

ELEMENTAL COMPOSITION OF RAINWATER IN MERSİN, AN URBAN SITE IN THE NORTH EASTERN MEDITERRANEAN

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ABSTRACT

Rainwater samples collected at urban sites of Mersin, an industrialized city 800,000 population on the southern coast of Turkey, during the year 2004 were analyzed to determine soluble and insoluble concentrations of trace elements, pH and conductivity. The soluble phase was obtained by filtering of rainwater from 0.45 μm size filters and the insoluble phase by HF:HNO₃ digestion of the material collected on filter paper. Al, Ba, Cd, Cr, Co, Cu, Fe, Mn, Ni, Pb, Sr and Zn were analyzed in both phases and Na, K, Ca and Mg in the dissolved phase by ICP-AES. Precipitation sampled at two central and two suburban sites were used to examine the spatial and temporal variability of rainwater constituents. The pH varied from 4.8 to 8.5 with an average value of 6.0, therefore considered alkaline. Concentrations of trace elements were in the order of Ca > Na > Fe > Mg > Al > K > Zn > Sr > Mn > Pb > Ni > Cr > Cu > Co > Ba > Cd. Terrigenous particles were shown to be the main source of trace elements. Trace elements grouped according to crustal Enrichment Factors (EFs calculated with respect to Al normalization) showed the precipitation not to be enriched in Ba, K, Fe, Mn and Mg compared to the upper crust composition. Na, Sr, Cr, Ca, Ni, Cu and Co are moderately enriched while Zn, Pb and Cd are highly enriched, most probably by other sources; e.g. sea, vegetation and human activities.

Key Words: Rainwater, Trace elements, North-Eastern Mediterranean, Enrichment factors, Mersin

1. INTRODUCTION

There is considerable interest in the atmospheric trace elements since they are increasingly being introduced into the environment as pollutants (Nriagu and Pacyna, 1988). Their chemistry in the atmosphere is influenced by different sources of gases and aerosols both can be originated from natural (crustal, marine biogenic) and/or anthropogenic emissions. During precipitation events, these gases and aerosols are incorporated into raindrops and this so-called washed-out processes play an important role in atmospheric deposition mechanisms of trace elements to the aquatic and/or terrestrial ecosystems (Barrie *et al.*, 1987). From this point of view, it is

possible to obtain important information about the atmospheric trace element reservoirs and the air quality of the local atmosphere through chemical analyses of precipitation.

Mersin is a big and industrialized city located on the south-eastern coast of Turkey, affected by increased air pollution following a rapid increase in its population in recent years. Serious research to determine air pollution levels for the city has not been conducted until present, excluding the intermittent measurements of gaseous SO₂ and particulate matter performed by the Regional Directorate of Environment of İçel (İçel Çevre İl Müdürlüğü). Precipitation samples have been collected continuously for one year at four different urban stations in Mersin. The samples were analysed for pH, conductivity and trace elemental composition. Al, Ba, Cd, Cr, Co, Cu, Fe, Mn, Ni, Pb, Sr and Zn were analyzed in both soluble and insoluble phases while Na, K, Ca and Mg were analyzed only in the soluble phase by ICP-AES.

The aim of this study was to determine the elemental composition of Mersin precipitation. For this purpose different origins of trace elements are discussed with the preliminary data obtained on the total, soluble and insoluble phase of rainwater samples collected between December 2003-June 2004, using enrichment factors, phase distribution and correlations between trace elements.

2. EXPERIMENTAL

2.1. Sampling Stations

Mersin as an industrialized city with more than a million inhabitants is the site for various industries (e.g. petroleum refinery, thermal power plant, soda, chromium, fertilizer and glass production), almost all situated in the industrial district east of the city. Four sampling stations were selected within the residential area of the city (Figure 1), located at roofs of private buildings based on practical and safety considerations. Station 1 is located in Çiftlikköy Campus of Mersin University, at an approximate height of 60 m from sea-level, on the slopes of Taurus Mountains. The campus is surrounded by agricultural land, mainly lemon groves. Sampling buckets of 30 cm diameter made out of HDPE (high density polyethylene) were deployed at the roof of Mersin Vocational School, a building with central heating and therefore no active chimney. Station 2 is located on the roof of a private building in the newly developing residential area of Yenişehir - Menteş Mahallesi, surrounded by a low density of small private houses and gardens, far from active chimneys. A rain-gauge (Akım Elektronik, Pluviograph, Model PHD5-02) with a special facility for rainwater sampling were deployed at Station 2. Station 3 and Station 4 were located at roofs of a private house and a business center, both heated by electricity, near the highly populated center of the city under the direct influence of other residential heating and dense traffic activity in the area.

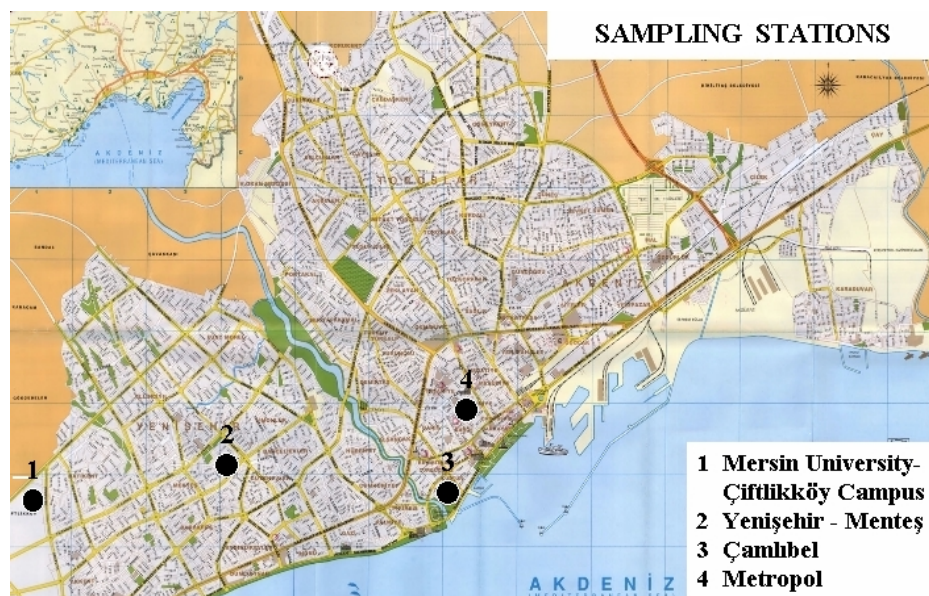


Figure 1. The location of the sampling stations of precipitation in Mersin.

2.2. Analytical Procedure

Sampling buckets, bottles and all glassware used in the laboratory have been washed first with detergent and rinsed with double distilled deionized water. Laboratory equipment have been additionally soaked in 1 M HNO₃ washing solution for 48 h and rinsed with distilled, deionized water several times prior to usage. Precipitation samples collected on an event basis were immediately brought to the laboratory after cessation of the particular rain event. The buckets were tightly sealed with a clean plastic lid in order to avoid contamination during transport to the laboratory. After measuring their volume, the samples were filtered through a 0.45 µm pore size membrane filter (MFS, cellulose acetate, 47 mm diameter) to separate insoluble particles by applying gentle negative pressure and divided into aliquots for different analyses. Subsamples of precipitation were transferred in rigorously cleansed PE (polyethylene) bottles and preserved at +4°C. Aliquots for major trace metal analysis were preserved by acidification with 0.1 M HNO₃ before storage. Filter samples were preserved at -18°C in a deep-freeze until analysis time.

Membrane filter samples have been digested according to the procedure given in UNEP (1995), using a microwave digestion oven (MARS 5, Microwave Accelerated Reaction System, CEM Microwave Technology Ltd.) at the Central Research Laboratory of Mustafa Kemal University. Total (HF) decomposition method has been applied with little modification in the adjustment of the microwave oven's power and timing. In digestion of samples HF and Aqua Regia (1:3 v/v HNO₃ and HCl) mixture have been used. Digested samples were diluted to 50 mL volume by double distilled de-ionized water and then transferred into polyethylene bottles in order to preserve them at +4°C until analysis time.

The pH in rainwater was measured by a Mettler Toledo MP120 pH-meter (accuracy of 0.01 pH unit). Conductivity measurements were performed with a DIST H198300/3-4 Conductivity/TDS Meters with automatic temperature compensation. A Varian Liberty II Model ICP-AES at the Central Research Laboratory of Mustafa Kemal University was used for the analysis of trace elements in both soluble and insoluble phases of precipitation. The ICP-AES with axial torch was controlled by PC Pentium III. Plasma power was 1.0 kW and integration time was 1.5 sec. with three replicates. The detection limits of Na, Ca, K and Mg were found to be 0.004, 0.010, 0.005 and 0.003 mg/L, respectively. The reproducibility was better than 4 % for these metals. Detection limits for the other elements were 3.0 $\mu\text{g L}^{-1}$ for Fe and Zn, 2.0 $\mu\text{g L}^{-1}$ for Al and Mn, 1.4 $\mu\text{g L}^{-1}$ for Pb, 0.9 $\mu\text{g L}^{-1}$ for Sr, 0.7 $\mu\text{g L}^{-1}$ for Co and Ni, 0.5 $\mu\text{g L}^{-1}$ for Cu, 0.4 $\mu\text{g L}^{-1}$ for Cr, 0.1 $\mu\text{g L}^{-1}$ for Ba and Cd. Standard solutions for trace elements have been prepared daily from 1000 ppm stock MERCK ICP Multi-element Standard solution IV.

The same procedures have been applied to five field blanks collected within the sampling period. Approximately 200 mL of distilled, de-ionized water was poured into the cleaned sampling bucket and deployed at the precipitation sampling stations. The concentration of field and laboratory blanks measured throughout the study were all below the detection limit of the measured trace elements.

3. RESULTS AND DISCUSSION

3.1. pH and Conductivity

A total of 158 samples collected during one year period from four different stations in Mersin. The mean pH of precipitation, calculated from the volume weighted H^+ concentration, was found to be 6.0. Out of 158 samples, 95 % reflects alkaline pH of precipitation, as compared to 5.6 pH of rainwater at equilibrium with atmospheric CO_2 . The observed alkalinity of rainwater is mostly due to the high loading of particulate matter present in the local atmosphere of Mersin. The suspended particulate matter which is rich in carbonate/bicarbonate of calcium, buffers the acidity of rainwater (Özsoy and Saydam, 2000).

Electrical conductivity of the precipitation samples was found to be highly variable, within a range of 0 -1300 $\mu\text{S cm}^{-1}$. The geometric mean conductivity of the 156 samples was $39.7 \pm 3.53 \mu\text{S cm}^{-1}$. The volume weighted mean total aluminium concentration of 101 precipitation samples was 347.8 $\mu\text{g L}^{-1}$. The relationship between electrical conductivity and total aluminium concentration is presented in Figure 2, representing a high positive correlation ($r = 0.81$) between the two parameters. Precipitation samples with relatively high concentrations of aluminium, hence mineral dust, had very high conductivity, most probably due to the high content of soluble solids, high ion adsorption capacity of mineral dust surfaces and adsorption-desorption processes taking place between the solid and liquid phases.

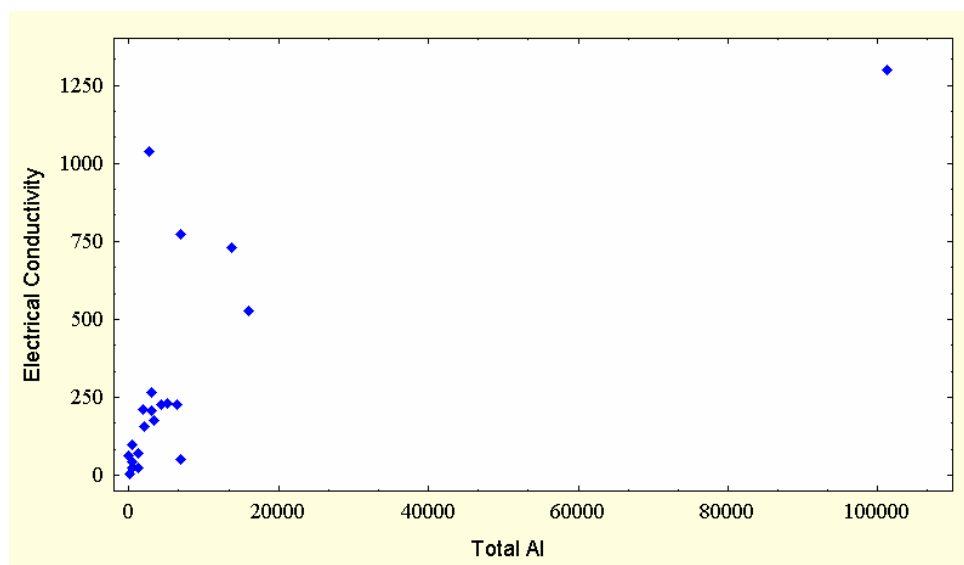


Figure 2. The relationship between the electrical conductivity ($\mu\text{S cm}^{-1}$) and total aluminium concentrations ($\mu\text{g L}^{-1}$) in Mersin precipitation.

3.2. Solubility of Trace Elements

Volume weighted mean (VWM) concentrations of the trace elements in the soluble and insoluble phases of precipitation are presented in Table 1. Concentrations of trace elements were in the order of $\text{Ca} > \text{Na} > \text{Fe} > \text{Mg} > \text{Al} > \text{K} > \text{Zn} > \text{Sr} > \text{Mn} > \text{Pb} > \text{Ni} > \text{Cr} > \text{Cu} > \text{Co} > \text{Ba} > \text{Cd}$. Terrigenous particles were shown to be the main source of the measured elements.

Percentage solubilities of trace elements are found to be in the order of $\text{Fe} < \text{Al} < \text{Mn} < \text{Cr} < \text{Ba} < \text{Cu} < \text{Ni} < \text{Pb} < \text{Cd} < \text{Co} < \text{Zn} < \text{Sr}$. According to their solubility, measured elements can be evaluated into three groups: The first group includes crustal elements such as Fe, Al and Mn which have less than 15% solubility in precipitation. The second group includes Cr, Ba, Cu, Ni and Pb which are moderately soluble in precipitation (solubilities ranging between 20 and 50 %). The third group includes the soluble and mainly anthropogenic elements such as Cd, Co and Zn (ranging between 50 and 80%). Our data are similar to Guieu *et al.*, 1997 concerning Al, Cu, Pb and Zn. On the other hand, the solubility of Fe (0.3%) in Mersin precipitation was found to be much lower than the value (6.2%) reported for Erdemli-Mersin (a rural-coastal area) precipitation (Özsoy and Saydam, 2001). Solubilities of trace elements are a function of several parameters such as pH, the amount of precipitation and the type of aerosols scavenged from the atmosphere during wash-out processes (Chester *et al.*, 1993a; Spokes *et al.*, 1994). This study have been conducted in the urban atmosphere and the volume weighted mean pH value of this study (6.0) was found to be higher than the pH value of 4.95 reported for the precipitation conducted in rural atmosphere of Mersin. Therefore, pH and the aerosol type might be the reason of the discrepancy between the solubility of iron found in this study and reported in Özsoy and Saydam, 2001.

Table 1. Volume weighted mean concentrations of the measured trace elements in Mersin precipitation. Concentrations are in $\mu\text{g L}^{-1}$. n refers to the number of samples.

Element	n	Soluble	Insoluble	Total	%Solubility
Ca ²⁺	153	3360	-	3360	-
K ⁺	153	170	-	170	-
Mg ²⁺	153	410	-	410	-
Na ⁺	153	990	-	990	-
Al	101	6.5	341.3	347.8	1.9
Ba	101	1.14	2.57	3.71	30.7
Cd	101	0.45	0.41	0.86	52.3
Co	101	3.06	1.94	5.00	61.2
Cr	101	1.54	6.11	7.65	20.1
Cu	101	2.63	3.43	6.06	43.4
Fe	101	2.42	766.5	768.9	0.3
Mn	101	2.05	13.52	15.57	13.2
Ni	101	3.99	5.11	9.10	43.9
Pb	101	6.12	7.15	13.27	46.1
Sr	101	14.8	3.75	18.53	79.8
Zn	101	36.3	10.4	46.7	77.7

3.3. Enrichment Factors

Enrichment Factors (EFs) provide information on the extent to which trace metal concentrations in aerosols or precipitation are enriched or depleted relative to crustal and marine sources (Duce *et al.*, 1975; Chester *et al.*, 1993b). They are often used to emphasize the natural or anthropic metals enrichment. A value of 10 is generally used to highlight this enrichment. Other sources, different than the crustal or marine ones, explain enrichment factors higher than 10.

The enrichment factor for an element x is defined as:

$$EF_{\text{crust}} = (x/\text{Al})_{\text{rain}} / (x/\text{Al})_{\text{crust}} \quad (1)$$

$$EF_{\text{marine}} = (x/\text{Na})_{\text{rain}} / (x/\text{Na})_{\text{marine}} \quad (2)$$

Where x, Al and Na are concentrations, the subscript “rain” denotes the concentration ratio in the precipitation, and the subscripts “crust” and “marine” denote the ratios in the appropriate reference materials (Zoller *et al.*, 1974). In this study, the average composition of upper crust (Rudnick and Gao, 2003) was used as crustal reference materials. The crustal EFs, based on volume weighted mean total concentrations of trace elements are presented in Table 2.

Table 2. Enrichment Factors (EFs) of trace elements in Mersin precipitation, with respect to crust.

Element	EF _{crust}
Ba	1
Fe	5
Mn	5
Mg	6
Ca	31
Na	10
K	2
Cd	2274
Co	68
Cr	20
Cu	51
Ni	45
Pb	183
Sr	14
Zn	164

EF_{crust} for trace elements presented in Table 2 have been grouped into non-enriched, moderately enriched and highly enriched classes, as in the following:

1. Non-enriched elements: Al (the crustal indicator), Ba, K, Fe, Mn, Mg, Na, with volume weighted mean EF_{crust} values of 1-10.
2. Moderately enriched elements: Sr, Cr, Ca, Ni, Cu, Co, with EF_{crust} values in the range of 10-10².
3. Highly enriched elements: Zn, Pb and Cd, having volume weighted mean EF_{crust} values in the range of 10²->10³

Among the highly enriched elements Zn and especially Pb and Cd are predominantly of anthropogenic origin. Zn and Cd have many common sources, the non-ferrous metal industry accounting for the largest fraction of Zn and Cd emitted (Nriagu and Pacyna, 1988). The largest contribution of Pb to the atmosphere is gasoline combustion, accounting for about 60% of the total anthropogenic emission in Europe (Pacyna, 1984). EF_{crust} values of mainly anthropogenic elements e.g. Zn, Cd, Pb, obtained from this study were found to be approximately, order of magnitude lower than the EF_{crust} values reported for İskenderun (EF_{Zn}:1333, EF_{Cd}:25055, EF_{Pb}:1474, Örnektekin and Çakmaklı, 2003) most likely due to the difference between the volume weighted mean Al concentrations of Mersin (347.8 µg L⁻¹) and İskenderun precipitation (30.04 µg L⁻¹). Enrichment Factors might be evaluated as pollution indicators with respect to upper crust mean composition. However, the EF values have to be used with caution in this type of comparisons. This caution is needed especially when anthropogenic elements are used as tracers, since part of the

variability in EF can come not from the element itself but from the variability of the reference element (Al concentration).

3.4. Wet Deposition Fluxes

Wet deposition flux of the trace elements ($F_w = \text{mg m}^{-2}$) can be calculated using the relationship;

$$F_w = C_w \cdot P \quad (3)$$

Where C_w is the total (soluble+insoluble) trace element concentration in precipitation and, P is the rainfall. Since, trace element analyses have not been completed yet, approximate annual wet deposition fluxes have been calculated based on the volume weighted mean concentrations of the measured trace elements and cumulative precipitation. The total wet deposition flux of aluminium was found to be 564 mg m^{-2} during the sampling period (December 2003 – June 2004). This value corresponds to an annual flux of approximately 1128 mg m^{-2} . This value is in good agreement with the value reported for a rural area in Mersin (1118 mg m^{-2} , Özsoy and Saydam, 2000). These wet deposition fluxes of aluminium are the highest values among reported values from various stations around the world. These results confirm that the eastern Mediterranean atmosphere is heavily loaded by mineral dust sporadically transported from arid regions (Özsoy and Saydam, 2000).

Among the mainly anthropogenic elements, the wet deposition flux of Zn (76 mg m^{-2}) was found to be considerably higher than those of the other anthropogenic elements e.g. Pb, Ni, Cr, Cu, Co and Cd.

4. CONCLUSIONS

Rainfall samples collected during the December 2003 – June 2004 period were analyzed to determine the trace elemental composition and to describe general characteristics of precipitation in Mersin. The results show that the rainwater in Mersin is typically of alkaline character with volume weighted mean pH of 6.0. Mainly Ca^{2+} ions were found to be responsible for neutralizing the acidity of rainwater. Electrical conductivity of the precipitation samples was found to be highly variable. Precipitation samples with relatively high concentrations of aluminium, hence mineral dust, had very high conductivity, most probably due to the high content of soluble solids. Solubilities of the measured trace elements have been investigated and the lowest solubilities were found for the crustal elements (e.g. Fe, Al and Mn) while the highest solubilities were obtained for mainly anthropogenic elements (e.g. Cd, Co and Zn). Trace elements grouped according to crustal Enrichment Factors, showed the precipitation not to be enriched in Ba, K, Fe, Mn and Mg compared to the upper crust mean composition. Na, Sr, Cr, Ca, Ni, Cu and Co are moderately enriched while Zn, Pb and Cd are highly enriched, most probably by other sources; e.g. sea, vegetation and human activities. Wet depositional fluxes of trace elements were in the order of $\text{Ca} > \text{Na} > \text{Fe} > \text{Mg} >$

Al > K > Zn > Sr > Mn > Pb > Ni > Cr > Cu > Co > Ba > Cd. The highest wet depositional fluxes calculated for both marine originated (Ca, Na, Mg) and crustal (Fe and Al) elements suggest that Mersin is under the influence of natural atmospheric sources rather than anthropogenic sources.

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