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Chemical and isotopic characterisation of bulk deposition in the Louros basin (Epirus, Greece)

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ABSTRACT

About 120 rainwater samples were collected through a network of five bulk collectors in the area of the Louros basin (Epirus, Greece) during the wet season from October 2008 to August 2009. They were analysed for their isotopic (δD and $\delta^{18}O$) and chemical (H^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+, F^-, Cl^-, Br^-, NO_3^-, SO_4^{2-}) composition.
A local meteoric water line (δD‰ = 5.80 ± 0.02 $\delta^{18}O$‰ + 0.02 ± 0.12) and a local isotopic lapse rate (−0.18 $\delta^{18}O$‰/100 m) were obtained considering the volume-weighted means of the five sampling sites. These results agree well with those obtained in nearby areas.
The chemical composition of the samples allows to identify an almost entirely marine origin for chloride and sodium with decreasing deposition values at increasing distance from the coast. Nitrate and ammonium are almost completely of anthropogenic origin, calcium and potassium are overwhelmingly geogenic, sulphate has a prevailingly anthropogenic origin with a significant marine contribution and magnesium has a mixed marine and soil dust origin. Finally, as for most of the Mediterranean area, rainwater acidity is buffered by the dissolution of the abundant geogenic carbonate aerosol.

1. Introduction

Precipitations are an important part of the global hydrologic cycle representing a net transfer of oceanic vapour towards the continental areas (Gimeno et al., 2012). The spatial and temporal rainfall distribution in Greece varies greatly. The lowest mean annual rainfall amounts (about 350 mm) are found in the south-eastern regions of central Greece (Attica and Cyclades islands), while in the mountainous areas of western Greece, they exceed 2000 mm. The Pindos mountains and the western mountains in Peloponnese and Creta form a strong divide between the western rainside and the eastern rainshadow areas (Pnevmatikos and Katsoulis, 2006).

Precipitations are also an important pathway through which nutrients and toxic elements are deposited to soils and surface waters (Norton and Vesely, 2003). Precipitation chemistry is the result of complex interactions between the dynamics of clouds and microphysical processes, as well as a series of atmospheric chemical reactions that occur in the interior of and below the clouds. The first process responsible for chemical composition of precipitation is the vapour condensation on CCN (cloud condensation nuclei). The main source for CCN is the sea salt aerosol thus providing abundant marine elements in growing cloud droplets. Acidity and ion concentration in rainwater depend on the intensity of constituent sources, their incorporation into the system, physical and chemical transformation during the process of cloud formation and washout below the cloud. Although atmospheric precipitation is usually slightly acid due to the natural occurrences of sulfur, nitrogen and CO_2, alterations in its chemical composition as well as in pH levels have been noted in several places in the world. Rain is the most effective scavenging factor for removing particulate and gaseous pollutants from the atmosphere thereby affecting the chemical composition and the pH of precipitations. The acidity level depends on the neutralization produced by certain rainwater

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components such as NH_3, $CaCO_3$ and hydroxides (Seinfeld and Pandis, 1998).

Precipitation samples can be subdivided basing on sampling methodology in wet-only, dry-only and bulk deposition. Significant differences of chemical composition have been evidenced where samples were collected contemporaneously (Al-Momani, 2008; Izquierdo and Avila, 2012). Wet deposition is delivered to the earth's surface in the form of rain, snow and mist while dry deposition of gases and particles occurs by turbulent transfer and by gravitational settling on land and over water surfaces. Bulk deposition is considered to be approximately the sum of wet and dry deposition and, except for very arid climates, the contribution of the former prevails on the latter (Al-Momani, 2008; Izquierdo and Avila, 2012). The collection of wet and dry deposition requires complex instrumentations powered by electricity while bulk deposition samplers are simple devices with no need of electric connection. Therefore bulk deposition collectors are generally recommended for networks operated at remote sites (Izquierdo and Avila, 2012).

Also the isotopic composition of precipitation is the result of several processes affecting cloud water since droplets formation. Oceans usually represent the main source of vapour entering into the hydrological cycle even if other seas can also provide important fraction of vapour. Air masses transport large amounts of vapour that can condense to form clouds and precipitations. Strong fractionation processes characterise any phase change. As a consequence the final isotopic composition of precipitation is the result of the whole path starting from sea evaporation up to condensation and falling to the ground. In the central Mediterranean the relationship between the air circulation systems and isotopic composition has been investigated by Liotta et al. (2008). The authors highlighted that during cyclogenesis the contribution of vapour from the Mediterranean can be recognized in the isotopic composition of precipitations. In this sense, important information on the origin of the vapour can be obtained from the deuterium excess as defined by Dansgaard (1964) as $d = \delta D - 8 \times \delta^{18}O$. A further important parameter that can be derived from the isotopic composition of precipitation is the oxygen isotopic lapse rate, defined as the variation of isotopic composition with altitude and generally expressed as $\delta^{18}O$‰/100 m. Precipitation chemistry and isotopic composition has been also studied in many urban and rural areas of the Mediterranean Sea area (Aiuppa et al., 2006; Al-Momani et al., 1995a,b, 2008; Avila and Alarcon, 1999; Celle-Jeanton et al., 2001; D'Alessandro et al., 2004; Gat and Carmi, 1970; Ladouche et al., 2009; Liotta et al., 2006a; Panettiere et al., 2000) and in other parts of the world (Scholl et al., 1996; Keene et al., 1986; Poage and Chamberlain, 2001). Some studies on the chemical (Anatolaki and Tsitouridou, 2009; Glavas and Moschonas, 2002; Kita et al., 2004; Samara et al., 1992; Tsitouridou and Anatolaki, 2007) and isotopic (Dotsika et al., 2010 and references therein) composition of precipitation were also made in Greece, but until now there is a lack of data in the north-western part of the country (Epirus). The present study aims at filling the knowledge gaps on precipitation chemistry and isotopic composition in this area thus providing a complete and necessary dataset to characterise precipitation in Greece and allowing a effective comparison with the surrounding areas and with other Mediterranean areas. In addition, since the isotopic composition of precipitation also reflect climatic changes, the characterization of the isotopic signature of meteoric water could be useful for the definition of long term changes at the global scale. It presents the analytical results of the precipitation samples collected in the frame of a wider research on hydrology and hydrogeochemistry of the Louros basin (Katsanou, 2012), from October 2008 to August 2009, focusing on geographical and temporal variability of isotopic composition, deuterium excess, oxygen isotopic lapse rate, precipitation acidity, main ions' concentrations and sources.

2. Study area and methods

2.1. The Louros basin

The study area is located in the Epirus region at the northwestern part of Greece, including the drainage basin of Louros River, which occupies an area of 952 km^2 (Fig. 1). Louros River has a length of 73.52 km and discharges into Amvrakikos gulf to the south with an average flow of 10.6 m^3/s.

Morphologically, the Louros karstic system is characterised by high elongated mountain ranges and narrow valleys, due to tectonics (anticline and syncline structures) and geological conditions of the region with a dominance of lithologic alternation between limestones and flysch.

Geologically the basin is hosted in the formations of the Ionian geotectonic zone (Aubouin, 1959). The older formations of the study area consist of evaporitic layers of Triassic age which outcrop at the centre of the study area. They are overlain by a thick sequence of carbonate and clastic rocks reflecting a continuous sedimentation from Late Triassic to Upper Eocene (Skourtsis-Coroneou and Solakius, 1999). Oligocene flysch extends at the margins of Louros basin, whereas at the lower part Neogene and Pleistocene sediments as well as Holocene fluvial deposits overlie these formations (Macleod and Vita-Finzi, 1982). Carbonate formations are the major units constituting the highlands of the study area. These units include dolomites, the Pantokrator Limestone, the Vigla Limestone, Late Senonian limestones, Paleocene–Eocene limestones, and Posidonian chert (Skourtsis-Coroneou et al., 1995; Skourtsis-Coroneou and Manacos, 1995; Rigakis and Karakitsios, 1998).

The most important aquifers in the broader area have been developed in carbonate rocks (mainly Pantokrator and Upper Senonian limestones). These formations show high permeability due to their intense karstification and fracture porosity and their occurrence is extended especially in the upper parts of Louros draining basin.

2.2. Precipitation regime of the area

Climate of Greece can be characterised as mild temperate, to continental, changing with the influence of geographical position and relief (Boltsis, 1986). The rainfall in the region is mainly associated with disturbances within the zone of westerlies entering the Mediterranean from the Atlantic Ocean and/or disturbances forming mainly in the north-western basin of the Mediterranean and crossing the region during the rainy season (October–April) (Maheras and Anagnostopoulou, 2003). The transport of moisture from the Western to the Eastern Mediterranean corresponds to the generation (or intensification) of cyclones in the western Mediterranean and their following eastward motion. A characteristic pattern of the spatial variability of the precipitation in the Eastern Mediterranean appears in