



Geochemical and isotopic study to determine sources and processes affecting nitrate and sulphate in groundwater influenced by intensive human activity - carbonate aquifer Gliwice (southern Poland)



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ABSTRACT

A multi-species, multi-stable-isotope approach ($\delta^{15}\text{N}_{\text{NO}_3}$, $\delta^{18}\text{O}_{\text{NO}_3}$, $\delta^{34}\text{S}_{\text{SO}_4}$, $\delta^{18}\text{O}_{\text{SO}_4}$, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta^2\text{H}_{\text{H}_2\text{O}}$) was used together with environmental tracers (Ar, Ne, CFC-11 and CFC-12) and geochemical modelling to characterize sources and processes controlling concentrations of NO_3^- and SO_4^{2-} in groundwater of the carbonate aquifer Gliwice (southern Poland). The study area represents a strongly transformed environment with a range of human activities i.a. Agriculture, urbanization and industry. The $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ indicated that most samples contained NO_3^- of mixed sources: artificial fertilizers, municipal and industrial sewage, while very good correlation between NO_3^- and CFC-12 suggested that nitrate originated primarily from residential and industrial sewage. Conversely, isotopic composition of sulphate in groundwater suggested agriculture as well as oxidation of sulphides as dominant. The conclusion was supported by the comparison of CFCs and sulphate concentrations which revealed no relevant correlation. Geochemical modelling confirmed the presence of sulphate reduction in areas where isotopic analyses were not possible due to undetectable sulphate. Thus, the integrated application of stable isotopes, environmental tracers, groundwater chemistry and geochemical modelling shows a complex origin of groundwater pollution in the study area as well as variety of geochemical processes controlling chemistry of groundwater in a triple-porosity aquifer influenced by different types of human activity.

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1. Introduction

Groundwater is the primary source of potable water in many regions worldwide. Intensive development of human activities in the second half of the 20th century caused a significant degradation of groundwater quality and consequently reduced available resources of drinking water. Among numerous substances that contribute to groundwater pollution, nitrate and sulphate are cited most frequently (eg. Vadillo et al., 2005; Bottrell et al., 2008; Vitòria et al., 2008; Puig et al., 2013). Potential sources of these compounds in groundwater include: synthetic and organic fertilizers, leakage from sewer systems, septic tanks, municipal and industrial landfills, atmospheric deposition and mine tailings. Sulphate in groundwater may also originate from natural sources like dissolution of sulphur-containing minerals, e.g. gypsum or pyrite. A requirement of

protecting and restoring a good quality of groundwater was implemented by the Water Framework Directive (2000/60/EC). The goals cannot be achieved without a proper identification of pollution sources as well as processes controlling concentration of contaminants along a groundwater flow path (Kendall et al., 2007).

Application of isotope tracers ($\delta^{15}\text{N}_{\text{NO}_3}$, $\delta^{18}\text{O}_{\text{NO}_3}$, $\delta^{34}\text{S}_{\text{SO}_4}$, $\delta^{18}\text{O}_{\text{SO}_4}$) in identifying sources and fate of SO_4^{2-} and NO_3^- in groundwater has been successfully done for several decades (Mariotti et al., 1988; Böttcher et al., 1990; Aravena and Robertson, 1998; Moncaster et al., 2000; Negrel and Pauwels, 2004; Taylor et al., 2006; Bottrell et al., 2008; Heaton et al., 2012; Jahangir et al., 2012; Saccon et al., 2013; Czekaj et al., 2016 among others). Stable isotope abundances measured in nitrate help to distinguish between natural and synthetic fertilizers, manure and atmospheric deposition as typical sources of nitrate in groundwater. In case of sulphate, the isotopic composition allows to discern sulphates coming from oxidation of sulphides, dissolution of evaporite minerals or anthropogenic sources. Additionally, the isotopic method provides a powerful tool in tracing the processes that can influence

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original isotopic signature of nitrate and sulphate, like microbial reduction or mixing (Mariotti et al., 1988; Dogramaci et al., 2001). Nonetheless, in many cases the proper identification of contaminant sources is complicated by: (i) temporal and spatial variation in isotopic signature of different sources, (ii) the problem that different sources can have partially overlapping isotopic compositions and (iii) presence of biogeochemical processes that cause isotopic fractionation and change the original isotopic signature of sulphate or nitrate (Kendall et al., 2007). To improve the investigation, multi-isotopes, multi-tracers and/or groundwater dating methods are used in many studies (Katz et al., 2001; Zoellmann et al., 2001). For instance, chlorofluorocarbons (CFCs) are gaseous tracers used to calculate age and flow regime of young groundwater (eg. Cook et al., 2005; Gooddy et al., 2006), and to help assess historical application rate of nitrate (Böhlke and Denver, 1995; Katz et al., 2001; Knowles et al., 2010). In urban regions concentrations of CFCs in groundwater likely exceed atmospherically-derived levels due to local contamination (Knowles et al., 2010), and this feature can be applied to identify urban-derived compounds like nitrate or sulphate. Noble gases (e.g. Ar, Ne) are now routinely used to obtain recharge temperature of groundwater – necessary for proper interpretation of concentration of gaseous tracers.

A relevant problem in identifying sources of groundwater pollution occurs in areas influenced by multiple types of human activity, e.g. industry, urbanization and various agricultural activities, which operate in the same area or very close to each other. A perfect example of such problematic conditions can be found in southern Poland, in the Upper Silesian Industrial Region (USIR), known for significant concentration of various types of industry and a high population density. At the same time agriculture is well developed on the edge of the region. Therefore, carbonate aquifers located at the fringe of the USIR are highly vulnerable to pollution associated with different types of industrial activity, farming and urbanization. Additionally, transport and biogeochemical transformation of contaminants are strongly affected by the porosity structure of the aquifers, which represent fissured-karst-porous media systems.

The aim of this study was to evaluate an impact of different types of human activity on sulphate and nitrate concentrations in a triple-porosity aquifer using chemical analyses, multi-isotopes ($\delta^{15}\text{N}_{\text{NO}_3}$, $\delta^{18}\text{O}_{\text{NO}_3}$, $\delta^{34}\text{S}_{\text{SO}_4}$, $\delta^{18}\text{O}_{\text{SO}_4}$, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta^2\text{H}_{\text{H}_2\text{O}}$), multi-tracers (Ar, Ne, CFC-11 and CFC-12) and geochemical modelling. A combination of a geochemical and multi-isotopic survey with measurements of anthropogenic gaseous tracers is a novel approach that can significantly improve identification of pollution sources, whereas numerical modelling serves as a complementary tool where isotopic composition could not be measured in groundwater.

2. Study area

The carbonate aquifer Gliwice, located in southern Poland, is a 450 km² area that belongs to the Silesian-Cracow Triassic carbonate formation. The aquifer system is composed of limestones and dolomites deposited during the Lower and Middle Triassic. The total thickness of these layers can reach up to 200 m in the central and western parts according to the tectonic blocks that form the basin basement (Sitek et al., 2009). The top of the Triassic carbonate aquifer is overlain by thick Miocene and Quaternary deposits in the western part of the aquifer and by Quaternary deposits in the east. The Miocene deposits are composed of clayey sediments with minor sands, marls and gypsum, of a maximum thickness up to 200 m (Alexandrowicz, 1997). The Quaternary deposits in the study area have diversified lithology and a thickness ranging from 0 to over 80 m in the buried valleys (Lewandowski, 1993; Bardziński and

Lewandowski, 2000).

Hydrogeologically two main units can be determined: the Quaternary aquifer and the Triassic aquifer. The former is of minor importance due to small thickness and poor water quality; the latter is one of the strategic reservoirs of abundant potable water in southern Poland. The Triassic aquifer is a triple porosity medium: fissured-karst-porous, disrupted by faults with an average hydraulic conductivity of 6×10^{-5} m/s (obtained from the pumping tests) (Rózkowski, 1990; Kowalczyk, 2003; Sitek et al., 2009; Sitek, 2014). It consists of two aquifer layers of middle and lower Triassic age, which were initially separated by marls but are now hydraulically connected due to diagenetic processes (dolomitization) and human activities (mining and boreholes). Therefore, these two layers are considered as a single Triassic aquifer complex. The Triassic aquifer is confined in the western part (Fig. 1), separated from the phreatic Quaternary aquifer by the Miocene aquiclude. In the eastern part the aquifer outcrops or is covered by permeable or semi-permeable Quaternary deposits with a thickness ranging from a few to 10–15 m and up to 40 m in the small buried valley of the Stoia River (Rózkowski, 1990; Kowalczyk, 2003; Sitek et al., 2009). Groundwater in the Triassic aquifer would naturally flow from the north-east towards the south-west, in accordance with the dip of the layers. However, flow patterns are strongly deformed by heavy pumping by the large well fields and, to a lesser extent, by semipermeable faults (Sitek, 2014). The groundwater abstraction decreased after the period of overexploitation in 1970s and 1980s (Rózkowski and Wilk, 1980; Rózkowski, 1990), but still remains very high – at the level of about 65–75 000 m³/d. In areas where pumping wells are located close to the Drama River, river water can infiltrate into the Triassic aquifer, which was confirmed by flow measurements in the field in 2009, 2010 and 2014, modelling studies (Sitek, 2014) and residence times of water based on the environmental tracers (Jakóbczyk and Kowalczyk, 2012).

The study area is characterized by strong anthropogenic activity at the surface as well as below ground. The beginning of the ore-mining industry in Tarnowskie Góry dates back to the 12th century (Grzechnik, 1980) and it ceased in the early 20th. Nowadays, industry (mainly metallurgy, metal and chemical industries) dominates in Tarnowskie Góry (north-east) and in Gliwice (south-east). An important element of the industrial activity in Tarnowskie Góry is the former chemical plant (Fig. 1) that produced silk paper and a wide range of chemical compounds from the end of the 19th century to 1995 (Rubin and Witkowski, 2003; Witkowski et al., 2008). Chemical wastes together with sludge from a sewage treatment plant had been stored in the unsealed landfills before they were transferred to the new landfills called Central Waste Disposal Facility in the years 2002–2005. Still, a huge amount of chemical wastes migrate into the aquifer from the polluted soil that was left. The north-eastern and south-western parts of the Gliwice aquifer are also urbanized – more than 60,000 people live in Tarnowskie Góry town and over 180,000 inhabitants live in Gliwice but only the northern districts of the latter town lie within the Gliwice aquifer. The remaining part of the study area is dominated by farmlands, forests, wastelands and rural residential areas. In spite of the industrial character of the study site, agriculture plays a significant role, particularly in the vicinity of Tarnowskie Góry, where croplands are sometimes located at the outcrops of Triassic carbonate rocks covered by a thin layer of Quaternary deposits. In 2010, 24 livestock farms were active in the study area, including 17 poultry farms, 6 pig farms and 1 horse stud. Another important problem is the application of organic fertilizers (mainly poultry and pig manure) to the fields, which is hard to assess quantitatively. The organic animal wastes are mostly spread out within the municipality where the farms are located or they are applied to the neighbouring fields. Apart from the animal manure, synthetic

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