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Contribution of marine and continental aerosols to the content of major ions in the precipitation of the central Mediterranean

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Abstract

The region of the investigated receptor is situated in the southern part of the Adriatic Sea in the Mediterranean. The measuring station is located on the seashore, which, being considered as a border area, is representative for the qualitative and quantitative estimation of the influence of marine and continental aerosols on the content of major ions in precipitation. In the sampling period, precipitation in the region of the investigated receptor was more abundant during the summer and autumn than during the winter and spring. The most frequent precipitation heights were up to 20 mm, while high precipitation came exclusively from the continental region. The results of the measurements of ions readily soluble in water were used for the differentiation of marine from continental contributions of primary and secondary aerosols to their content in the precipitation. Using PCA, it was shown that main contribution of Cl^-, Na^+ and Mg^{2+} came from primary marine aerosols, while the contribution from continental sources was dominant for the content of SO_4^{2-}, NO_3^-, NH_4^+ and Ca^{2+} in the precipitation. The continental origin of Ca^{2+} was from a primary source, while SO_4^{2-}, NO_3^- and NH_4^+ were representatives of secondary aerosols produced by reactions between acid oxides and alkaline species in the atmosphere, but SO_4^{2-} and NO_3^- also exist in the precipitation as free acids. The origin of the trace elements Cd, Cu, Pb and Zn in the precipitation came from anthropogenic emission sources. The results obtained in this work are based on experimental data from 609 samples collected during the period 1995–2000.

Keywords: Precipitation; Major ions; Trace elements; Principal component analysis

1. Introduction

The atmosphere in the Mediterranean is affected by air masses coming from Sahara desert or from polluted regions of North and East Europe. Strong influence of these two major sources (Saharan dust and pollution aerosols originating from Europe) on the chemical composition of the precipitation in the Mediterranean is well established (Koçak et al., 2004; Glavas and Moschonas, 2002; Avila and Alarcon, 1999; Al-Momani et al., 1995; Samara and Tsitouridou, 2000). Additionally, chemical composition of rainwater varies from site to site due to the influence of local sources (Kulshrestha et al., 2003). The acidity of the precipitation depends on the availability of the acid precursors and alkaline species. In the regions which are exposed to

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strong influence of SO_2 and NO_x gases, originating mostly from combustion of fossil fuels and industrial processes, and where no natural cleansing mechanism of the atmosphere exists, low pH values are expected. The neutralization of acidity occurs, even in areas which have high SO_2, and NO_x emissions, when atmosphere is highly loaded with alkaline species, such as $CaCO_3$ from airborne dust (Saxena et al., 1996; Glavas and Moschonas, 2002; Al-Momani, 2003) and/or NH_3 originating from agricultural, industrial and even natural activities (Schuurkes et al., 1988; Zunckel et al., 2003). The neutralization of the precipitation acidity is a characteristic for the Mediterranean region due to $CaCO_3$, originating from Saharan dust and calcareous soil of the Mediterranean Sea coasts (Avila and Alarcon, 1999; Glavas and Moschonas, 2002).

Sulphate, nitrate and ammonium ions are formed in the atmosphere by gas-particle conversion processes. Sulphate and nitrate aerosol are mainly formed from the reaction of sulphuric acid and nitric acid with alkaline species in the atmosphere, e.g. ammonia, sea salt or dust. Ammonium salts obtained by reaction with NH_3 are the most important under environmental conditions (Lee and Atkins, 1994; Langford et al., 1992). The sulphates in the atmosphere can also originate from other sources: e.g. marine sea spray aerosol, gypsum $CaSO_4{\cdot}2H_2O$ from (re-suspended) dust from the Sahara (Avila and Alarcon, 1999; Glavas and Moschonas, 2002), etc. Sulphuric acid is obtained by the oxidation of SO_2, which was either directly emitted to the atmosphere (burning of fossil fuels, industrial processes, volcanoes, combustion of biomasses) or by the oxidation of lower oxidation state sulphur compounds, mainly DMS, which is the dominant source of SO_2 in marine atmosphere (Seinfeld and Pandis, 1998). The precursors of nitric acid are NO_x, primarily originating from combustion of fossil fuels in high temperature processes (traffic, power plants, industry, domestic fireboxes), soil (microbiological activity), combustion of biomass, lightning, etc. (Seinfeld and Pandis, 1998). The main natural sources of NH_3 are the decay of vegetation in soils, wild animals and oceans, while the anthropogenic sources are global livestock farming, the employment of fertilizers in agriculture, and the combustion of biomass (Seinfeld and Pandis, 1998). Far away from land, the only significant source of NH_3 is the ocean where it is obtained by the decay of N-containing organic compounds and of the secretion of zooplanktons.

The primary pollutants SO_2 and NO_x and their secondary products H_2SO_4, HNO_3, SO_4^{2-}, NO_3^-, as well as their subsequent reaction products $(NH_4)_2SO_4$ and NH_4NO_3 are continuously removed from the atmosphere by dry and wet deposition processes. Although wet deposition is very efficient, it is sporadic by nature. The residence time of SO_2 and NO_x in the troposphere is 1–3 days (Glavas and Moschonas, 2002), while the residence time of sulphates and nitrates is somewhat longer: for nitrates it is 3–9 days (Seinfeld and Pandis, 1998), and it can even be 10 days for sulphates during dry periods in the Mediterranean region (Luria et al., 1996).

Na^+, K^+, Ca^{2+}, Mg^{2+} originate mainly from natural sources: from marine aerosol, rocks and soil resuspension and forest fires, while most of the Cd^{2+}, Pb^{2+}, Zn^{2+} and Cu^{2+} in precipitation comes from anthropogenic emission sources (traffic, industry) but natural sources, such as volcanic eruptions and resuspension, also contribute (Đorđević et al., 2004, 2005).

Determination of chemical composition of rainwater, provides an understanding of the source types that contribute to rainwater chemistry, and enhances the understanding of the local and regional dispersion of pollutants and their potential impacts on ecosystems through deposition processes (Zunckel et al., 2003).

The main goal of this study was the differentiation of marine and continental aerosol contribution to the content of anions and cations in precipitation in the Mediterranean region. The differentiation was based on analysis of precipitation samples and processing of the obtained database by Principal Component Analysis (PCA).

Study area. The investigated receptor is situated in the coastal belt of a region of the Mediterranean (Fig. 1). The coastal belt is a narrow zone separated from the continental region by a mountain range and has a typical Mediterranean climate. Precipitation samples were collected at a measuring site located in the area of the Hydrometeorological station Herceg Novi (18°33′ N, 42°27′ E). The Hydrometeorological station is situated in the eastern outskirts of Herceg Novi on the coast of the south Adriatic Sea (Đorđević et al., 2004, 2005). The

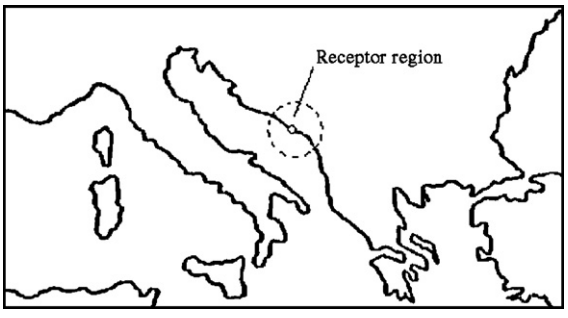

Fig. 1. Location of the Sampling Station.