



# Prediction of sources of metal pollution in rainwater in Istanbul, Turkey using factor analysis and long-range transport models

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## ABSTRACT

In this study, major (Na, K, Al, Ca and Mg) and trace (Pb, Ni, Fe, Cu, Cr, Co, and V) elements in 43 rain samples were measured and their concentrations were statistically analysed. The samples were collected during October 2007 and May 2008 at the campus of Fatih University, which is located in Istanbul at 41.09° longitude and 28.61° latitude and is in the Büyükcçekmece watershed area. Rainwater samples were collected using a purpose-built wet-only rain sampler designed and constructed at the Fatih University Department of Environmental Engineering. Major and trace metals in rainwater were measured using Graphite Furnace Atomic Absorption Spectrometer (GFAAS) and Flame Atomic Absorption Spectrometer (FAAS) techniques. Statistical analyses show that the highest concentrations were observed for Al and Fe, which are mainly lithophilic elements. The lowest concentrations were measured for Co. Crustal Enrichment Factor (EF<sub>c</sub>) calculations clarified that rainwater samples were not enriched with Mg, K, Ca, Na or Fe, but were moderately to extremely enriched with Cr, Co, Ni, Cu, V, and Pb. The latter elements were attributed to a mix of local and long-range anthropogenic sources. Factor analysis calculations resulted in five factors with eigenvalues greater than unity. To further elucidate the geographical contribution from these factors, a potential source contribution function (PSCF) model was calculated from the highest quartile of the factor-score trajectories for the five extracted factors. The PSCF results show that a significant fraction of the measured anthropogenic pollutants was transported to the sampling area from source regions in Europe, Russia, southern and northern Mediterranean countries and industrial zones west of Turkey.

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## 1. Introduction

Istanbul is located between the continents of Asia and Europe, separated by the Bosphorus Strait. The city is affected by regional and global pressure systems and located along the transport pathways of air parcels coming primarily from Europe, the Black Sea and Russia during winter and autumn and from the Mediterranean and Africa during spring and summer. For this reason, studies focusing on the potential contribution of long-range sources to wet precipitation samples collected in Istanbul have both local and global importance.

Studying wet precipitation in Istanbul is of further importance in light of the decreasing amount and quality of surface water in the city. Surface water reservoirs in Istanbul were nearly emptied following an extraordinary drought during the summer of 2008. The chemistry of the precipitation from rainfall events that followed this drought period is representative of the main factors characterising the chemical composition of Istanbul's water reserves. Istanbul and its surroundings have a rich flora and extensive forest tracts that can be damaged by acid deposition. Finally, Istanbul is home to hundreds of precious and unique historical buildings, monuments and other structures, to the extent that the city is known as "the timeless city." Acidic precipitation deteriorates monuments and historical buildings, and it is thus important to uncover the sources of pollution affecting precipitation chemistry.

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The scientific literature contains a limited number of studies regarding rainwater chemistry in Istanbul (Gulsoy et al., 1999; Okay et al., 2002; Akkoyunlu and Tayanc, 2003; Başak and Alagha, 2004; Saylan et al., 2002; Saylan et al., 2009). To our knowledge, the first study carried out was by Gulsoy et al. (1999). Between January and October 1999, they collected urban precipitation samples in three different regions of Istanbul having different urbanisation characteristics. Major ions were analysed, and it was concluded that there was a clear effect of urban heating on rain chemistry. The pH of the collected samples ranged from 3.96 to 8.46 with an average of 6.15. Only 18.6% of the collected samples were acidic (i.e., having a pH value less than 5.6, which characterises typical precipitation). Most of the acidic events were recorded during January, a few in early April, and only one in October. Aerosols containing calcium and ammonium were the dominant neutralising agents.

Okay et al. (2002) collected wet deposition samples from August 1993 to November 1995 in Kaynarca, located in the southeast of Istanbul. They measured major cations and anions and found an average pH value of 5.59, lower than that found by Gulsoy et al. (1999). In addition to evaluating the seasonality of their data, they also used statistical methods to determine the chemical sources of the measured ions using enrichment factors based on crustal and marine sources. Cyclones identified from 00 GMT surface maps and 500 hPa geopotential height maps were used to evaluate the trajectories of air parcels affecting the region during rain events. Their trajectory analyses showed high sulphate- and nitrate-containing rain events associated with cyclones originating in locations from Europe to Istanbul.

In another study, Akkoyunlu and Tayanc (2003) collected wet deposition samples (54 wet-only and 21 bulk samples) in four different regions of Istanbul — Topkapı, Bağcılar, Maltepe and Göztepe — between January and May 2001. They measured major cations and anions and found an average pH of 5.26 for their wet samples. This value is the lowest average pH ever measured in Istanbul (Gulsoy et al., 1999; Okay et al., 2002; Akkoyunlu and Tayanc, 2003; Başak and Alagha, 2004; Saylan et al., 2009). Enrichment factors were used to define possible enrichment sources, and the results from this analysis were in close agreement with those of previously mentioned studies.

Başak and Alagha (2004) collected 79 bulk precipitation samples in Büyükçekmece, Istanbul between October 2001 and July 2002. This study was the first in Istanbul to concentrate on both trace elements and major ions. The average pH was 5.58, similar to that of the rain samples collected in Kaynarca (Okay et al., 2002). Atmospheric sources of ions and trace elements in the Büyükçekmece data were evaluated using a variety of statistical methods, including enrichment factors and correlation analyses. They concluded that acid neutralisation in the samples was the result of calcium, not ammonium, ions.

In a recent study, Akkoyunlu and Tayanc (2008) sequentially collected wet precipitation data during four different rainstorms. Samples were collected between October 2003 and February 2004. They concentrated on ionic composition and variations during sub-events along with the prevailing atmospheric conditions during the storms. They found that the first sub-event of each storm had higher pH values than the subsequent events due to atmospheric washout.

The most recent study of wet deposition in Istanbul employed back trajectory analysis of samples collected from two different regions (urban and forest) in Istanbul between November 1997 and June 1998 (Saylan et al., 2009). The authors designed a sequential rain sampler that collected samples from sub-events of a rainstorm at 10-minute intervals. The arithmetic mean of the pH was 6.0. Most ions in the samples reached Istanbul from the WSW, WNW and NNE directions. This study served as one of the most important attempts to evaluate the effects of long-range transport on the chemical composition of rain in Istanbul.

Building upon the previous work, the main goals of our study are: i) to evaluate the trace element composition of wet-only precipitation samples collected in Büyükçekmece, Istanbul, ii) to employ statistical tests and models to differentiate possible source factors, and iii) to use backward trajectory analysis together with extracted source factors to calculate the potential contributions of distant sources to the trace element content of the samples.

## 2. Methods and materials

### 2.1. Study area

The sampling area is located in the Büyükçekmece Lake watershed at Fatih University (41.09° N, 28.61° E), a suburban area in Istanbul. The lake provides Istanbul with 30% of its potable water. The maximum depth does not exceed 4 m. Fish such as grey mullet, carp and bream are found in the lake (Başak and Alagha, 2004). The sampling area and location are given in Fig. 1.

The rainwater sampling collection campaign began in November 2007 and ran until June 2008. A total of 43 samples were collected during this period.

### 2.2. Wet-only rain sampler

Rainwater samples were collected using a purpose-made wet-only rain sampler designed and manufactured at the Air Pollution Laboratory, Department of Environmental Engineering, Fatih University. The sampler allows wet-only samples to be collected during a rain event and can be kept closed during the dry periods to eliminate the contribution of dry deposition. The sampler design is shown in Fig. 2.

Dry deposition samples were collected from the dry bucket of the sampler, which consists of a High Density Polyethylene (HDPE) container. When there was no rainfall for a one-week period and the sampler's dry bucket was continually opened, the dry samples were obtained by washing the dry bucket with 100 mL of de-ionised distilled water.

After a rainfall event, samples were collected and immediately transported to the laboratory. Any snow samples collected in the sampling bucket were brought to the laboratory and allowed to melt at room temperature before measurement or filtration.

### 2.3. Volume, pH and conductivity measurement

The volume, pH and specific conductivity of the rain samples were determined immediately after collection. First, the volume was determined by comparing the volume of the sample with

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