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Original Research

Chemical Characteristics of Settled Particles during a Dust-Storm

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Abstract

Major synoptic systems bring desert dust from Arabia and the Sahara to Anatolia, Turkey. A study of particulate matter (PM) associated metal content such as As, Al, Cr, Cd, Co, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Sn, and Zn, etc., has been carried out for Diyarbakir, SE Anatolia, Turkey. Results show that the PM_{10} levels during a dust storm were much higher than in a non-dust-storm period and that four metals (Fe, Al, Cr, Mn) were dominant in settled particles. This research does not only provide background data for air quality management, but also provides valuable information about the chemical composition of the particles.

Keywords: air pollution, dust storm, metal, particulate matter, Anatolia, Turkey

Introduction

A dust storm is a physical phenomenon associated with suitable meteorological conditions over arid and semi-arid regions and it is generated when a gust front passes over these regions or when the wind force exceeds the threshold value above which loose sand and dust are removed from the dry surface [1, 2]. According to the Earth Observatory (earthobservatory.nasa.gov/intense) dust outbreaks are considered natural hazards, which may affect global and regional radiative balance, modify cloud microphysical properties, trigger tropical cyclone activity, disturb atmospheric heating and stability, and influence photolysis rates, ozone chemistry, ecosystems, marine environments, phytoplankton, and human health [3]. The residence time of dust particles depends on dust-particle size, meteorological conditions, and wind speed and precipitation that favor dry and wet deposition, respectively. Atmospheric aerosols consist of particles of both natural and anthropogenic origin. The impact of mineral dust aerosols on the Earth's system depends mainly on particle characteristics such as size, shape, and mineralogy, which are initially determined by the terrestrial sources from which the soil sediments are entrained. While these characteristics can change during dust transport. Crustal aerosols influence atmospheric radiative balance through the scattering and absorption processes, and by acting as cloud condensation nuclei when sulfation and nitration occur. Dust particles frequently act as surfaces on which gaseous species react; a reaction surface for atmospheric gas/particle interactions related to nitrogen and sulfur cycles and acid/base balance; and a source for a number of trace substances, and the secondary particulate matter (PM) may greatly increase when dust particles are present in the atmosphere [4, 5].

The composition of atmospheric PM is important relative to their effects on visibility biogeochemical cycles and human health [6]. Desert dusts are probably the most abundant and massive type of PM present in the atmosphere worldwide. The Sahara produces more aeolian soil dust than any other world desert, and Saharan dust has an important impact on climatic processes, nutrient cycles, soil formation, and sediment cycles [7]. Saharan dust has important influences on nutrient dynamics and biogeochemical cycling in both oceanic and terrestrial ecosystems in North Africa and far beyond, due to frequent long-range transport across the Atlantic Ocean, the Mediterranean Sea, the Red

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Sea, to the Americas, Europe, and the Middle East. Recently, poor management of the Earth's drylands, such as neglecting the fallow system, is increasing dust storms from desert borders and changing both local and global climates, and impacting local economies [8, 9]. The mineral dust adds directly to anthropogenic particulate pollution, and mineral dust particles are coated by anthropogenic pollutants such as sulfates, nitrates, pesticides, PAHs and heavy metals [10-15]. It can also carry several thousand types of microorganisms that can affect plant, animal, and human health.

Atmospheric pollution is one of the major sources of heavy metal contamination. Elemental content of airborne particulate matter can provide important information on the degree of atmospheric pollution and further evaluation of the potential health risk to the population. Several epidemiological studies have shown positive correlation between different aerosol characteristics and increased human morbidity and mortality [16, 17]. Moreover, the airborne particles significantly influence several atmospheric processes, for example the formation of clouds and changes in the radiative transfer of solar radiation. For these reasons it is necessary to know their chemical composition and physical characteristics in order to understand their behavior and impact [18]. To achieve this, we need availability of data that is as reliable and complete as possible. However, the analytical techniques most frequently used to monitor PM require expensive and time-consuming procedures to collect, process and analyze samples [19]. The September 2008 dust events have been verified by most ground-based stations and satellite observations. The dust was transported north out of the Syrian Desert into Iraq, Syria, and Jordan.

This article investigates the impact of the dust storm on Diyarbakir's atmosphere by examining PM_{10} concentrations and the concentrations of some elements found in dust particles. This study will provide valuable information on the chemical characteristics of dust storm particulates.

Materials and Methods

Diyarbakir (40º14'N, 37º55'E, 670 m above sea level), a metropolitan city with a population of 3 million, is located in SE Anatolia, of Turkey. Sampling of dust particles was carried out during 9 September 2008, at a site located in a suburban area to the east of Diyarbakir city center, between the main University Campus, Dicle University, and Diyarbakir airport. The sampling site was chosen for this study because the levels of emissions of anthropogenic air pollutants are very low. Eight sites in addition to that in the University Campus that are least influenced by local sources were selected to investigate the influence of a September 2008 dust storm on Diyarbakir's atmosphere. Settled dust particles were collected in polyethylene cylindrical containers (dimensions: 40 cm in diameter, 20 cm in height) installed on 25 cm high tripods for a three day period located at about 1.0 m above the ground in order to eliminate the effect of soil or dust resuspension.

Table 1. Operating conditions for two-stage digestion in the microwave oven.

Step 1			
TºC	140	160	190
Ta (min)[a]	5	3	5
Time (min)[b]	5	10	20
Step 2			
TºC	160	100	–
Ta (min)[a]	3	1	–
Time (min)[b]	15	15	–

[a] Waiting time at desired temperature
[b] The time between the two successive temperatures

Twenty-four samples of settled airborne dust were collected on 9 September 2008. The samples were stored in polyethylene plastic bags right after sampling and preserved in a refrigerator. They were dried in an oven in 105ºC. All the procedures were strictly quality-controlled to avoid any possible contamination of the samples [20]. Hourly PM_{10} mass concentrations on 9 September 2008 and daily average levels of PM_{10} in September 2008 were obtained by the Ministry of Environmental and Forestry Air Quality Monitoring Network of Turkey in Diyarbakir.

Reagents used were Merck suprapur when available or analytical grade and used without further purification. Nitric acid (HNO_3, 65%), hydrofluoric acid (HF, 40%) and boric acid (H_3BO_3, saturated solution) were analytical grade reagents. Deionized-distilled water was used throughout and was directly obtained from a Milli-Q system (Millipore, USA). Dust particles were digested using Berghof MWS-3 model microwave digestion system. The Optima model 2100 DV Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) was used for determining the chemical elements in the dust-digested samples.

The two-stage digestion was carried out as follows: a portion of 0.2 g of the dried sample was weighed and transferred into a pressure-resistant PTFE vessel; the mixture of acids (HNO_3 +HF, 5:2 ml) was added. The vessel was closed and heated in the microwave oven in the shedule described in Table 1. The vessels were removed and carefully vented in a fume hood after cooling to room temperature in a water-bath. After the venting procedure, a 30 ml solution of boric acid (H_3BO_3, saturated solution) was quickly added to each sample. Crystalization of CaF_2 was avoided by the addition of boric acid. The vessels were returned to the microwave oven and the second processing was applied to the samples under the same temperature shedule. The reaction mixture was subjected to evaporation by use of the evaporation module in order to remove the acids after final digestion. Then the residue was dissolved in Milli-Q water and filtrated, and the filtrate was diluted into 50 ml. The ICP-OES measurements of Al, Fe, Mn, As, Cr, Cu, Cd, Co, Mo, Ni, Pb, Se, Sb, Sn, and Zn

were performed for the diluted solutions. A total of six samples were evenly spaced in the microwave oven carousel for microwave acid digestion (MW-AD).

Analysis of dust particles for all the elements of interest was carried out with ICP-OES; average detection limits for all measurements are listed in Table 2. The most sensitive line without spectral interferences in the sample matrix was used for analysis.

Results and Discussion

A dust storm swept across SE Anatolia provinces, dramatically affecting daily life on 9 September 2008. Flights were canceled, and visibility was nearly zero even for drivers in the afternoon as the dust grew thicker. It was impossible to see the water of the Dicle (Tigris) River below. Soil dust particles transported from loess regions in s Syrian dust storm highly influence air quality. Diyarbakir is the greatest settlement in SE Anatolia of Turkey, located near the Dicle (Tigris) river [21]. Settled atmospheric particles were collected in Diyarbakir in order to identify their properties. The particles were analyzed for major and trace element concentrations. The most simple and reliable analytical methods consisting of ICP-OES were applied for the elemental analysis of dust particles due to their higher selectivity and lower interference problems from other elements [22]. The results demonstrate the critical importance of sample treatment prior to the destructive analysis by ICP. Table 2 shows the concentration of 15 chemical elements in settled dust particles in Diyarbakir. Al and Fe oxides are the major components in which Al and Fe crustal element oxides show high concentrations. The metal analysis showed that high concentrations were detected mainly for the four typical dust elements during the dust storm event, i.e. Fe, Al, Cr, and Mn. The mean concentrations for these dust elements were 19620, 9672, 431.8, and 394.1 $mg \cdot kg^{-1}$, respectively. The other estimated elements represent lower concentrations. Arid and semi-arid regions in the Middle East are considered the major sources for mineral dust by various trace elements such as Fe and Al in the atmosphere [23]. Most of the heavy metals and persistent organic compounds come from anthropogenic sources and are transported over long distances with air and water. These compounds are known to be toxic, and several reports indicate that they are present in ecosystems all over the world. Of all types of dusts found of Diyarbakir, the most highly enriched in trace toxic elements are settled dust particles. Metals are an important and emergent class of carcinogens and are dispersed in the atmosphere at a rate higher than that expected from natural processes, mostly due to anthropogenic activities in which metals are involved. Anthropogenic particles generated at industrial locations travel to nearby populated areas influenced by prevailing meteorological factors. Exposure to ultrafine aerosol particles containing toxic heavy metals is one of the most important considerations in assessing the risks by airborne pollutants. The carcinogenic potential of many metals is a major issue in investigating human health risks to exposure.

Table 2. Analytical wavelengths(λ), detection limits (LOD), and average concentrations of the chemical elements in the settled dust particles in Diyarbakir for 9 September 2008.

Chemical Element	λ (nm)	LOD	Concentration, $mg \cdot kg^{-1}$
Cd	228.804	0.5	1.33±0.22
Co	228.616	0.5	15.63±1.03
Cu	327.293	0.5	39.81±2.44
Fe	238.204	0.5	19620.65±121
Mn	257.610	0.5	394.1±12.03
Ni	231.604	1.0	79.02±3.68
Pb	220.353	1.0	28.75±1.24
Zn	206.200	1.0	22.87±2.16
Cr	267.716	0.5	431.80±18.15
Sn	189.927	2.0	84.48±7.58
As	188.979	2.5	23.45±2.33
Al	396.153	2.0	9672.04±89.62
Mo	202.031	1.0	2.35±0.15
Se	196.026	1.0	<1.0
Sb	206.836	2.5	<1.0

A great number of studies have shown the adverse effects of PM on human health. For example, PM_{10} has important health implications through inhalation, which can be deposited in the lungs. High concentrations of metals associated with these inhalable particles, such as Pb, Cd, V, Fe, Zn, Cr, Ni, Mn, and Cu, are potentially toxic to humans [6, 12]. Heavy metals influence the toxicity of airborne particulate matter. Some heavy metals play an important role in the nutrition of plants, animals or humans (Mn, V, Cr, Ni, Cu, and Zn), but if they occur in excess, they may produce certain toxic effects. The others (Cd, Hg, Pb) are toxic even in very low concentrations. Metals are redox active and can therefore induce or catalyze chemical change, leading to production of free radicals, which have a known ability to cause tissue inflammation [18].

The analysis of elemental composition plays an important role in the chemical characterization of PM and provides interesting data, not only for the evaluation of its impact on human health and environment, but also for the identification of specific emission sources. It is widely recognized, furthermore, that the study of elemental solubility provides useful information about the biological and environmental availability of specific elements in dust particles. Dust outbreaks may also greatly increase the ambient air levels of PMs recorded by air-quality monitoring networks. The particle measurements over Diyarbakir are performed by the Environmental and Forestry Air Quality Monitoring Network, which monitors aerosol concentrations, in terms of PM_{10}, on an hourly basis. The dynamics

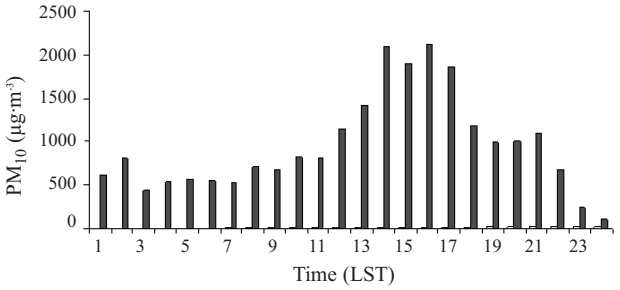

Fig. 1. Hourly levels of PM_{10} measured at Diyarbakir (Turkey) on 9 September 2008.

of PM_{10} concentrations measured at Diyarbakir showed a significant peak in PM_{10} on 9 September 2008 (Fig. 1). The examined data refer to hourly concentration measurements in September 2008, from which the daily averaged values were obtained (Fig. 2) showing the daily mean levels of PM_{10} ($\mu g \cdot m^{-3}$) measured at Diyarbakir during 9 September. Diyarbakir Air Monitoring Station measured the highest levels of PM_{10} (with hourly average concentrations of 2116.1 $\mu g \cdot m^{-3}$) at 16:00 LST on September 9 at a rural station in Diyarbakir. A daily average of PM_{10} was determined at 745.3 $\mu g \cdot m^{-3}$ on September 9, while the September average PM_{10} was 95.1 $\mu g \cdot m^{-3}$ at Diyarbakir and even in neighboring cities. PM_{10} concentrations after the dust storm were found to be much higher than those before the storm. The highest PM_{10} concentration was observed on 9 September and the concentration gradually decreased as the episode developed. This implies that some of the PM_{10} components might not be effectively removed but might remain for 1 or 2 days longer in the atmosphere.

The increase of dust episodes is probably due to a rapid increase of soil loss and desertification by industrialization, forest fires, and reckless deforestation in the Middle East. The World Health Organization has periodically reviewed the evidence on air pollution and health and recommended guidelines to adequately protect public health [23]. The low precipitation in the Mediterranean basin favors the long residence time of PM in the atmosphere, with a consequent impact on air quality [4]. Aerosols in industrial areas are also highly heterogeneous, containing inorganic and organic compounds from local as well as transported sources.

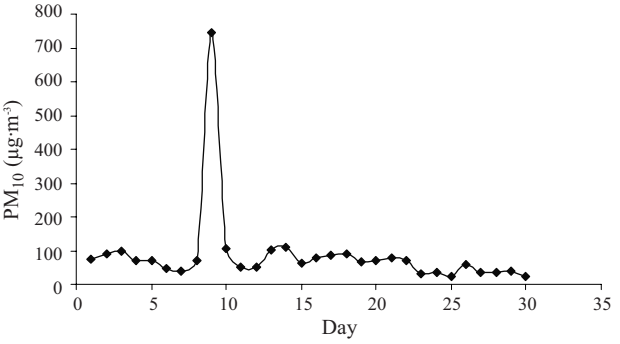

Fig. 2. Daily average levels of PM_{10} measured at Diyarbakir (Turkey) on 9 September 2008.

Conclusions

Very high PM_{10} concentrations in Diyarbakir and SE Anatolia in Turkey were observed on 9 September 2008, leading to two dates with unpredictably excessive concentrations. The study concluded that the toxicity of the dust aerosols is not only owing to PM_{10} concentrations, but it is in association with the chemical fractions in the settled dust particles. In this paper, we used a procedure for the chemical analysis of elements, i.e., As, Al, Cr, Cd, Co, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Sn, and Zn, in the dust particles. The procedure applied the measurement technique (ICP-OES) to the analysis of individual samples. A study on dust particle metal composition showed that Fe (19.62 $g \cdot kg^{-1}$) and Al (9.672 $g \cdot kg^{-1}$) were the most abundant species in dust storm particles. Moreover, Cr (0.4318 $g \cdot kg^{-1}$) and Mn (0.3941 $g \cdot kg^{-1}$) exhibited higher concentrations, followed by Fe and Al. The other chemical elements represented lower concentrations. Relative abundances of the remaining chemical elements follow the order: Sn (84.48 $mg \cdot kg^{-1}$) > Ni (79.02 $mg \cdot kg^{-1}$) > Cu (39.81 $mg \cdot kg^{-1}$) > Pb (28.75 $mg \cdot kg^{-1}$) > As (23.45 $mg \cdot kg^{-1}$) > Zn (22.87 $mg \cdot kg^{-1}$) > Co (15.63 $mg \cdot kg^{-1}$) > Mo (2.35 $mg \cdot kg^{-1}$) > Cd (1.33 $mg \cdot kg^{-1}$). Se and Sb were not detected.

References

1. CAO J., LEE S., ZHENG X., HO K., ZHANG X., GUO H., CHOWJ.C.,WANG H. Characterization of dust storms to Hong Kong in April 1998. Water, Air, and Soil Pollution: Focus. **3**, 213, **2003**.
2. GOUDIE A.S. Dust storms: Recent developments. J Environ Manage. **90**, 89, **2009**.
3. KASKAOUTIS D.G., KAMBEZIDIS H.D., NASTOS P.T., KOSMOPOULOS P.G. Study on an intense dust storm over Greece. Atmos. Environ. **42**, 6884, **2008**.
4. QUEROL X., PEY J., PANDOLFI M., ALASTUEY A., CUSACK M., PEREZ N., MORENO T., VIANA M., MIHALOPOULOS N., KALLOS G., KLEANTHOUS S., African dust contributions to mean ambient PM_{10} mass-levels across the Mediterranean Basin. Atmos. Environ. **43**, 4266, **2009**.
5. BADARINATH K. V .S., KHAROL S. K., KASKAOUTİS D. G., SHARMA A. R., RAMASWAMY V., KAMBEZIDIS H. D. Long-range transport of dust aerosols over the Arabian Sea and Indian region A case study using satellite data and ground-based measurements. Global Planet. Change, **72**, 164, **2010**.
6. KOCAK M., MIHALOPOULOS N., KUBILAY N. Origin and source regions of PM_{10} in the Eastern Mediterranean atmosphere. Atmos. Research, **92**, 464, **2009**.
7. GOUDİE A.S., MİDDLETON N.J. Saharan dust storms: nature and consequences Earth-Science Reviews **56**, 179, **2001**.
8. PERRINO C., CANEPARI S., CATRAMBONE M., TORRE S.D., RANTICA E., SARGOLINI T. Influence of natural events on the concentration and composition of atmospheric particulate matter. Atmos. Environ. **43**, 4766, **2009**.
9. ZHANG R., HAN Z., SHEN Z., CAO J. Continuous measurement of number concentrations and elemental composi-

tion of aerosol particles for a dust storm event in Beijing. Adv. Atmos. Sci. **25**, 89, **2008**.
10. GANOR E., STUPP A., ALPERT P.A., Method to determine the effect of mineral dust aerosols on air quality. Atmos. Environ. **43**, 5463, **2009**.
11. HAMAMCI C., GUMGUM B., AKBA O., ERDOGAN S., Lead in urban street dust in Diyarbakir, Turkey. Fresen. Environ. Bull. **6**, 430, **1997**.
12. AYDIN I., AYDIN F., SAYDUT A., BAKIRDERE E.G., HAMAMCI C., Hazardous metal geochemistry of sedimentary phosphate rock used for fertilizer (Mazıdag, SE Anatolia, Turkey). Microchem. J. **96**, 247, **2010**.
13. TURKUM A., PEKEY B., PEKEY H., TUNCEL G., Comparison of sources affecting chemical compositions of aerosol and rainwater at different locations in Turkey. Atmos. Research., **89**, 306, **2008**.
14. VANDERSTRAETEN P., LENELLE Y., MEURRENS A., CARATI D., BRENIG L., DELCLOO A., OFFER Z.Y., ZAADY E. Dust storm origin from Sahara covering Western Europe:A case study. Atmos. Environ. **42**, 5489, **2008**.
15. ABED A.M., KUISI M.A., KHAIR H.A.,Characterization of the Khamaseen (spring) dust in Jordan. Atmos. Environ. **43**, 2868, **2009**.
16. CURTIS L., REA W., SMITH-WILLIS P., FENYVES E., PAN Y., Adverse health effects of outdoor air pollutants. Environ. Int. **32**, 815, **2006**.
17. ISIK B., HAMAMCI C., ISIK R. Effect of winter air pollution on lipid peroxidation product levels of patients with chronic obstructive pulmonary disease. Asian J. Chem. **18**, 1433, **2006**.
18. MERESOVA J., FLOREK M., HOLY K., JESKOVSKY M., SYKORA I., FRONTASYEVA M.V., PAVLOV S.S., BUJDOS M., Evaluation of elemental content in air-borne particulate matter in low-level atmosphere of Bratislava. Atmos. Environ. **42**, 8079, **2008**.
19. KORCZ M., FUDALA J., KLIS C., Estimation of wind blown dust emissions in Europe and its vicinity. Atmos. Environ. **43**, 1410, **2009**.
20. JIRIES A.,EL-HASAN T., MANASRAH W. Qualitative evaluation of the mineralogical and chemical composition of dry deposition in the central and southern highlands of Jordan. Chemosphere. **48**, 933, **2002**.
21. ERDOGAN S., BAYSAL A., AKBA O., MERDIVAN M., HAMAMCI C. Relationship between wintertime atmospheric particulate matter and meteorological conditions in Diyarbakir (Turkey). Asian. J. Chem. **19**, 1703, **2007**.
22. TA W., XIAO Z., QU J., YANG G., WANG T., Characteristics of dust particles from the desert/Gobi area of northwestern China during dust-storm periods. Environ. Geology. **43**, 667, **2003**.
23. KALDERON-ASAEL B., EREL Y., SANDLER A., DAYAN U. Mineralogical and chemical characterization of suspended atmospheric particles over the east Mediterranean based on synoptic-scale circulation patterns. Atmos. Environ. **43**, 3963, **2009**.