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Sources Effecting Rain Water Composition Over the Eastern Mediterranean Sea

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Abstract

Determination of source types of chemical composition of wet deposition samples is important for solving problems in inland and aquatic ecosystems. This is especially essential for the oligotrophic environments like Mediterranean. For this purpose, in between 1992 and 1999, 387 rain samples were collected at Eastern Mediterranean coast of Turkey and were analyzed with atomic absorption spectrometry (AAS), inductively coupled plasma (ICP), ion chromatography (IC) and Nessler's colorimetric methods for the determination of Mg, Ca, K, Na, Cd, Cu, Pb, Al, Ni, Cr, Zn and Fe elements and SO_4^{2-}, NO_3^-, NH_4^+ and Cl^- ions. A receptor oriented method, positive matrix factorization (PMF), was applied to the data set in order to determine the source types that contribute to the rain water. The method resulted with two natural and three anthropogenic sources. Natural sources were from soil and sea. Three anthropogenic sources were named as free acidity factor, NO_3^- factor and SO_4^{2-} factor.

Introduction

Precipitation is an effective and quick removal process for pollutants present in the atmosphere both in the gas and aerosol phases. The composition and chemistry of the precipitation are important research subjects for the last three decades because of the increased awareness towards the aquatic and terrestrial problems due to nutrient and acid deposition [1, 2]. Even though it is well known that Mediterranean Sea has an oligotrophic nature, there are very few studies conducted over the region for the identification of nutrient and acid deposition.

This study aims to determine the levels and sources of pollutants measured in rain water at Eastern Mediterranean coast of Turkey. To determine the sources of pollutants a receptor oriented method, Positive Matrix Factorization was used [3].

Materials & Methods

Rain water samples were collected at the Mediterranean coast of Turkey (31.0 E, 36.8 N), using a wet-only sampler (Andersen, acid precipitation sampler), between 1992 and 1999. In this period a total of 387 wet-only rain water samples were collected. Concentrations of ions (Cl^-, NO_3^- and SO_4^{2-}) were measured using a Varian, Model 2010 HPLC coupled with a VYDAC 302 IC anion exchange column. Ammonium ion was determined by the direct Nesslerization using a Unicam 8625 UV–Vis spectrometer. pH was determined with a Radiometer PHM 80 portable pH meter.

Samples for the element (Ca, Na, K, Mg, Al, Cd, Cu, Fe, Cr, Ni, Pb and Zn) analyses were acidified in the field and then sent to the laboratory. Since all elements were not soluble in water, samples were first filtered through 0.45 μm pore sized cellulose acetate filter. Both soluble (filtrate) and insoluble fractions of the elements were analyzed by atomic absorption spectrometry (Perkin Elmer 1100B spectrometer coupled to a HGA 70 electrothermal analyzer). Filters that contain insoluble fractions of elements were dissolved in microwave oven using HNO_3 – HF mixture before analysis. Dissolved fraction (filtrate) was directly injected to spectrometer. Total concentrations of elements were calculated by summing their soluble and insoluble concentrations.

Positive Matrix Factorization (PMF) is a multivariate factor analysis tool that decomposes a matrix of speciated sample data into two matrices—factor contributions and factor profiles—which then need to be interpreted by an analyst as to what source types are represented. In PMF, species with missing or below detection limit values are included by assigning large uncertainties, and therefore a small weight, to these data.

Results

In this study, PMF was applied to data set containing measured concentrations of elements and ions in all of the 387 samples. In order to achieve optimum solution 3 to 8 factor solutions were analyzed. In all of the results, variance, source profiles and standard errors were evaluated. In order to achieve the optimum solution, crustal enrichment factor was calculated with factor profiles. As a result, it is determined that Eastern Mediterranean rain water is affected from five sources. The variances of the each factor are given in Table 1. First factor was identified as free acidity factor. Second factor explains most of the variances of crustal elements and hence, named as crustal factor. Third factor is dominated with sea salt ions, sodium and chlorine, and named as sea salt factor. Fourth and fifth factors were dominated with nitrate and sulphate ions and named as nitrate factor and sulphate factor, respectively.

Table 1. Variances of each source affecting Eastern Mediterranean rain water composition

	Factor 1	**Factor 2**	**Factor 3**	**Factor 4**	**Factor 5**
$\mathbf{Na^+}$	0.30	2.24	96.47	0.03	0.01
$\mathbf{Cl^-}$	0.55	0.01	96.44	0.01	1.98
Al	0.00	92.74	2.07	3.94	0.01
Fe	0.01	92.15	0.00	0.00	7.84
$\mathbf{Ca^{2+}}$	0.32	70.18	9.60	0.64	13.09
$\mathbf{K^+}$	0.06	45.53	36.21	1.01	8.40
$\mathbf{Mg^{2+}}$	0.61	51.96	39.60	1.61	0.00
$\mathbf{H^+}$	98.52	0.24	0.17	0.15	0.41
$\mathbf{SO_4^{2-}}$	0.42	1.74	1.26	2.38	91.79
$\mathbf{NO_3^-}$	0.25	0.04	0.62	98.75	0.03
$\mathbf{NH_4^+}$	0.00	98.03	0.01	1.94	0.02
Cd	0.30	54.71	0.03	27.31	10.88
Cu	0.53	36.41	3.28	34.15	14.69
Pb	4.47	39.60	0.35	28.69	9.87
Ni	1.51	61.30	1.67	27.16	0.62
Cr	0.00	53.35	0.01	44.14	1.18
Zn	2.98	60.16	0.19	15.25	9.13

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