Research paper

Hydrogeochemistry of Alpine springs from North Slovenia: Insights from stable isotopes

Tjaša Kanduč [a,*], Nataša Mori [b], David Kocman [a], Vekoslava Stibilj [a], Fausto Grassa [c]

[a] Department of Environmental Science, Jožef Stefan Institute, Jamova cesta 39, Ljubljana 1000, Slovenia
[b] National Institute of Biology, Department of freshwater and terrestrial ecosystems research, Večna pot 111, 1000 Ljubljana, Slovenia
[c] Istituto Nazionale di Geofisica e Vulcanologia. Sezione di Palermo, Via Ugo La Malfa, 153, 90144, Palermo, Italy

ABSTRACT

Spring water chemistry and carbon cycling in our study mainly depend on geological composition of the aquifer. The investigated Alpine springs in Slovenia represent waters strongly influenced by chemical weathering of Mesozoic limestone and dolomite, only one spring was located in Permo-Carboniferous shales. The carbon isotopic composition of dissolved inorganic carbon (DIC) and suspended organic carbon (POC) as well as major solute concentrations yielded insights into the origin of carbon in Alpine spring waters. The major solute composition was dominated by carbonic acid dissolution of calcite. Waters were generally close to saturation with respect to calcite, and dissolved CO_2 was up to fortyfold supersaturated relative to the atmosphere. $\delta^{13}C$ of DIC indicates the portion of soil CO_2 contributed in water and is related with soil thickness of infiltrating water in aquifer and could be therefore used as a tool for vulnerability assessment. The $\delta^{13}C$ of DIC ranged from $-15.8‰$ to $-1.5‰$ and indicated less and more vulnerable aquifers. Mass balances of carbon for spring waters draining carbonate rocks suggest that carbonate dissolution contributes from approximately 49% to 86% and degradation of organic matter from 13.7% to 51.4%, depending on spring and its relation with rock type, soil environment, and geomorphic position. Stable oxygen isotope composition of water ($\delta^{18}O_{H2O}$), and tritium values range from -12.2 to $-9.3‰$ and from 6.4 to 9.8 TU, respectively and indicate recharge from modern precipitation. According to active decay of tritium and tritium in modern precipitation the age of spring waters are estimated to be about 2.6 years for springs located in Julian Alps, about 5 years for springs located in Karavanke and about 5 years for springs located in Kamniško–Savinjske Alps.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Approximately 25% of the world's drinking water comes from karst groundwater systems (Drew and Hoetzl, 1999). In Slovenia, approximately half of the population is supplied by karst waters. In Slovenia, karst is developed where Devonian to Miocene age carbonate rocks are present at or near the land surface. Slovenian karst systems are divided into three units, based on geological, hydrological and morphological conditions: Alpine karst, Dinaric karst and Dinaric-alpine intermediary and isolated karst (Habič, 1969). Alpine karst is present in mountainous regions of the northwestern and northern parts of Slovenia. Although a significant portion of groundwater is discharged from alpine karst, capacities of the alpine springs are not yet fully known (Petrič, 2004). As the degree of pollution in sparsely inhabited mountainous areas is still relatively low and amount of stored groundwater is large, alpine aquifers are invaluable reservoirs of drinking water and an important potential water source also for

the future. At the same time, as highly heterogeneous and anisotropic environments they are particularly vulnerable to pollution. Due to fast infiltration and groundwater flow, which can transport pollutants rapidly in karst conduits over large distances, the rate of their self-cleaning capacity is low (Petrič, 2004). To adequately protect them, better understanding of their characteristics and dynamics is necessary (Petrič, 2004). Karst aquifers in Slovenia are also known for their heterogeneity and irregular complex flow patterns which make them more difficult to model and demand specific modeling approaches (Janža, 2010). Slovenian alpine karst springs also significantly contribute to the discharge of major alpine rivers, which drain to the Sava River. Alluvial aquifers associated with the Sava River are a major groundwater resource for the country.

Hydrochemistry and stable isotope compositions of karst spring waters provide critical information regarding sources of groundwater recharge, timing of recharge, water-rock interaction along flow paths, and mixing of distinct groundwater bodies. Ionic and isotopic concentrations can be easily changed or fractionated in aquifers through processes such as plant activity (O'Leary, 1988), isotopic exchange with surrounding materials, mineral or gas dissolution (Deines et al., 1974; Lesniak and Sakai, 1989), or redox reactions such as denitrification

---

(Bottcher et al., 1990), sulfate reduction (Sakai, 1968; Machel et al., 1995), sulfide oxidation (Fry et al., 1988), or methanogenesis (Klass, 1984) along the flow path. Carbon isotopes are used to assess the origin of dissolved inorganic carbon (DIC), which is the main species in waters draining carbonate watersheds, and particulate organic carbon (POC), which is also an important parameter in food web studies of biota within watersheds. Concentrations of DIC and its stable carbon isotope ratios ($\delta^{13}C_{DIC}$) are governed by processes occurring in the soil–aquifer system, and these vary seasonally. Changes in DIC concentrations result from carbon addition or removal from the DIC pool, whereas changes of $\delta^{13}C_{DIC}$ result from the fractionation accompanying transformation of carbon or from mixing of carbon from different sources. The major sources of carbon to aquifer DIC loads are dissolution of carbonate minerals, soil CO_2 derived from root respiration and from microbial decomposition of organic matter (often mainly of terrestrial origin but also including aquatic production). The major processes removing DIC in aquifer systems is carbonate mineral precipitation (Atekwana and Krishnamurthy, 1998). Water isotopic composition ($\delta^{18}O$ or δD) behaves conservatively in low-temperature aquifer environments (Kendall et al., 1995). As a result, researchers have often used stable isotope composition of water as tracers for determining the water provenance (Epstein and Mayeda, 1953; Kennedy et al., 1986; Taylor et al., 1992; Mayo and Loucks, 1995; Katz et al., 1997; Cartwright et al., 2000; Larsen et al., 2001).

In this study, we used hydrochemical (Mg^{2+}/Ca^{2+} ratios) and isotope (carbon, oxygen, hydrogen and tritium) tracers to characterize: 1) water–rock interactions, 2) origin of carbon and biogeochemical processes, and 3) recharge area and flow paths of some of the most important Alpine aquifers in northern Slovenia. A thorough knowledge of hydrogeochemical characteristics of Alpine springs is important for interpretation of the sources of waters and origins of solutes, which could be used as an additional tool in vulnerability estimation, risk assessment analysis and groundwater management practice.

2. Hydro-geological and meteorological characteristics

In aquifer studies, the uncertainty about recharges sources and processes along flowpaths is the major consideration. In this study, spatially distributed data on meteorology, hydrogeology and land use were used for the characterization of the springs, using the advantages of Geographical Information System (GIS) technology. This makes characterization of springs easier and more objective, though constrained by the quality of the input data. For each of the springs, characteristics presented in Table 1 and Fig. 1 were extracted from corresponding GIS maps prepared by the Environmental Agency of the Republic of Slovenia (EARS) and the Geological Survey of Slovenia, respectively, using the ArcGIS 9.3 software (ESRI).

Investigated springs are located within valleys of high mountainous areas composed of carbonate rocks, predominantly Triassic age limestone with some dolomite and dolomitized limestone. Rocks are well karstified and different surface and underground karst features are developed. The dominant hydrogelological units are highly permeable karst-fissured aquifers with fissured porosity. In some areas, where dolomite is more prevalent, fissured aquifers are slightly less permeable (Buser, 1987). More detailed hydro-geological descriptions of springs are presented in Table 1.

The climate of the region is alpine, with a mean annual temperature of 4 to 9 °C and annual precipitation from 1721 to 2335 mm (Ogrin, 1998). The majority of springs are situated along deep, narrow Alpine valleys at altitudes from 645 to 941 m. Three of them emerge higher on the slopes with altitudes of 1107–1236 m (Table 1). Precipitation and infiltration data for all springs are presented in Table 1. The vegetation of springs is composed of C3 plants (mixed forest, grasslands and coniferous forest) and is described in detail for the Sava River watershed elsewhere (Kanduč et al., 2007a). All the springs are part of the larger Sava River watershed (Fig. 1). Locations of Alpine karst springs as well

as their hydrogeological characteristics are presented on Fig. 1 and Table 1.

Groundwater resources are divided into three subgroups: intergranular aquifers, karstic aquifers and fissured aquifers according to EU Water Framework Directive. Intergranular aquifers are a geological medium where porosity is a consequence of contact between grains in sediment and rock, while karstic aquifers are a geological medium where channel porosity prevails and fissured aquifers are a geological medium where the porosity of fissures and joints are predominant, although intergranular and channel porosity may also be present (Brenčič et al., 2009). In our study all types of aquifers were investigated (Table 1).

3. Sampling protocols and field measurements

Sampling was performed during 3 different seasons (spring = June, summer = August/September and autumn = October/November) in years 2009 and 2010. Samples for stable isotope and tritium analyses were taken only in year 2010. Temperature, dissolved oxygen (DO) and conductivity of the spring waters were measured under the water surface in spring. Temperature and conductivity were measured using a WTW Multiline P4, TetraCon 325, respectively. Dissolved oxygen (DO) was measured with WTW Multiline P4, CellOx 325 and pH was measured using a WTW pH 540 GLP, with a SenTix 81. Discharge was measured using an OTT ADC flow meter at each spring and during each sample collection. Data of estimated discharges were calculated according to flow velocity and surface area of the springs (Table 1).

Sample aliquots collected for cation (pre-treated with HNO_3), anion and alkalinity analyses were passed through a 0.45 μm nylon filter into HDPE bottles and kept refrigerated until analyzed. Samples for $\delta^{13}C_{DIC}$ analyses were stored in glass serum bottles filled with no headspace and sealed with septa caps.

Samples for stable carbon isotope analysis of particulate organic carbon ($\delta^{13}C_{POC}$) in all 2010 sampling seasons were collected in LDPE bottles (5 liters from each location). In addition, carbonate rocks of Mesozoic age from all locations (except of Perkova pušča (location 9), which is located in Permo-Carboniferous clastics rocks), were sampled from outcrops for stable carbon analyses ($\delta^{13}C_{caco3}$).

For $\delta^{18}O$ and δD analyses samples were collected in 30 ml HDPE bottles with no filtering. For tritium analyses 1 l of sample was collected per location.

4. Laboratory analyses

Alkalinity was measured using Gran titrations (Clesceri et al., 1998). For waters investigated in Sava River watershed it was found out that regression between alkalinity and DIC concentrations was 96% when both were measured (Kanduč et al., 2007b). Cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) and anions (SO_4^{2-}, NO_3^-, Cl^-) were measured by ion chromatography (Metrohm, 761 Compact IC) with a precision of $\pm 2\%$. Analytical uncertainty is estimated between 10-20%. Detection limits for Ca^{2+}, Mg^{2+}, Na^+ and K^+ are 0.035 mg/l. Detection limits for NO_3^-, SO_4^{2-} and Cl^- are 0.01 mg/l.

The stable isotope composition of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) was determined with a Europa Scientific 20–20 continuous flow IRMS (isotope ratio mass spectrometer) with an ANCA–TG preparation module. Phosphoric acid (100%) was added (100–200 μl) to a septum-sealed vial which was then purged with pure He. The water sample (6 ml) was injected into the septum tube and headspace CO_2 was measured (modified after Miyajima et al., 1995; Spötl, 2005). In order to determine the optimal extraction procedure for surface water samples, a standard solution of Na_2CO_3 (Carlo Erba) with a known $\delta^{13}C_{DIC}$ of -10.8 ± 0.2‰ was prepared with a concentration of 4.8 mM (for samples with an alkalinity from 1 to 4 mM).

The carbon stable isotope composition of particulate organic carbon ($\delta^{13}C_{POC}$) was determined with a Europa Scientific 20–20