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Main sources and processes affecting dissolved sulphates and nitrates in a small irrigated basin (Lerma Basin, Zaragoza, Spain): Isotopic characterization

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ABSTRACT

Irrigated agriculture affects the quality of water bodies receiving irrigation return flows by both salinization and nitrate pollution, which are controlled by site-specific factors such as geology or agriculture management. In this work, coupled hydrogeochemistry and isotopic data are used to determine the factors controlling water salinization and nitrate pollution in a small irrigated basin in Northeast Spain. This basin is representative of a large irrigated surface in the Middle Ebro Valley, presenting perched aquifers developed over Quaternary glacis and half of its surface under pressurized irrigation. Identification of the controlling factors and the differences between both environmental problems (salinization and nitrate pollution) were established through chemical composition and stable isotope analyses (δD and δ^{18}O-[H_2O]; δ^{34}S and δ^{18}O-[$SO_4{}^{2}$]; δ^{15}N and δ^{18}O-[$NO_3{}^{-}$]) of collected samples in groundwater, springs and surface water during the irrigated and the non-irrigated season. The isotopic composition of water indicated no significant evapoconcentration and a higher influence of irrigation water (rather than precipitation water) on the hydrology of the basin. Sulphate was used as a tracer for salinization. There was no positive correlation between nitrate and sulphate, indicating differences in the controlling factors for each compound. Sulphate content was significantly higher in surface water than in groundwater, and a mixture of soil and local gypsum sulphates explained the isotopic composition of most of the collected samples. One sampling location presented samples affected by fertilizers. Nitrate concentration was significantly lower in surface water than in groundwater, with synthetic fertilizers being the main source, especially the ammonia/urea components. The isotopic composition of surface water suggested a low degree of denitrification while circulating in a diffuse pathway over a low permeability substrate. All water quality information was incorporated into a conceptual model of the study site.

1. Introduction

After publication of the European Union Water Framework Directive (OJEC, 2000), all water bodies are required to achieve a *good* quality status by 2015. Agricultural practices affect soil and water qualities at a basin level and is regarded as the main source of diffuse pollution (Novotny, 1999). Specifically, irrigated agriculture results in considerable impacts on surface and groundwater due to the irrigation return flows that adversely affect water quality (García-Garizabal et al., 2012). The salinization of soils and water bodies as well as nitrate pollution are topics of special interest.

Although necessary for agriculture in semi-arid to arid environments, irrigation water can add salts or mobilize the salts stored in soils and geological materials and the application of agrochemicals can influence water quality by both adding solutes and enhancing natural weathering (Koh et al., 2007; Kume et al., 2010). The salinization of soils causes productivity losses, and, in water bodies that receive salt-enriched irrigation return flows, can affect both water supply systems and ecosystems (Duncan et al., 2008; Nielsen et al., 2003). As a consequence, the long-term sustainability of agriculture depends on protecting land and water resources from salinity (Thayalakumaran et al., 2007).

Nitrate pollution is a major concern in agricultural areas since high nitrate levels have been long regarded as dangerous for human health and ecosystems (Fan and Steinberg, 1996; Sutton et al., 2011). Nitrate pollution is indeed aggravated by the fact that other

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nitrogen forms (such as organic N or ammonia) are present in waters but not considered in most of the cases, neither in legislation (*e.g.*, Nitrates Directive, OJEC, 1991) nor in environmental studies (Sutton et al., 2011). Despite the fact that nitrate leaching varies considerably with climatic conditions (Elmi et al., 2004), the actual impact of nitrogen pollution on surface and groundwater depends on specific features of the area (such as soil types or the presence of reducing conditions in aquifers) and irrigation/fertilization management (*e.g.*, Schepers et al., 1995). Thus, an understanding of the fate of nitrate in natural waters is vital for managing risks associated with nitrate pollution, and to safeguard groundwater supplies and dependent surface waters.

Multi-isotopic studies coupled with hydrogeological and hydrochemical information have proved to be useful tools to assess the origin of solutes. For instance, Krouse (1980) suggested that δ^{34}S is a good tool to identify natural and anthropogenic sources of dissolved sulphate, especially in small study areas, where the sources of dissolved sulphate can be easily distinguished. In addition, numerous studies have used the sulphur isotopic composition coupled with the oxygen isotopic composition of the dissolved sulphate molecule to characterize the sources of dissolved sulphate in surface and groundwater (*e.g.*, Rock and Mayer, 2009; Houhou et al., 2010; Tichomirowa et al., 2010).

The different sources and processes that affect nitrate can also be evaluated through its isotopic compositions (*e.g.*, Baily et al., 2011; Kaown et al., 2009; Otero et al., 2009). Common sources of nitrate such as synthetic fertilizers, manure or sewage effluents present different isotopic compositions (*e.g.*, Kendall et al., 2007). Isotopic analysis distinguishes between nitrate and ammonia-type fertilizers, and different processes that affect dissolved nitrate can be identified. Among these processes, natural attenuation of nitrate pollution presents a characteristic trend in isotopic data, allowing for its detection and, in some cases, its quantification (Sebilo et al., 2003).

However, dual isotope analysis alone does not always provide conclusive information on sources and processes that these solutes have undergone (Kaown et al., 2009) and the information provided has to be considered in a qualitative way (Kendall et al., 2007). Chemical data and hydrological information should be simultaneously used to interpret isotopic compositions and also to determine the sources and biogeochemical history of solutes in the systems.

In this context, the results obtained in the monitoring of a small basin recently transformed into irrigation land are presented herein. The basin outlet has been monitored during the last decade (hydrological years 2004–2012), resulting in the detection of significant increasing trends in water flow (3.2 L s^{-1} $year^{-1}$) and nitrate concentration (5.4 mg L^{-1} $year^{-1}$), and decreasing trends in water salinity (indicated by the electrical conductivity of water corrected to 25 °C, −0.38 mS cm^{-1} $year^{-1}$) (Merchán et al., 2013). In this previous study (Merchán et al., 2013), the hydrology of the Lerma Gully is deeply described and its dynamics through the implementation of irrigation studied. The objectives of the present study were to determine the causes of these dynamics through the assessment of environmental indicators of both shallow groundwater and surface water. Specifically, we expose how selected isotopic data can significantly increase the qualitative knowledge of a hydrological system with several potential sources of salinity and nitrate.

2. Materials and methods

2.1. Description of study site

The study site is a small hydrological basin, Lerma Basin (7.38 km^2, Fig. 1), in which irrigation is applied to a high proportion of its surface. This basin is representative, regarding geology, hydrology and agronomy, of a broad range of land-water connected environments in the region (Causapé et al., 2004). It is located inside the municipality of Ejea de los Caballeros (Zaragoza, Spain), and presents a Continental to Mediterranean climate (Spanish National Agency of Meteorology, 2012) characterized by extreme temperatures along with irregularity and scarcity of precipitation. Temperatures can reach −18 °C during extreme winters and 40 °C during summer, with an average annual temperature of 14 °C. Average annual precipitation is 468 mm, with precipitation concentrated in Spring and Fall. Summers are dry, with occasional storms.

Two groups of geologic materials are found in Lerma Basin (ITGE, 1988; Fig. 1). A bottom layer of Tertiary materials composed by clay, marls and limestone (66% of its surface) is covered by a surface layer of 10 m maximum thickness of Quaternary materials consisting of stony gravel with a loamy matrix (glacis, 34%). A network of gullies developed over the glacis exposes Tertiary materials. Soils developed on Quaternary materials (Calcixerollic Xerochrepts, Soil Survey Staff, 1992) display loamy textures, 60–90 cm of effective depth, low salinity and small risk of erosion (slope <3%). On the other hand, soils developed on Tertiary materials (Typic Xerofluvent, Soil Survey Staff, 1992) present 30–45 cm of effective depth, high salinity and significant risk of erosion (slope >10%). These characteristics identified Quaternary soils as suitable for conversion into irrigated land (Beltrán, 1986) and, as a consequence, the irrigated area covers mainly the Quaternary surface. The high salinity of Tertiary materials is inherited, since it comes from sediments deposited in drying lake conditions in the centre of the Ebro Depression. For instance, there is a significant presence of soluble sulphate-bearing mineral in the basin, with tabular and nodular gypsum in a well-defined stratum (Fig. 1); gypsum is also present in other lithologies as cementation (ITGE, 1988).

Regarding hydrological behaviour, Quaternary materials present medium to high permeability, constituting free intergranular perched aquifers, whereas Tertiary materials present low to very low permeability. Precipitation and irrigation water infiltrate (vertically) through Quaternary materials until reaching Tertiary materials, where it flows horizontally. The main flow directions in the basin are from SE to NW (Fig. 1), following the network of gullies, and is determined mainly by the slope of the outcropping materials.

The network of gullies have excavated through the Quaternary materials until the Tertiary was reached. Thus, all the gullies are over Tertiary materials (Fig. 1) and the contact with Quaternary materials, where groundwater seeps feeding the gullies, is close to them. Before irrigation started, the flow in these streams occurred mainly during Spring and Fall, *i.e.*, in the rainy seasons (Abrahão et al., 2011a); after implementation of irrigation the Lerma Gully has become a perennial stream. In addition, it imposed a high waters period during the late summer along with, in general, lower salinities and higher nitrate concentrations (Merchán et al., 2013). These patterns were also observed in the aquifer, with maximum saturated thickness and seepage flow in late summer, after the irrigated season.

During Spring and Summer, Lerma Basin receives water from the Aragón River *via* the Bardenas irrigation channel. Pressurized irrigation systems cover 48% of the Lerma Basin surface. Typical Middle Ebro Valley crops are cultivated: maize, winter cereal, sunflower and vegetables. The most widespread crop was maize, which has also the highest irrigation rates (around 700 mm $year^{-1}$). Other common crops received 552 mm $year^{-1}$ (vegetables), 250 mm $year^{-1}$ (sunflower) or 160 mm $year^{-1}$ (winter cereal).

According to individual surveys, the estimated amount of synthetic nitrogen fertilizer applied in the plots is *ca.*