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Comparison of prediction methods for oxygen-18 isotope composition in shallow groundwater

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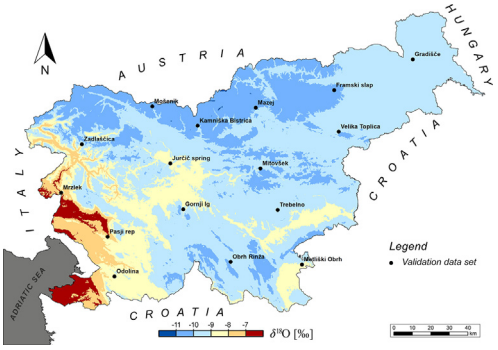
HIGHLIGHTS

- Isotopic composition of oxygen ($\delta^{18}O$) in groundwater in shallow aquifers was investigated.
- 83 groundwater sampling points during dry and wet periods (2009–2011)
- Different prediction models were used for prediction of $\delta^{18}O$ spatial distribution.
- Model parameters: distance from sea, elevation, and amount of precipitation
- Best groundwater $\delta^{18}O$ prediction model is artificial neural network.

GRAPHICAL ABSTRACT



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ABSTRACT

Groundwater is the most important source of drinking water in the world. Therefore, information on the quality and quantity is important, as is new information related to the characteristics of the aquifer and the recharge area. In the present study we focused on the isotope composition of oxygen ($\delta^{18}O$) in groundwater, which is a natural tracer and provides a better understanding of the water cycle, in terms of origin, dynamics and interaction. The groundwater $\delta^{18}O$ at 83 locations over the entire Slovenian territory was studied. Each location was sampled twice during the period 2009–2011. Geostatistical tools (such us ordinary kriging, simple and multiple linear regressions, and artificial neural networks were used and compared to select the best tool. Measured values of $\delta^{18}O$ in the groundwater were used as the dependent variable, while the spatial characteristics of the territory (elevation, distance from the sea and average annual precipitation) were used as independent variables. Based on validation data sets, the artificial neural network model proved to be the most suitable method for predicting $\delta^{18}O$ in the groundwater, since it produced the smallest deviations from the real/measured values in groundwater.

1. Introduction

Isotopes as environmental tracers have been used extensively during the past decades to study water cycles, to better understand the origin, dynamics (recharge areas, residence time in aquifers, etc.) and the interconnections of the different elements that constitute the hydrologic cycle (Clark and Fritz, 1997; Schiavo et al., 2009; Chandrajith et al., 2014). Usually the stable isotope composition of precipitation of oxygen-18 ($\delta^{18}O$), as well as deuterium ($\delta^{2}H$), is correlated with various environmental parameters that characterise the recharge areas of sampled water. Since the isotope composition of shallow groundwater is closely related to the isotope composition of precipitation, we can trace the origin of the groundwater, identify the groundwater recharge

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areas, and the dynamics, processes and quantification of mixing ratios of different water sources (Mezga et al., 2013). In most low-temperature environments, stable $\delta^{18}O$ and $\delta^{2}H$ isotopes behave conservatively in the sense that as they move through a recharge area, any interactions with oxygen and hydrogen in the organic and geologic materials in the recharge area will have a negligible effect on the ratios of isotopes in the water molecule (Kendall and McDonnell, 1998).

The main factors that influences the isotope composition ($\delta^{18}O$ and $\delta^{2}H$) of water are altitude (*altitude effect*) and the continental factor (*continental effect*). Alongside those two are other factors, e.g., the *temperature effect*, which is expressed by the local surface air temperature, the *amount effect*, which is governed by the amount of the precipitation (Dansgaard, 1964; Kendall and McDonnell, 1998; Araguás-Araguás et al., 2000; Mook, 2001; Cartwright et al., 2012; Giustini et al., 2016). The altitude effect is caused by increased precipitation at higher elevations due to the continuous cooling of the air mass pseudo-adiabatically down to below the dew point in an orographic precipitation system (Kendall and McDonnell, 1998). The effect describes decreasing $\delta^{18}O$ values in precipitation as elevation increases. According to Clark and Fritz (1997), and Eriksson (1983) the altitude effects in precipitation range from −0.1‰ to −0.6‰ $\delta^{18}O$/100 m. The calculated isotope altitude effects derived from groundwater samples are comparable to the estimated altitude effects in precipitation from the past researches in Slovenia and neighbouring countries. For example on the Slovenian territory, the altitude effect in precipitation ranges from −0.2‰ to −0.3‰ $\delta^{18}O$/100 m (Vreča et al., 2006; Brenčič and Poltnig, 2008). For Croatia and Slovenia jointly these values range between −0.37‰ and −0.26‰ $\delta^{18}O$/100 m (Horvatinčić et al., 2005). For other countries, such as for instance Austria, the altitude effect is estimated at −0.21‰ $\delta^{18}O$/100 m (Kralik et al., 2003) and the value for Italy is estimated to approximately −0.2‰ $\delta^{18}O$/100 m (Longinelli and Selmo, 2003). Based on the fact that isotope composition in the precipitation is reflected in the isotope composition of the groundwater, Mezga et al. (2013) calculated three altitude effects for groundwater, which follow the different precipitation intensity pattern, ranging from −0.25‰ $\delta^{18}O$ to −0.33‰ $\delta^{18}O$/100 m.

The continental effect is caused by the evaporation of water from the ocean (or the sea) into the atmosphere and the movement of air masses inland. Isotopic fractionation occurs during the movement of air masses, resulting in the depletion of heavy isotopes of oxygen (Ingraham, 1998) during said movement. Coastal precipitations are enriched with heavy isotopes, while the colder, inner continental regions receive precipitation depleted in heavy isotopes and exhibit strong seasonal differences (Clark and Fritz, 1997). The estimated continental effect for France is around −3.2‰ $\delta^{18}O$/1000 km (Millot et al., 2010), while for Europe in general the figure is roughly −2.0‰ $\delta^{18}O$/1000 km (Rozanski et al., 1993). For Slovenia, the estimated continental effect in groundwater is approximately −8.3‰ $\delta^{18}O$/1000 km (Mezga et al., 2013).

Both $\delta^{18}O$ and $\delta^{2}H$ in precipitation have been monitored and collected on a global scale since 1961 as part of the Global Network of Isotopes in Precipitation (GNIP) (IAEA/WMO, 2016). In Slovenia, water isotopes in precipitation have been systematically monitored since 1981, but only in Ljubljana (Pezdič, 1999). Still, in the past 37 years, the number of additional sampling points has been growing constantly and now stands at 30 (Vreča and Malenšek, 2016). While these datasets exhibit sufficient temporal density, their spatial distribution is not sufficient for use in prediction models. Also, many isotope studies of groundwater in Slovenia have been performed on individual aquifers. Prior to this study, only one study presented the general characteristics of the $\delta^{18}O$ and the determination of the altitude and the continental effects of groundwater for the entire territory of Slovenia (Mezga et al., 2013). However, during this study spatial modelling of $\delta^{18}O$ in groundwater was performed countrywide based on sample results gathered from various groundwater bodies. Mezga et al. (2013) produced point values of mean $\delta^{18}O$ at each sampling point as well as for groundwater bodies in Slovenia, but the measured isotopic data was not spatially modelled.

Many studies from around the world show spatial distribution of the $\delta^{18}O$ in groundwater or in the precipitation as derived using some general interpolation methods, i.e. ordinary kriging, IDW (Melchiorre et al., 2009; Van der Veer et al., 2009), multiple linear regression (Kendall and Coplen, 2001; Bowen and Revenaugh, 2003; Lachniet and Patterson, 2009; Capilla et al., 2011; Terzer et al., 2013), as well as spatial modelling with a methodology developed by Bowen and Wilkinson, 2002 (Dutton et al., 2005; Dotsika et al., 2010; West et al., 2014), and supported by the Geographical Information System (GIS).

Producing quality regional or continental-level spatial models usually calls for large sets of sampling points distributed equally throughout the study area, which is not only expensive but also time consuming. To tackle this challenge, we strived to find the most appropriate method to precisely predict modelled values that would provide the best estimation of real $\delta^{18}O$ values in groundwater at locations of different elevations and climates, where groundwater was not sampled. While each of the commonly applied methods has its advantages and drawbacks, problems with the interpolation of geo-related datasets are commonly linked to noise in the data (as a result of sampling and analytical errors), and to inability to incorporate outliers and attributive variables, which cannot be measured by using nominal scale (like rock or soil type) in the model. Finding the right method to establish the right model and approach "close to real values" in nature (in aquifers) could reduce the time and number of locations required for groundwater sampling in the field, and could reduce costs as well. However, it must be stressed that these models and methods are no substitute for real field measurements. However they can help us draw general conclusions about the sources of groundwater bodies and help us make better decisions about groundwater management.

2. Study area

In order to model the spatial distribution of isotope compositions of groundwater that incorporate all of the aforementioned variables (continental and altitude effects, amount of precipitation), the test area should exhibit clearly expressed differences in all three factors. Because the Slovenian territory is very diverse, it presents a quite appropriate area for testing different prediction methods. It is located near the coast and stretches towards the inland, with seasonal variations in annual precipitation and a diverse landscape (lowlands and mountainous areas).

Slovenia is a Central European country with an area of 20,273 km^2, located at approximately 46°N latitude and about 15°E altitude, and situated between Austria, Italy, Croatia and Hungary (Fig. 1). The average altitude of the Slovenian territory is 557 m a.s.l. The highest altitudes are found in the northwest (2864 m a.s.l.), where high mountains dominate, while the lowest altitudes stretch along the coast in the southwest, and in the east, on the Pannonian plains (Perko, 1998).

Slovenia's heterogenic climate is mainly the result of its geographic position with its temperate latitudes and significant diversity in its relief. With the exception of the high-mountain and mountain climates in the northwest of the country, Slovenia has a moderately warm and humid climate, which is divided into sub-Mediterranean, which influences the southwest of the country, and temperate continental, which characterises the majority of its territory (Rakovec and Vrhovec, 2007).

The highest amounts of annual precipitation occur in the western part the country, in the Julian Alps and Kamnik-Savinja Alps (over 2500 mm) and at the south-western edges of the high Dinaric plateaus (Snežnik Mt.). The amount of precipitation decreases as distance from the sea increases, i.e. from the southwest and the west, across the central part (1000–1300 mm) of Slovenia, to its eastern and north-eastern parts (<900 mm) (Zupančič, 1998). The prevailing precipitation trajectories are observed in the southwest-northeast direction. Most of the important precipitation air masses generally come from the