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Methods to investigate the geochemistry of groundwaters with values for nitrogen compounds below the detection limit

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ABSTRACT

Groundwaters, like other natural waters, are solutions of a variety of substances in the solvent water. Human impact upon groundwater systems has created many environmental problems so that hydrogeochemical studies related to pollution have become very important. In this context high abundance of nitrogen species, particularly nitrates, can cause adverse health effects, their main sources being fertilizer, animal or human waste, natural soil organic matter, nitrogen fixation and rain. Graphical representations of hydrogeochemical data (for example molar ratio diagrams, stochiometric diagrams, triangular diagrams, mixing diagrams) pose considerable problems if statistical evaluations have to be performed. In fact, since hydrochemical data are compositional (proportional data), their sample space is the simplex, a constrained space where the application of the standard geometrical approach may provide misleading information. In this paper classical binary diagrams used to investigate the whole chemistry of water as well as the behaviour of nitrogen species were substituted by new equivalent graphs coherent with the properties of compositional data, thus opening new perspectives in the evaluation of geochemical processes affecting water resources. Moreover, since nitrogen species are often affected by the presence of numerous data below the detection limit, their role was investigated by considering different imputation methods, and evaluating their performance in the sub-composition NH_4^+, NO_2^-, NO_3^-. The first phase of the analysis did not consider the presence of data below the detection limit but subsequently, step by step, the possibility to recuperate this type of information was explored. The opportunity to recover information about data below the detection limit from the variance–covariance structure of the whole composition (Ca^{2+}, Mg^{2+}, K^+, Na^+, HCO_3^-, $Cl^-$and SO_4^{2-} and available nitrogen data) was also investigated by considering a multivariate framework. The approaches, coherent with compositional data analysis theory, pointed out interesting aspects of 1) the relationships in the sub-composition of NH_4^+, NO_2^-, and NO_3^-, giving us a different perception of the background level of these species as well as of their source; 2) the effects on the variance–covariance structure of the whole composition (main anions and cations and nitrogen species); and 3) the loss of information about the covariance between chemical variables (coherence of geochemical behaviour), which is able to affect the understanding of geochemical systems.

1. Introduction

Groundwater constitutes the largest reservoir of freshwater in the world, accounting for over 97% of all freshwaters available on earth (excluding glaciers and ice caps). The remaining 3% is mainly composed by surface water (lakes, rivers, wetlands) and soil moisture. Until recently, focus on groundwater mainly concerned its use as drinking water (e.g., about 75% of European Union residents depend on groundwater for their water supply), but it is also an important resource for industry (e.g., cooling waters) and agriculture (irrigation). It has however become increasingly obvious that groundwater should not only be viewed as a water supply reservoir, but it should also be protected for its environmental value. Groundwater plays an essential role in the hydrological cycle and it is critical for maintaining wetlands and river flows, acting as a buffer during dry periods. In fact, it provides the base flow (i.e., the water which feeds rivers all year round) to surface water systems, many of which are used for water supply and recreation. Since groundwater moves slowly through the subsurface, the impact of anthropogenic activities may also continue for a long time (Wang et al., 2013).

Modern agricultural practice is a major cause of environmental pollution, significantly perturbing on the planetary scale nitrogen- and phosphorus biogeochemical cycles (Galloway, 1998; Herivaux et al., 2013). Human activities resulting mainly from the manufacture of

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fertilizer for food production and the cultivation of leguminous crops are able to convert around 120 million tonnes of N_2 from the atmosphere per year into reactive forms, a quantity that is more than the combined effects from all the Earth's terrestrial processes (Erisman et al., 2013; Fowler et al., 2013). Much of this added reactive nitrogen ends up in the environment, polluting waterways and the coastal zone, accumulating in land systems and adding a number of gases to the atmosphere. Moreover, nitrous oxide is one of the most important non-CO_2 greenhouse gases.

The situation posed by the changes to the natural biogeochemical cycles of nitrogen and phosphorous has produced an attempt to define a planetary boundary for their flows, which could be considered as a safety threshold (Rockström et al., 2009). However, notwithstanding the attention of public institution, since the mid-1950s the concentration of nitrate in groundwater and surface waters has increased in many countries due to fertilizer use or from manure due to animals (Capri et al., 2009; Hutchins, 2012; Kuhr et al., 2013; Su et al., 2013). Comparable problems are also known from many developing countries (i.e., Berner and Berner, 1996; Gupta and Gupta, 2013; Weiskel and Howes, 1992) and nitrate is now considered one of the main contaminants (Gupta and Gupta, 2013; Kuhr et al., 2013; Liu et al., 2013; Lockhart et al., 2013; Su et al., 2013; Yetis et al., 2013; Zhang et al., 2013). In Europe the Nitrates Directive 91/676/CEE aims to reduce and prevent water pollution caused by nitrates from agricultural sources, under the Water Framework Directive (WFD) (European Commission, 2008), setting a maximum allowable concentration to 50 mg/L. Since methemoglobinemia has not been reported where water contains less than 10 mg/L of NO_3^-, this level has been adopted by the U.S. Environmental Protection Agency as the standard in the Primary Drinking Water Regulations (O'Riordan and Bentham, 1993; Shuval and Gruener, 1974; World Health Organisation, 1993). In Italy, according to the National Legislative Decree n. 31/01, NH_4^+, NO_2^- and NO_3^- concentrations in potable water should not overcome the Maximum Admissible Concentration (MAC) values of 0.50, 0.50 and 50 mg/L, respectively.

From a geochemical point of view the identification of the origin of nitrogen in water is a complex process because it occurs in solution in different forms, it is a major constituent of the atmosphere and it is highly involved in biogeochemical cycles as an essential component of living tissue, animal and plants (Erisman et al., 2013; Fowler et al., 2013; Wick et al., 2012).

In aquatic environments the nitrate ion (NO_3^-) is the stable form of combined nitrogen for oxygenated systems. Although chemically inert, it can be reduced by microbial action. The nitrite ion (NO_2^-) contains nitrogen in a relatively unstable oxidation state. Chemical and biological processes can further reduce nitrite to various compounds or oxidise it to nitrate.

As a rule, ammonium is quickly absorbed by the rock matrix of the soil, whereas nitrate is not bound and can move with soil water and therefore it can be potentially lost, through leaching processes. Microbial nitrification, oxidation of ammonium through nitrite to nitrate by means of microorganisms under aerobic conditions, is the unique process where nitrate is formed in natural systems (Baird, 2001).

Surface waters are predominantly polluted by nitrate from surface run-off, sub-surface flow or groundwater exchange. Intensive agricultural production, domestic and industrial wastes, sewage and atmospheric nitrogen pollution are considered to be the main sources of nitrate contamination in water (e.g., Fenech et al., 2012; Fukada et al., 2004; Nisi et al., 2005; Panno et al., 2008).

Kendall (1998), Widory et al. (2004), Panno et al. (2008), Xue et al. (2009) and Fenech et al. (2012) demonstrated that nitrogen isotopes may be used to distinguish between different pollution sources by comparing the $\delta^{15}N$ values of the groundwater potential discharge. Shallow groundwaters in residential areas tend to show nitrogen isotope signatures indicative of a sewage source. Studies by Barrett et al. (1999) and Yang et al. (1999) identified sewage as the reason for nitrate pollution in urban groundwaters by means of the nitrate and chloride ratio. On the condition that all chloride is leached and 20–60% of the nitrogen oxidised and leached to groundwater, the NO_3^-/Cl^- ratio is expected to range from 1.8 to 5.3. A high NO_3^-/Cl^- ratio is indicative of a sewage source and a close agreement between the two values would suggest a single pollution source.

In this paper the behaviour of the nitrogen species NO_3^-, NO_2^- and NH_4^+ (mg/L) was investigated in the groundwater of the Arezzo plain, Tuscany, central Italy, an area particularly prone to pollution due to human water waste, agriculture and stock-farming (Vaselli et al., 2007). The chemical features of the waters and the role of the nitrogen pollutant species were analysed by using classical binary diagrams (e.g. molar ratio, stoichiometric and ternary diagrams). Graphical alternatives coherent with the properties of compositional data, based on the concept of the balance between parts, were consequently proposed, improving statistical evaluation of the results and giving us a valid alternative to the classical approach.

Due to the presence of values below the detection limits for the nitrogen species (<0.01 mg/L for NH_4^+, NO_3^-; <0.001 mg/L for NO_2^-), the role of this type of information was recovered adopting appropriate substitution methods (Martín-Fernández et al., 2003, 2012). The performance of different imputation methods was evaluated both for the subcomposition NH_4^+, NO_2^-, NO_3^- and the whole composition adding the nitrogen species to the content of Ca^{2+}, Mg^{2+}, K^+, Na^+, HCO_3^-, Cl^- and SO_4^{2-}.

2. Case study: geological and hydrogeological outlines

The study area is located in Tuscany (central Italy) where the geological setting is characterised by sedimentary formations piled up to form the Northern Apennines thrust fold belt that developed during the Tertiary in a continental collisional regime (Vai, 2001). The compressive phase was followed by an extensional regime since the Upper Miocene–Pliocene times. This phase produced in the western Apennines a “horst-and-graben” tectonics, originating continental and marine basins (e.g., Abbate et al., 1970; Boccaletti et al., 1999). The Arezzo basin can be considered a portion of a wider Plio-Quaternary fluvio-lacustrine area (Fig. 1A). This basin is a structural depression limited to the North and to the East by the Pratomagno and Chianti belts (not reported in Fig. 1A), respectively, and to the South and East by two NW–SE to NNW–SSE-oriented tectonic lineaments (Arbia–Val Marecchia transversal and Chitignano normal faults) and NE-verging thrust faults with their associated ramp anticlines and footwall synclines (Fig. 1A) (Sani et al., 2009 and references therein). Along these tectonic discontinuities CO_2-rich manifestations are either naturally discharged or exploited by private companies down to the depth of 1000 m (Vaselli et al., 2011).

The Arezzo basin is dominated by sedimentary deposits (Fig. 1B) which lie above the turbiditic Cervarola–Falterona (Eocene–Middle Miocene) formation. Commonly the latter is found in the topographic high outcrops. The central part of the basin is mainly filled by Pliocene and Quaternary sediments, which are referred to fluvio-lacustrine and alluvial (Arno river) successions (Fig. 1B) accumulated in two main depositional phases (Sani et al., 2009 and references therein).

Three main aquifers were recognised in the Arezzo basin: i) a relatively deep (generally >60 m) aquifer hosted in Tertiary sandstone formations; ii) an intermediate (20–30 m) aquifer located in the Quaternary fluvio-lacustrine sediments and iii) a shallow (5–10 m) aquifer in recent alluvial sediments. The shallow aquifer is more frequently exposed to the anthropogenic pressure, whereas the deep aquifer is relatively unpolluted, although the quality of the latter is occasionally compromised by the presence of CO_2-rich uprising fluids in the north-western sector of the basin (Vaselli et al., 2007, 2011). It is quite well documented that the anthropogenic input is contributing with a variety of contaminants that spoil the shallow aquifer, whose