were exposed to the atmosphere for a sampling period of 30 to 44 days. It should be noted that the measurements represent dry deposition only, as there was no rainfall during the sampling period.

The dry deposits (settleable particulates) were quantitatively tranferred from the collectors to quartz crucible using milli-Q water. The content of the crucibles was dried at 105 °C to a constant mass, and then it was weighed and the quantity of dustfall was computed in $\mu g/m^2$ month. About 0.10 g of the dired samples was accurately weighed and extracted with concentrated ultra-pure nitric acid, sonicated for 30 min in a test tube heater for one hour, left overnight, and then the solutions were filtered and diluted with 1% HNO_3 in 25 mL polyethylene volumetric flask to the mark. The blanks were treated in a similar way to the samples.

Suspended particulate matter was collected simultaneously from these sites by drawing air through weighed Whatman membrane filters (47 mm in diameter, 0.2 μm pore size). The suspended particles were collected for 12-hr periods using a low-volume air sampler (Stuplex Air Division, Brooklyn, NY, USA), at a flow rate of 20 L/min The sampler was mounted 10 m above the ground so that dust would not be collected from the ground and only local airbone particulates would be obtained. Pb, Cu, Cd, and Zn were leached from the air particulate samples by treating the filter samples with 5 ml concentrated nitric acid, 1 mL HCl (both acids were of ultra-purity) and 19 mL Milli-Q water. The samples were left overnight after being treated in an ultrasonic cleaner for 30 min, and then filtered. The filtrate was evaporated to near dryness and filled to 25 mL with 1% nitric acid (ultra-pure). Blank filters were treated in a similar manner to the samples.

Pb, Zn, Cu and Cd in the dustfall as well as in the suspended particulate samples were analytically determined using Graphite Furnace Atomic Absorption Spectrophotometry (GF-AAS) with a Varian Model, GTA 100.

Results and Discussion

Heavy Metal Concentrations in Air

The average level of particulate matter collected on the filters was 0.417 mg/cm^2 and the range was from 0.06 mg/cm^2 at site 11, which represents a suburban area, to 0.56 mg/cm^2 at site 9, which is an urban area with heavy traffic and a large bus station.

The levels of Zn, Cu, Pb and Cd in the atmosphere of Amman are summarized in Table 1. Zinc was recorded in the highest quantities 21.6-1539 ng/m^3, while Cd had the lowest levels 0.20-16.6 ng/m^3. The highest levels of heavy metals were found in densely populated parts of the city with high traffic density, such as sites 7, 9, 12, and 14. The large variability in the concentration range and standard deviation was expected, since the samples were collected from different sampling sites, which are characterized by different types of activity and different pollution sources.

Table 1. Atmospheric concentrations of Zn, Cu, Pb, and Cd (ng/m^3) in Amman (n=51,3 samples were taken from each site).

Element	Mean±SD	Min	Max
Zn	344±582	21.6	1539.0
Cu	170±224	6.4	1139.0
Pb	291±223	2.2	1091.2
Cd	3.8±3.6	0.2	16.6

The correlation coefficient (r) was calculated from the element concentrations in order to predict the possibility of a common source. The r values were low, except for the correlation between Pb and Cd (r = 0.76), which may indicate that these metals have a common source; possibly automobile emissions.

Table 2 represents a comparison of the heavy metal concentraitons in the atmosphere of Amman with other places worldwide. The table illustrates that our values are generally higher than those found in Cairo[3], the Black Sea[12] and New-Zealand[14] Bombay[22] for lead and comparable to those found in Santiago[13] for zinc. However, our values are much lower than those found in Riyadh[2] for Cu and Pb and comparable to those found in Bombay[8] for Cd, Cu, and Pb.

Table 2. Average atmospheric levels of Zn, Cu, Pb, and Cd (ng/m^3) compared with other results reported in the literature.

Location	Zn	Cu	Pb	Cd	Reference
Bombay/India	600	116	300	5	8
Riyadh/Saudi Arabia	207	1257	1850	-	2
Black Sea	-	-	51	-	12
Santiago/Chile	310	220	-	-	13
Cairo/Egypt	428	904	47.6	-	3
New Zealand	34.9	10.4	112.6	0.41	14
Amman	344	170	291	3.8	This study

Dry Deposition

The average quantity of settleable particulates deposited at the seventeen sampling sites was 163.6 mg/m^2.day, and the range was from 80.4 mg/m^2.day at site 6 to 212.4 mg/m^2.day at site 7. The mean value in this study is lower than that found in other places such as Jamaica[6], 198.6 mg/m^2. day, and Cairo[3], 475 mg/m^2. day. These figures may indicate that Amman is less polluted than Jamaica and also significantly less polluted than Cairo in terms of settleable particulate matter.

The dry deposition was sampled and analyzed for zinc copper, lead, and cadmium. The results are shown in Table 3. A large variation in the concentrations of these metals was observed. The table shows that zinc has the highest and cadmium has the lowest levels. This phenomenon is similar to that found for the suspended particulates shown in Table 1. A comparison of the average concentrations of heavy metals in suspended and settleable particles, expressed in terms of μg/g, shows higher values in suspended particles; about 2, 8, 7.5 and 4.8 times higher for Zn, Cu, Pb, and Cd, respectively. This indicates that a small portion of these heavy metals are removed from the atmosphere by gravitational settling, which may be due to the small particle size of the suspended dust, causing them to be suspended for long periods in the air.

Table 3. A heavy metal concentrations (μg/g) in dustfall in Amman (n=51, 3 samples were taken from each site).

Element	Mean±SD	Min	Max
Zn	505±476	65.1	1754.8
Cu	94±202	7.1	882.2
Pb	74±49	17.9	182.9
Cd	3.1±3.3	0.3	12.0

The enrichment coefficients of the heavy metals were estimated and these are summarized in Table 4. The enrichment coefficient was computed as the ratio of the heavy metal concentration in the settleable particulates (dustfall) to the concentration in the soil collected and analyzed at the same time[6]. The values in the table indicate high enrichment of the dustfall with Zn, Pb and Cu. The high values of enrichment coefficients suggest that these elements are anthopogenic in origin, for example, from the emissions of motor vehicles. The enrichment coefficient for Cd was close to unity, which suggests that the origin of the cadmium is mostly the local soil.

The dry deposition rates (fluxes) of the heavy metals are shown in Table 5. Zinc had the highest rate, and Cd the lowest rate of deposition. This is consistent with the conclusions drawn from Table 3. Zince had the highest deposition rate as well as the lowest distribution ratio in suspended to settleable particles.

Table 4. Enrichment factor of heavy metals deposites at the 17 sampling sites in Amman.

Element	Enrichment factor	
	Average	Range
Zn	12.14	1.78-35.88
Cu	6.06	0.59-54.46
Pb	11.74	3.14-25.76
Cd	1.11	0.45-3.75

Table 5. Fluxes of Zn, Cu, Pb and Cd (μg m^{-2} mon^{-1}) in dry deposition in Amman.

Element	Mean±SD	Min	Max
Zn	2474.4±2596	385.0	9262.8
Cu	462.8±1057	20.1	4656.8
Pb	349.8±245	64.9	990.1
Cd	12.5±12.7	1.2	45.7

An evaluation of the relationships between the fluxes of the heavy metals revealed that some correlations exist, such as those between Cu and Zn (r = 0.66), Cu and Cd (r = 0.65), and Zn and Cd (r = 0.48). These values may indicate that these metals have a common source.

A comparison of our results with other data worldwide (Table 6) indicates that our Zn and Cu levels are higher than those recorded in Jamaica[6], the North Sea[15] and the West Mediterranean[16], but they are lower than those recorded in Bombay[8]. The cadmium level in the present study is also higher than those determined in these places, except for Jamaica[5] and the North Sea[15]. However, the lead levels are comparable to other values found worldwide.

Table 6. Fluxes of heavy metals (μg m^{-2} mon^{-1} compared with other results reported in the literature.

Location	Zn	Cu	Pb	Cd	Reference
Bombay/India	3097.0	785.8	269.9	3.28	8
North Sea	920.5	167.7	453.7	19.4	15
Jamaica	1525.5	332.1	450.4	184.8	6
W. Mediterranean	361.6	31.6	345.2	4.3	16
Amman	2474.4	462.8	349.8	12.5	This study

Dividing the deposition fluxes by the atmospheric concentrations of the metals gives the dry deposition velocities. Table 7 summarizes the mean dry deposition velocities of Zn, Cu, Pb, and Cd in the atmosphere of Amman. Large variations in the deposition velocities were observed. Zinc shows the highest deposition velocity while Pb has the lowest. Table 8 shows some values for deposition speeds found by other investigators. Generally our results show lower deposition speed than most of those in the table. This may be due to local sources and meteorological factors. The low deposition speeds indicate that these elements may be present in small particles, which will have low deposition velocities.

Table 7. Deposition velocities of Zn, Cu, Pb, and Cd (cm s^{-1}) in Amman.

Element	Mean	Min	Max
Zn	0.274	0.023	0.564
Cu	0.104	0.030	0.401
Pb	0.046	0.010	0.110
Cd	0.125	0.023	0.431

Table 8. Deposition velocities (cm s^{-1}) heavy metals compared with some results reported in the literature.

Zn	Cu	Pb	Cd	Reference
0.50	-	<0.50	-	17
-	-	0.30	-	18
0.40	0.29	-	0.20	19
0.50	0.81	0.28	0.10	8
-	-	0.25-1.80	-	4
0.35	0.48	0.25	0.39	15
-	-	0.04	0.05	20
0.22	0.22	0.22	0.22	21
0.27	0.10	0.05	0.12	This work

Conclusions

Based on our study of toxic heavy metals in the atmosphere of Amman the following conclusions can be drawn:

Zinc is the major heavy metal pollutant in settleable as well as suspended particles. However, Cadmium is the most minor pollutant in both types of particle.

The concentrations (μ/g) of Zn, Cu, Pb, and Cd are higher in suspended than in settleable paticulate matter. This may indicate that these heavy metals exist as fine particles. The dry deposition velocities

of the studied elements were generally found to be lower than others found worldwide. The enrichment coefficients of the heavy metals in the dustfall were found to be greater than the unity, which suggests that the sources are anthropogenic.

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