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Chemical modeling of groundwater in the Banat Plain, southwestern Romania, with elevated As content and co-occurring species by combining diagrams and unsupervised multivariate statistical approaches

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HIGHLIGHTS

- Groundwater naturally enriched with inorganic arsenic species.
- Classification of groundwater sources using Fuzzy Hierarchical Cross-Clustering.
- PO_4^{3-}—AsO_4^{3-} ion exchange and water-rocks interactions as sources of As.
- Na^+—F^-—pH cluster as marker for As naturally enriched groundwater.
- Co-occurrence of As species and F^- under the influence of HCO_3^- and alkaline pH.

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ABSTRACT

The study proposes a combined model based on diagrams (Gibbs, Piper, Stuyfzand Hydrogeochemical Classification System) and unsupervised statistical approaches (Cluster Analysis, Principal Component Analysis, Fuzzy Principal Component Analysis, Fuzzy Hierarchical Cross-Clustering) to describe natural enrichment of inorganic arsenic and co-occurring species in groundwater in the Banat Plain, southwestern Romania. Speciation of inorganic As (arsenite, arsenate), ion concentrations (Na^+, K^+, Ca^{2+}, Mg^{2+}, HCO_3^-, Cl^-, F^-, SO_4^{2-}, PO_4^{3-}, NO_3^-), pH, redox potential, conductivity and total dissolved substances were performed. Classical diagrams provided the hydrochemical characterization, while statistical approaches were helpful to establish (i) the mechanism of naturally occurring of As and F^- species and the anthropogenic one for NO_3^-, SO_4^{2-}, PO_4^{3-} and K^+ and (ii) classification of groundwater based on content of arsenic species. The HCO_3^- type of local groundwater and alkaline pH (8.31–8.49) were found to be responsible for the enrichment of arsenic species and occurrence of F^- but by different paths. The PO_4^{3-}—AsO_4^{3-} ion exchange, water-rock interaction (silicates hydrolysis and desorption from clay) were associated to arsenate enrichment in the oxidizing aquifer. Fuzzy Hierarchical Cross-Clustering was the strongest tool for the rapid simultaneous classification of groundwaters as a function of arsenic content and hydrogeochemical characteristics. The approach indicated the Na^+—F^-—pH cluster as marker for groundwater with naturally elevated As and highlighted which parameters need to be monitored. A chemical conceptual model illustrating the natural and anthropogenic paths and enrichment of As and co-occurring species in the local groundwater supported by mineralogical analysis of rocks was established.

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1. Introduction

Groundwater is one of the most significant sources for drinking water as well as for human activities in industrial, agricultural, household, recreational and other fields. In arid and semi-arid regions groundwater is often the sole source of drinking water for local human communities. Because of the groundwater-mineral matrix interaction, some chemical parameters can occur in high concentrations even in the absence of anthropogenic sources. In these circumstances the assessment of groundwater quality and health risk was the subject of several studies (Aksever et al., 2015; Cuoco et al., 2015; Esmaeili-Vardanjani et al., 2015; Al-Harbi et al., 2014; Kelepertzis, 2014; Shankar et al., 2011; Carrillo-Rivera et al., 2002). One of the most common chemical species naturally occurring in groundwater is arsenic in inorganic form following water-rock interaction. Thus more than 500 million people living in the so-called „arsenic endemic" regions such as West Bengal India, Bangladesh, China, Vietnam, Taiwan, Northern Chile, Mexico, USA, and Central and Eastern Europe are chronically exposed to arsenic from drinking water (1–10000 μg L^{-1}) (Sarkar and Paul, 2016; Panagiotaras et al., 2012; Amini et al., 2008; Smedley and Kinniburgh, 2002). In Europe, the Pannonian Basin including eastern Hungary, western Romania, northern Serbia, northeastern Croatia and southern Slovakia, is characterized by an elevated As content, which poses health risks to more than 1000000 inhabitants via drinking water (Romanian National Institute of Statistics, 2012; Rowland et al., 2011; Dimkic et al., 2010; Gurzau and Gurzau, 2001). Examination of groundwater with elevated As concentration and the mechanisms related to its occurrence are public health and environmental concerns in the world (Chakraborti et al., 2016; Frederick et al., 2016; Sarkar and Paul, 2016; Rahman et al., 2015a; Biswas et al., 2014a; Sorg et al., 2014; Bonte et al., 2013; Ghosh and Sar, 2013; Rango et al., 2013). Besides the well-known carcinogenicity of inorganic arsenic species, studies indicated the risk associated to other diseases such as anemia, arsenicosis, vascular and heart diseases, neurological, or neuro-physiological diseases or risk for spontaneous pregnancy loss via drinking water consumption from wells with arsenic below or above of maximum contaminant level (MCL) (Chakraborti et al., 2016; Sarkar and Paul, 2016; Neamtiu et al., 2015; Rahman et al., 2015a, 2015b; Surdu et al., 2015; Bloom et al., 2010, 2014).

World Health Organization (WHO) and U.S. Environmental Protection Agency (EPA) adopted the value of 10 μg L^{-1} arsenic as MCL in drinking water (U.S. EPA, 2001 and WHO, 2004). Based on Water Framework Directive (WFD) (2000/60/EC), EU countries adopted the Groundwater Directive (GWD) with the aim to protect all bodies of surface water and groundwater from pollution and established measures and Environmental Quality Standards (EQS) so that inland and coastal water resources to achieve "good status" (Crane and Babut, 2007; Crane et al., 2007; Directive 2006/118/EC). Member states have established threshold values (TVs) for groundwater bodies depending on hydrogeological conditions and natural background levels (NBLs) at least for contaminants referred to as risk factors from natural or anthropogenic sources (As, Cd, Pb, Hg, NH_4^+, Cl^-, SO_4^{2-}, NO_3^-) and synthetic substances (trichloroethylene, tetrachloroetylene) (Annex 3 to Directive 2006/118/EC). In Romania, there were established TVs for all groundwater bodies according to NBLs (Order 621/2014; Radu et al., 2010).

The simple examination of the results for hazardous chemicals in groundwater in relation with guideline values is not satisfactory for explaining and understanding their behavior in groundwater. Multivariate supervised/unsupervised statistical approaches are needed to reveal hidden relationships between chemical parameters and to establish the relevant characteristics for classification, grouping and delineation of groundwater sources (Cuoco et al., 2015; Esmaeili-Vardanjani et al., 2015; Spanos et al., 2015; Sener and Sener, 2015; Al-Harbi et al., 2014; Kelepertzis, 2014; Kim et al., 2014; Sappa et al., 2014).

The aim of this study was to provide a chemical modeling of groundwater in the Banat Plain, south-western Romania, for a deeper understanding of occurrence of high level of As and co-occurring species F^-, SO_4^{2-}, PO_4^{3-} and NO_3^-. The model is based on a combination of classical diagrams (Gibbs, Piper and Stuyfzand Hydrogeochemical Classification System (SHCS)) and unsupervised chemometric methods such as Cluster Analysis (CA), Principal Component Analysis (PCA), Fuzzy Principal Component Analysis (FPCA) and Fuzzy Hierarchical Cross-Clustering (FHCC). Usefulness of the model was demonstrated on water samples collected from shallow groundwater body (GW-ROBA03) and depth groundwater body (GW-ROBA18) labeled according to water body delineation in Romania. Besides speciation of inorganic As (arsenite, arsenate) other hydrogeochemical characteristics were investigated such as ion concentrations (Na^+, K^+, Ca^{2+}, Mg^{2+}, HCO_3^-, Cl^-, F^-, SO_4^{2-}, PO_4^{3-}, NO_3^-), pH, redox potential (E_h), electrical conductivity (EC) and total dissolved substances (TDS). The chemical conceptual model describing the pathway and enrichment of As and co-occurring species in the local groundwater was coupled with hydrogeochemical and mineralogical analysis of the aquifer rocks and land use activities. In this model both natural via water-rock interaction and ion-exchange, and anthropogenic sources associated to land use activities were identified. The present study was an attempt to examine the occurrence of the elevated As species in an oxidizing aquifer rather than to assess the quality of the groundwater.

2. Materials and methods

2.1. Site description, water sample collection and preservation

The study-area is situated in the Banat Plain, Bega and Timis Rivers Basin, south-western Romania and belongs to the eastern margin of the Panonian Basin that accumulated very thick deposits during the Neogene and Quaternary. The Banat Plain was formed as a result of the activity of rivers during the Quaternary that transported and deposited detrital sediments as a succession of cross bedded layers and alluvial fans. The thickness of the Quaternary deposits may reach tens to hundreds m and they are generally coarse-grained with discontinuous finer intercalations (Mutihac, 1990; Enciu et al., 2014). Beneath the Quaternary deposits, and completely covered by them, the Pliocene fluvio-lacustrine sediments are also detrital, generally finer gained. Their thickness increases from east to west from about 100 m to more than 1000 m. The two superposed groundwater bodies, GW-ROBA03 and GW-ROBA18, were identified in the Banat Plain by the Romanian Water Authority and classified as shallow/phreatic aquifer and deeper confined aquifer (ANAR, 2015).

GW-ROBA03 is developed until 15 m in flood plains and terraces, and until 30 m in interfluves and the overlaying strata are represented by clays, sandy clays, silty clays, silts, argillaceous silts and sandy silts. The main lithological units of the aquifer GW-ROBA03 are presented in Supplementary material 1 (Radu and Radu, 2011). The shallow aquifer is exploited mainly through low yield domestic wells. The main flow direction is from north-east to south-west, with a hydraulic gradient of 0.1–2.0‰. The effective porosity is between 5 and 25% and the hydraulic conductivity ranges between 6 and 68 m d^{-1}. The depth of the water table is less than 5 m in most cases. The aquifer is recharged through precipitations and hydraulic connection with the rivers. Due to the permeability of the covering sediments, GW-ROBA03 is relatively vulnerable to contamination through the human settlements in the