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ORIGINAL ARTICLE

Evaluation of the atmospheric chloride deposition in the Danube hydrological zone of Bulgaria

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Abstract Estimation of the long-term groundwater recharge based on the chloride mass balance method is easy for practical applications. This method is reliable only if the atmospheric chloride deposition is known. The direct measuring of this deposition is difficult and time consuming. In this study, the chloride deposition at the catchment scale is assessed based on the export of chloride with river waters (including baseflow), as the net groundwater recharge in the studied catchments is usually low, and its contribution to the exports of salts is insignificant. For the purpose of this study, a 25-year-long time series of discharge and chloride content (from 1951 to 1975) is processed, as the quality of river waters for this period is considered natural and unaffected by human activity in the studied catchments. The obtained value of the atmospheric chloride deposition for North Bulgaria is in the range of 2.5–2.8 $g/m^2/a$ based on representative stations. This is the first estimate of the atmospheric chloride deposition in the country, which may be used for assessment of the long-term groundwater recharge in North Bulgaria.

Keywords Chloride deposition · Groundwater · Recharge · Bulgaria

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Abbreviations

CMB Chloride mass balance
ICP Inductively coupled plasma

Introduction

Groundwater recharge is characterized by large temporal and spatial variability (de Vries and Simmers 2002). Its quantification is important for water management, as the recharge represents the renewable water resource of the aquifer. As part of the hydrological cycle, the groundwater recharged to the aquifer is characterized by the quantity and quality of the precipitation water. The chloride concentration in groundwater is governed both by the water budget and the chloride input. The chloride mass balance (CMB) method is a powerful and easy-to-use technique to evaluate the long-term recharge values (Custodio 2010). However, it requires the values of the atmospheric chloride deposition, including both the wet (with precipitation) and dry (with dust) components. The common approach to estimate the atmospheric chloride deposition includes a monitoring network for precipitation quality over a period of at least several years (Custodio 2010).

During the last decades, the quality of rainwater has been the subject of intense research. The primary goal of the networks was to detect acid rains of anthropogenic origin having detrimental impact on the environment and human health. Therefore, sulfates and nitrogen compounds were most often determined. The European Air Chemistry Network includes more than 50 stations in northern and central Europe since 1955 (Rodhe and Granat 1984). The National Atmospheric Deposition Program has measured the concentrations of the major chemical species in precipitation since 1978 in 280 sites across the United States

(Lamb and Bowersox 2000). Nowadays, numerous networks on precipitation chemistry exist in North America, Europe, China, Australia, etc., some of them with long-term history (e.g., Lehmann et al. 2005; Fowler et al. 2007; Izquierdo et al. 2012; Li et al. 2012).

The atmospheric chloride deposition depends on prevailing winds that change both seasonally and annually. The proximity of the ocean has a strong influence on the concentration in rainwater, as shown by many studies carried out in Spain, Portugal, France, etc. (Alcala and Custodio 2008; Santos et al. 2011; Salles et al. 2008). For the study sites located near the seashore, the trajectory of winds is important—it was proven for Portugal that air masses transported from the Atlantic Ocean bear three times more salts compared to the continental winds (Santos et al. 2011). As a result, coastal areas are characterized by strong spatial variability in chloride deposition (Guan et al. 2010a).

In continental areas such as Eastern Europe there are very few studies concerning the chemical composition of rainwater, although some exist in Poland and the Czech Republic (Arsene et al. 2007). Based on the analyses of rainwater samples, the evaluated wet deposition of chloride in a study area from NE Romania was 0.57 $g/m^2/a$ for the period 2003/2004–2006 (Arsene et al. 2007).

In Bulgaria the monitoring network for the chemical composition of rainwater is established with the purpose of detecting acid precipitations that is the object of scientific and public interest (Iordanova 2006). Their origin is explained by the high concentration of sulfur and nitrogen compounds in the atmosphere due to human activity. Therefore, the measured parameters are mainly pH values, sulfates and nitrates in precipitation samples. Some of them were analyzed for macro and micro-components by ICP analyses. The chloride content is not measured on a regular basis and is often below the detection level.

Both wet and dry deposition rates are needed for the CMB method, i.e., the bulk deposition. As mentioned before, wet deposition fluxes of measured ions are defined, i.e., chemicals in rain water. The dry deposition is defined as the gases and particles that are deposited on the ground and vegetated surfaces. It is determined as the difference between bulk and wet deposition. The dry deposition may be rather large, for example in the USA it is assessed as one half of the total deposition (Szilagyi et al. 2011), and for a study area in France its is about 40 % of the total deposition (Salles et al. 2008). Because analyzing bulk atmospheric chloride deposition is not always feasible, e.g. chloride concentration in rainfall can be very low, therefore, requiring special analytical methods and the difficulty in measuring the dry deposition, another method has been applied in the USA. This method is based on the exports of salts with river waters. Concentrations of sodium and chloride obtained from field sampling and discharge at the USGS gauges at the time of collection were used to estimate loads and exports for the 2009 water year (Steele and Aitkenhead-Peterson 2011). One advantage of the method is that no precipitation quality network is necessary. Another advantage is that the both wet and dry depositions are taken into account. The method is applicable for pristine and low-urbanized watersheds.

Guan et al. (2010b) evaluate applicability of chloride mass balance method in an area with historical forest clearance and conceptualize six catchment types in this respect.

In this study, the multiannual value of the atmospheric chloride deposition for the Danube hydrological zone of Bulgaria is evaluated at the catchment scale taking into account the specific features of the region. The export of salts from the catchments is mainly with the river waters; therefore the basic datasets are the discharge and chloride content in rivers.

In addition, the anthropogenic input of chloride salts is evaluated based on increase of chloride salts in the stream (for the period 2000–2005).

Study area description

The study area encompasses that part of North Bulgaria that belongs to the Danube River Basin, or the Danube hydrological zone (Figs. 1 and 2). Its area covers 42,837 km^2, which is about 38 % of the overall territory of Bulgaria.

The north boundary coincides with the Danube River. The Danubian plain is flat, weakly sloping in the north direction. Toward the south, the relief becomes hilly. The southern boundary of the Danube River Basin follows the Balkan Mountain range, with elevations up to 2,376 m (peak Botev).

The climate of Bulgaria is formed under the influence of the moisture-laden prevailing westerly winds and the intense cyclonic activity. The North Atlantic cyclones cause the thundercloud formation with related rainfall maximum during May–June typical for the most part of the country (Martinov 1991; Kopralev 2010).

The Mediterranean cyclones formed over the Tyrrhenian Sea (Western part of the Mediterranean Sea) are most frequent and well manifested in the cold half-year (Pisarski 1955; Martinov 1991). Although usually more pronounced in Southern Bulgaria, they often create quite substantial rain conditions which envelope the northern part of the country. They follow one of the three trajectories from west to east, the middle track ensuring a winter in the country with precipitation sum about normal (Pisarski 1955; Bocheva et al. 2007).