



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 glaciais 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 $\delta^{18}O$ -[H₂O]; $\delta^{34}S$ and $\delta^{18}O$ -[SO₄²⁻]; $\delta^{15}N$ and $\delta^{18}O$ -[NO₃⁻]) 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.

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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 $\delta^{34}\text{S}$ 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 ($3.2 \text{ L s}^{-1} \text{ year}^{-1}$) and nitrate concentration ($5.4 \text{ mg L}^{-1} \text{ year}^{-1}$), and decreasing trends in water salinity (indicated by the electrical conductivity of water corrected to 25°C , $-0.38 \text{ mS cm}^{-1} \text{ year}^{-1}$) (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.

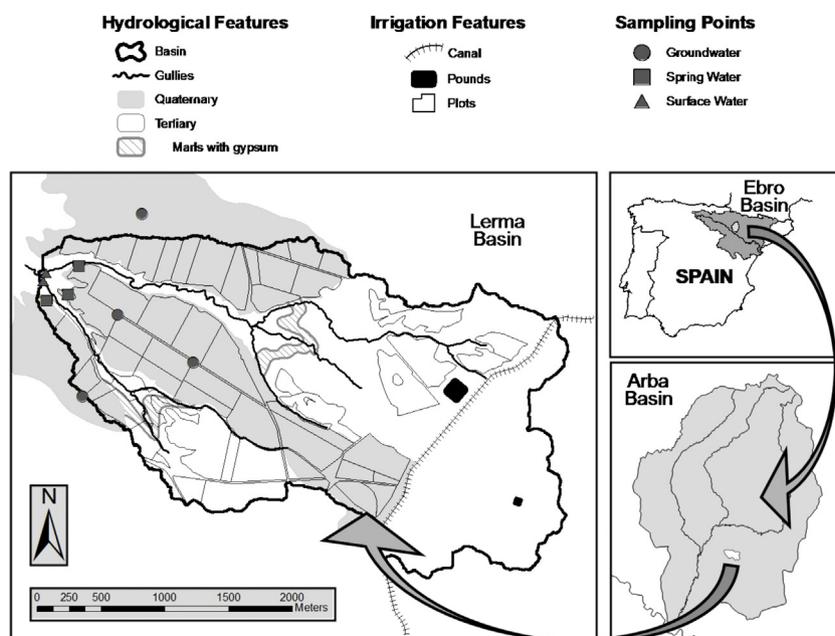


Fig. 1. Location map of Lerma Basin inside Arba and Ebro Basins, hydrological and irrigation features. Ground, spring and surface water monitoring points are depicted.

352 kg N ha⁻¹ year⁻¹ for maize, 143 kg N ha⁻¹ year⁻¹ for winter cereal, 104 kg N ha⁻¹ year⁻¹ for sunflower, and 56–124 kg N ha⁻¹ year⁻¹ for vegetables. Fertilization is performed in multiple applications throughout the growing season, using liquid fertilizers incorporated to irrigation water (mostly N32), urea and compound fertilizers (NPK). Maize fertilization is carried out mainly with N32 and urea fertilizers, with a pre-sowing application (around April) and 2–4 side-dressing applications (between June and August). Fertilization of other crops is quite more variable, depending on expected productions, weather conditions, etc.

The main environmental issues in Lerma Basin are salinization and nitrate pollution of downstream water bodies (Abrahão et al., 2011a,b). Arba River, which is the receiver of Lerma Gully waters, is the river that presented the highest increase in salinity and nitrate concentration in the Ebro Basin during the period 1975–2004 (CHE, 2006). In fact, Arba River was the first surface water body declared as *polluted by nitrate* in the entire Ebro Basin (MMARM, 2011). For this reason, the study area and its surrounding basins were designated as vulnerable areas to nitrate pollution in 2008 (BOA, 2009). An increase in knowledge on water bodies suffering severe water quality problems has been considered paramount by the Ebro Basin Water Authority (*In Spanish*: Confederación Hidrográfica del Ebro).

2.2. Hydrochemical and isotopic characterization

Samples were collected on July 27th 2011 (irrigated season, Summer) and January 10th 2012 (non-irrigated season, Winter), which represent high and low water seasons (high water levels in the gullies and aquifer occurred in late summer, at the end of the irrigated season). Samples were collected at least one week after the last precipitation event to avoid dilution and mixing effects. Samples were collected from four piezometers (groundwater samples, GW), two springs (SpW), and two gullies (surface waters, SW) in an approximate flow line (Fig. 1). These monitoring points were selected after preliminary analyses were carried out in a broader monitoring scheme. The piezometers were drilled in 2008 in the Quaternary materials to a depth between 6 and 8 m, until the Tertiary was reached, going around 50 cm inside the Tertiary materials. These materials were always dry 20 cm below the contact, which is a proof of their low permeability, since the Quaternary materials

just above were saturated. One of the piezometers appears out of the surface catchment (Fig. 1) but the chemical composition of the water in this aquifer was homogeneous (unpublished results from preliminary studies), so this piezometer is considered as representative of the groundwater in this section of the catchment.

The variability in the chemical composition of precipitation and irrigation water was very low (Abrahão et al., 2011b). Thus, only a sample of irrigation water and several samples of precipitation water were collected during the study period.

Field parameters (electrical conductivity corrected to 25 °C [EC], Temperature [T], pH, redox potential relative to hydrogen electrode [Eh], dissolved oxygen [DO] and alkalinity) were measured *in situ* just after sample collection. Samples were filtered using a 0.45 μm filter prior to analysis. Chemical parameters (Cl⁻, SO₄²⁻, HCO₃⁻, CO₃²⁻, Na⁺, K⁺, Ca²⁺, Mg²⁺, silica, NO₃⁻, NO₂⁻, NH₄⁺, Kjeldahl N [KN] and total organic carbon [TOC]) were analyzed by standard analytical methods at the Geological Survey of Spain (IGME) laboratories. Total-N was calculated by addition of NO₃⁻, NO₂⁻ and Kjeldahl N concentrations. Cations and silica were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES), and anions were determined by high performance ion chromatography (HPLC). When necessary, samples were diluted to obtain adequate responses from the analytical equipment. The sample for KN was acidulated immediately after collection with H₂SO₄ until pH < 2 and titration was utilized to measure the amount of ammonium sulphate obtained. TOC analysis was preceded by combustion and detected by non-dispersible infra-red emission using TOC-V analyzer Shimadzu. The cation-anion balance was cross-checked, and for all analytical results the error was under 6%.

Isotopic analysis included the nitrogen and oxygen isotopic composition of dissolved nitrate ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ -[NO₃⁻]), the sulphur and oxygen isotopic composition of dissolved sulphate ($\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ -[SO₄²⁻]) and the deuterium and oxygen isotopic composition of water (δD and $\delta^{18}\text{O}$ -[H₂O]). For $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ -[NO₃⁻], isotopic analyses were performed according to the anion exchange method proposed by Silva et al. (2000). For $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ -[SO₄²⁻], dissolved sulphate was precipitated as BaSO₄ by adding BaCl₂·H₂O after acidification with HCl and ebullition to prevent BaCO₃ precipitation. Deuterium and O isotopes of water were analyzed in

a Finnigan Matt Delta S Isotope Ratio Mass Spectrometer (IRMS) coupled to an automated line base on the equilibration between H-water and H₂ gas with a Pt catalyst, and between O-water and CO₂ gas following standard methods (Epstein and Mayeda, 1953). Results are reported in δ per mil relative to the international standards: VSMOW (Vienna Standard Mean Oceanic Water) for δ D and δ^{18} O, AIR (atmospheric N₂) for δ^{15} N, V-CDT (Vienna Canyon Diablo Troilite) for δ^{34} S. The reproducibility (1σ) was calculated using international and internal laboratory standards systematically interspersed in the analytical batches: $\pm 0.3\%$ for δ^{15} N-[NO₃⁻]; $\pm 0.3\%$ for δ^{34} S-[SO₄²⁻]; $\pm 1.5\%$ for δ D-[H₂O]; $\pm 0.5\%$ for δ^{18} O-[NO₃⁻], δ^{18} O-[SO₄²⁻] and δ^{18} O-[H₂O]. Isotopic analyses were carried out at the laboratory of the *Mineralogia Aplicada i Medi Ambient* research group and performed at the *Centres Científics i Tècnics* of the Universitat de Barcelona (CCiT-UB).

Additionally, four samples of nodular and tabular gypsum of a stratum present in the study zone (Fig. 1) were collected to characterize the isotopic signal of local gypsum. 0.2 g of gypsum samples were dissolved in 300 mL of distilled water and the dissolved sulphate obtained was analyzed using the procedure previously described for water samples.

2.3. Statistical treatment

For every studied variable, one-way ANOVA *post hoc* tests were performed to check if there were significant differences between sampling dates (irrigation season and non-irrigation season) or between sampling locations (groundwater, spring water or surface waters). The Bonferroni method was used in the ANOVA tests, which is the more appropriate when comparing groups with different number of observations. The level of significance was set to 5%. Even though technically samples taken in the same location in different dates are not independent, this approach was justified given the limited number of points on the basis of data exploration and is only used as a guide to assessing other data and not considered definitive itself. In addition, tests for regression between every combination of pairs of variables were performed. The statistical package Statgraphics (Statpoint Technologies, 2009) was used for the computation of the performed tests.

3. Results and discussion

Average EC, pH, Eh and DO of the water samples were 1.98 mS cm⁻¹, 7.7 pH units, 223 mV and 7.7 mg L⁻¹ for groundwater and 3.29 mS cm⁻¹, 8.2 pH units, 282 mV and 10.0 mg L⁻¹ for surface waters. Samples collected in springs presented intermediate values (Table 1). EC and pH were significantly higher in surface water than in groundwater. No significant differences were found between the irrigated and non-irrigated seasons in EC and pH. However, DO and Eh were higher during the non-irrigated season (winter), which is explained by the higher capacity of water to carry DO at lower temperatures.

Similarly, concentrations of major water constituents were different regarding groundwater, springs and surface water (Table 1). Concentrations of Cl⁻, SO₄²⁻ and Ca²⁺ in surface water were significantly higher than in groundwater. In the case of NO₃⁻, the concentration in surface water was significantly lower than in groundwater. The main increase in average concentration (comparing groundwater and surface water) was observed in SO₄²⁻ (116%) followed by Cl⁻ (86%). A negative correlation was found between SO₄²⁻ and NO₃⁻ (Fig. 2) in the study area, pointing to different processes controlling the concentration of these solutes. This result contrasts with some studies in agricultural areas where a positive correlation existed between SO₄²⁻ and NO₃⁻ (e.g., Nakano et al., 2008). According to the Piper classification, the majority

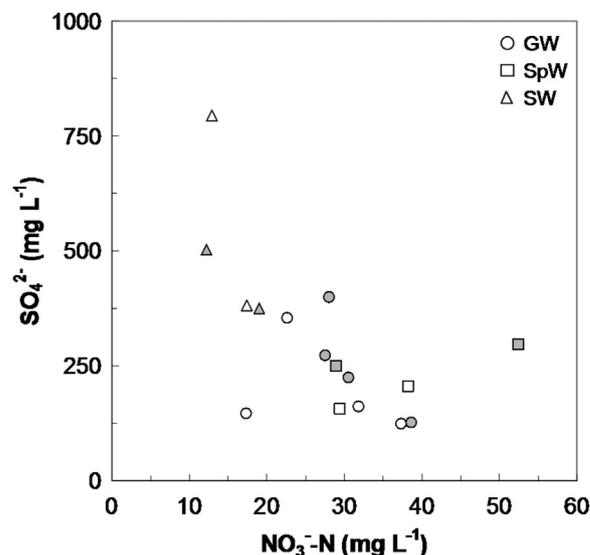


Fig. 2. Bivariate plot of NO₃⁻-N against SO₄²⁻ concentrations. GW: groundwater; SpW: spring water; SW: surface water. White symbols represent samples collected during the irrigated season whereas filled symbols represent samples collected during the non-irrigated season. No significant relationship was detected between the solutes.

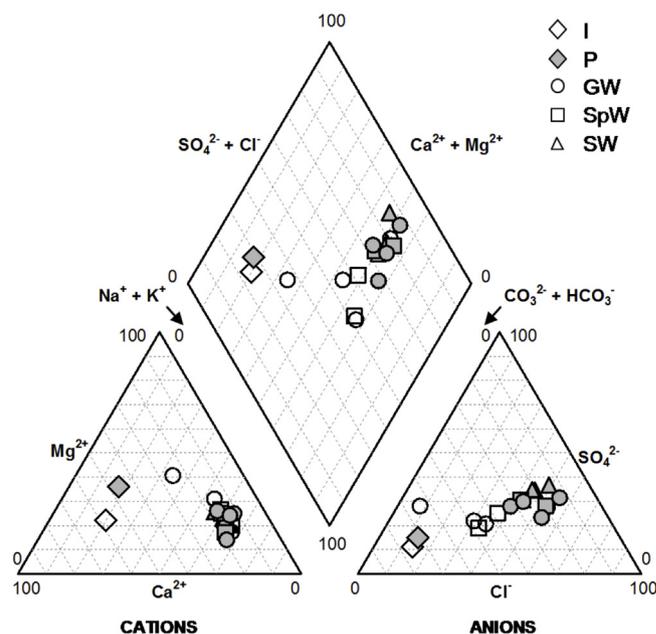


Fig. 3. Piper diagram of irrigation (I), precipitation (P), ground (GW), spring (SpW) and surface (SW) waters collected in Lerma Basin during the irrigated season (white symbols) and the non-irrigated season (filled symbols).

of Lerma Basin waters are Na⁺-(Cl⁻, SO₄²⁻) type (Fig. 3). Some samples tended to (Ca²⁺, Mg²⁺)-HCO₃⁻ water types, showing the influence of precipitation and irrigation waters, which are (Ca²⁺, Mg²⁺)-HCO₃⁻ types.

3.1. The influence of irrigation water on Lerma Basin

δ D-[H₂O] ranged between -56.7 and -45.0‰, with a median value of -49.3‰. δ^{18} O-[H₂O] ranged from -7.8 to -6.4‰, with a median value of -6.9‰ (Fig. 4 and Table 2). No significant differences were detected between the two sampling surveys or between ground, spring or surface waters for δ D-[H₂O] and δ^{18} O-[H₂O]. The local meteoric water line (LMWL, δ D = 7.6 · δ^{18} O + 4.8; Fig. 4),

Table 1
Field parameters and concentration of selected parameters in Lerma Basin water samples.

	Site Units	EC mScm^{-1}	pH	DO mg L^{-1}	Eh mV	HCO_3^- mg L^{-1}	SO_4^{2-} mg L^{-1}	Cl^- mg L^{-1}	Ca^{2+} mg L^{-1}	Mg^{2+} mg L^{-1}	Na^+ mg L^{-1}	K^+ mg L^{-1}	TOC mg L^{-1}	NO_3^- -N mg L^{-1}	TN mg L^{-1}
	Prec ^a	0.03	5.7	nd	nd	14.1	2.3	1.6	4	1	1.4	0.6	<0.5	0.5	nd
	Irr	0.33	8.1	nd	nd	161.7	19.3	18.3	48	8	11.4	1.1	1.3	0.2	nd
Irrigated season (27/07/2011)															
	P4	1.19	7.6	7.1	211	348	125	126	49	32	233	4.2	2.9	37.3	39.4
GW	P10	1.48	7.5	7.8	210	446	163	203	60	74	240	8.5	3.7	31.8	34.1
	P11	0.97	7.4	6.7	231	432	149	31	65	64	100	5.4	3.5	17.9	20.9
	P12	2.86	7.5	6.8	218	312	355	502	85	84	420	4.0	5.2	22.6	26.7
SpW	S1	1.81	7.5	7.0	193	506	157	205	59	50	307	5.2	4.1	29.4	31.5
	S2	1.78	8.2	7.7	194	400	206	224	64	68	279	7.8	3.8	38.2	29.5
SW	B1	2.60	8.2	9.1	253	420	381	395	93	79	398	6.6	4.7	17.4	19.3
	B2	4.28	8.2	8.7	226	590	795	764	154	132	754	5.5	5.1	12.9	15.6
Non-irrigated season (10/01/2012)															
	P4	1.10	7.8	9.4	225	186	127	134	50	22	197	3.1	2.4	38.6	40.3
GW	P10	1.94	7.8	8.1	223	289	225	380	53	71	342	6.3	3.9	30.5	33.7
	P11	1.71	7.6	6.3	236	310	273	294	74	70	291	5.1	3.8	27.5	28.7
	P12	2.83	8.0	9.0	229	211	400	522	79	88	433	3.5	4.9	28.0	28.6
SpW	S3 ^b	2.84	8.4	13.6	287	263	297	408	99	56	403	2.6	5.6	52.4	53.5
	S2	2.04	8.4	10.5	277	282	250	256	64	61	272	6.7	4.0	28.9	29.6
SW	B1	2.96	8.2	11.4	325	290	376	352	81	68	355	4.3	3.9	19.0	25.1
	B2	3.33	8.3	10.9	323	246	502	496	111	96	400	3.6	4.1	12.2	17.7
Averages															
	Irrigated season	2.12	7.8	7.6	217	432	291	306	79	73	341	5.9	4.1	25.9	27.1
	Non-irrigated season	2.34	8.1	9.9	266	260	306	355	76	67	337	4.4	4.1	29.6	32.1
	Significantly different?	No	No	Yes	Yes	Yes	No	No	No	No	No	No	No	No	No
GW		1.76	7.7	7.7	223	317	227	274	64	63	282	5.0	3.8	29.3	31.6
SpW		2.12	8.1	9.7	238	363	228	273	72	59	315	5.6	4.8	37.2	36.0
SW		3.29	8.2	10.0	282	387	514	502	110	94	477	5.0	4.4	15.4	19.4
	Significantly different?	Yes	Yes	No	No	No	Yes	Yes	Yes	Yes	No	No	No	Yes	Yes

nd: not determined.

^a Average data from several samples.

^b Spring S1 was dry in this sampling occasion and a nearby spring was sampled instead.

which is similar to the global meteoric water line (GMWL, Craig, 1961), is composed of $\delta^{18}\text{O}$ and δD values from modern rainfall, monitored over seven years at Zaragoza's Airport station (approximately 50 km southeast of Lerma Basin) as part of the Global Network for Isotopes in Precipitation (IAEA/WMO, 2006). The slope

of the best-fit straight line for the dataset is 6.7, which is lower than the LMWL of Zaragoza (Fig. 4). However, this value is higher than the range of values reported in literature as indicative of open water evaporation (from 2 to 6, Kehew, 2001), indicating that Lerma waters are not significantly evaporated under these

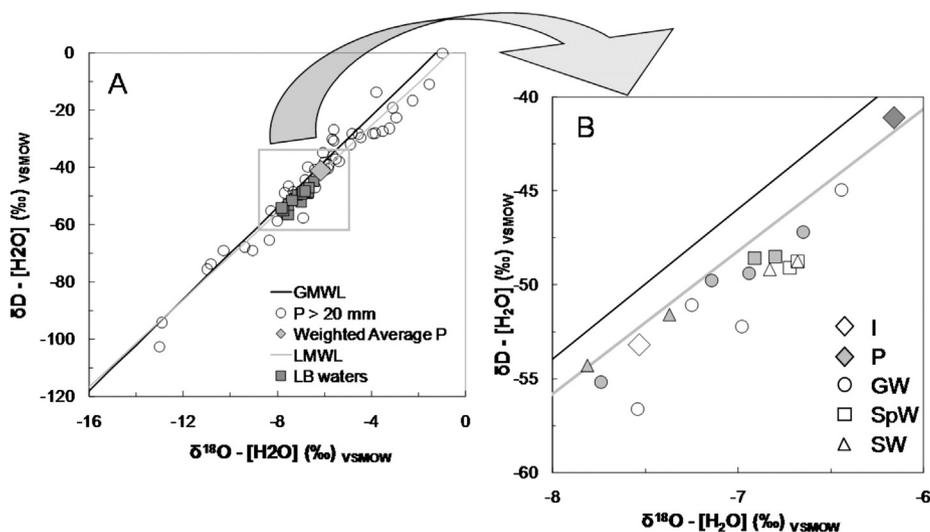


Fig. 4. (A) $\delta^{18}\text{O}$ vs. δD of the Global Meteoric Water Line (GMWL; Craig, 1961), precipitation events of more than 20 mm in Zaragoza (white circles), weighted average precipitation (grey diamond shapes), the Local Meteoric Water Line of Zaragoza (LMWL, IAEA/WMO, 2006), and samples collected in Lerma Basin (LB waters). (B) Details of Lerma Basin samples: irrigation (I), average precipitation (P), ground (GW), spring (SpW) and surface (SW) waters, collected during the irrigated season (white symbols) and the non-irrigated season (filled symbols).

Table 2
Isotopic data of Lerma Basin water samples.

Site Units	H ₂ O		SO ₄ ²⁻		NO ₃ ⁻		
	δ ² H ‰	δ ¹⁸ O ‰	δ ³⁴ S ‰	δ ¹⁸ O ‰	δ ¹⁵ N ‰	δ ¹⁸ O ‰	
Prec ^a	nd	nd	nd	nd	nd	nd	
Irr	-53.2	-7.5	nd	nd	nd	nd	
Irrigated season (27/07/2011)							
GW	P4	-51.1	-7.3	+8.4	+8.2	+3.5	+2.5
	P10	-45.0	-6.4	+6.6	+9.1	+5.3	+5.0
	P11	-56.7	-7.5	+5.6	+7.6	+3.0	+5.1
	P12	-52.2	-7.0	+7.2	+12.4	+6.3	+5.9
SpW	S1	-49.1	-6.7	+6.7	+7.7	+5.6	+5.3
	S2	-48.8	-6.7	+6.6	+8.6	+5.2	+4.0
SW	B1	-49.2	-6.8	+6.8	+12.7	+7.2	+7.0
	B2	-48.8	-6.7	+2.7	+13.7	+9.3	+13.8
Non-irrigated season (10/01/2012)							
GW	P4	-55.2	-7.7	+8.3	+7.3	+3.0	+4.6
	P10	-47.2	-6.7	+8.0	+10.5	+5.2	+12.8
	P11	-49.8	-7.1	+6.4	+9.7	nd	nd
	P12	-49.4	-6.9	+7.0	+12.4	+5.3	+21.4
SpW	S3 ^b	-48.5	-6.8	+6.6	+8.7	+5.6	+9.6
	S2	-48.6	-6.9	+6.5	+8.6	+5.7	+13.7
SW	B1	-51.6	-7.4	+6.6	+12.6	+6.3	+12.6
	B2	-54.3	-7.8	+3.4	+13.1	+8.2	+21.5
Averages							
Irrigated season	-50.1	-6.9	+6.3	+10.0	+5.7	+6.1	
Non-irrigated season	-50.6	-7.2	+6.6	+10.4	+5.6	+13.7	
Significantly different?	No	No	No	No	No	Yes	
GW	-50.8	-7.1	+7.2	+9.7	+4.5	+8.2	
SpW	-48.8	-6.8	+6.6	+8.4	+5.5	+8.2	
SW	-51.0	-7.2	+4.9	+13.0	+7.8	+13.7	
Significantly different?	No	No	Yes	Yes	Yes	No	

nd: not determined.

^a Average data from several samples.

^b Spring S1 was dry in this sampling occasion and a nearby spring was sampled instead.

conditions. However, the displacement of values to the right side of the LMWL could be a consequence of evaporation in the unsaturated zone, as specifically observed in a couple of groundwater samples (Fig. 4). Moreover, according to Han et al. (2011), deuterium excess (Dansgaard, 1964) generally decreases if the water evaporates significantly. This pattern was not clearly observed in Lerma Basin waters, pointing to low-significant evaporation. In addition, the enrichment in Cl⁻ (an indicator of water salinity) was not correlated with δ¹⁸O-[H₂O] (Fig. 5), indicating that mainly dilution (and not evaporation) accounts for the salinity increase (Portugal et al., 2005). Only surface water shows small seasonal variations during summer to higher values that can be interpreted as produced by evaporation, but isotopic variations are very small

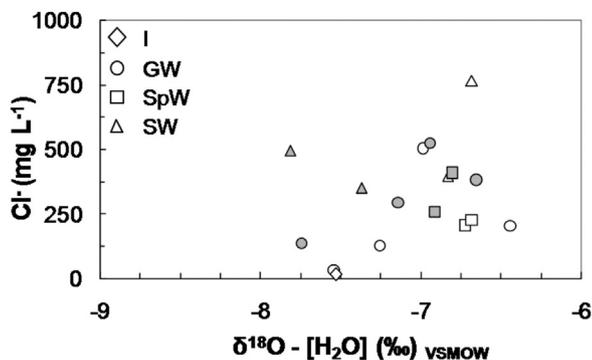


Fig. 5. δ¹⁸O-[H₂O] vs. chloride concentration in irrigation (I), ground (GW), spring (SpW) and surface (SW) waters during the irrigated (white symbols) and non-irrigated season (filled symbols). No correlation was detected between these two variables.

(<0.2 δ¹⁸O units and <1 δD units, near to the analytical error) indicating that evaporation is not a significant process.

The weighted average values of δD and δ¹⁸O in precipitation events (>20 mm) were -41.1‰ and -6.2‰, respectively. In a δD vs. δ¹⁸O diagram, samples collected in Lerma Basin were located between the isotopic compositions of average precipitation and irrigation waters. Although highly dispersed, they generally plot closer to the isotopic composition of irrigation water (Fig. 4), suggesting irrigation water had a higher influence on the increase in water flow observed during the last decade.

With the isotopic composition of average weighted precipitation water (δD_P = -41.1‰ and δ¹⁸O_P = -6.2‰), irrigation water (δD_I = -53.2‰ and δ¹⁸O_I = -7.5‰) and an estimation of Lerma Basin waters (δD_{LB} = -49.3‰ and δ¹⁸O_{LB} = -6.9‰, computed as the median of all the collected samples), precipitation contribution (X_P) was computed using a simple mass balance (Eq. (1)):

$$X_P \delta D_P + (1 - X_P) \delta D_I = \delta D_{LB} \quad (1)$$

A similar equation was applied for δ¹⁸O and X_P values were 0.32 and 0.46 respectively. According to this approach, irrigation water had more influence than precipitation water in the origin of Lerma Basin waters, with a contribution up to 60%. These results should be taken with caveat, due to the low number of samples and the dispersion in the isotopic values. However, they corroborate those of Merchán et al. (2013), who related increasing trends in Lerma Basin flows to the increase in irrigation, as no trends were detected for precipitation values. Thus, according to the aforementioned information and the mass balance carried out, Lerma Basin waters originate dominantly from irrigation water.

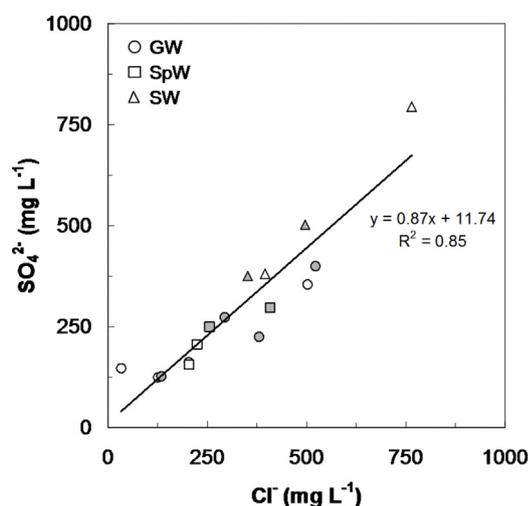


Fig. 6. Bivariate plot of Cl^- vs. SO_4^{2-} concentrations in ground (GW), spring (SpW) and surface (SW) waters of the Lerma Basin during the irrigated season (white symbols) and non-irrigated season (filled symbols). Best-fit line and correlation estimates.

3.2. Sulphate sources as indicators of salinity sources

Sulphate concentration was highly correlated to chloride concentration ($R^2=0.85$; Fig. 6) and to many other indicators of water salinity (e.g., EC). Moreover, sulphate presented the highest increase between low-salinity groundwater and high-salinity surface water (116% in average, Table 1). Thus, the origin of sulphate can be considered as representative of salinization processes. SO_4^{2-} concentration ranged from 125 to 795 mg L^{-1} , with significant differences between the sampling surveys. In general, sulphate concentration was higher during the non-irrigated season (winter). Sample B2 is an exception, with 58% more sulphate during the irrigated season. SO_4^{2-} averaged 226.6 mg L^{-1} in groundwater, 227.5 mg L^{-1} in spring water and 513.5 mg L^{-1} in surface water, being significantly higher in surface water.

$\delta^{34}\text{S}-[\text{SO}_4^{2-}]$ ranged from +2.7 to +8.4‰, with a median value of +6.6‰. $\delta^{18}\text{O}-[\text{SO}_4^{2-}]$ ranged from +7.3 to +13.7‰, with a median value of +9.4‰ (Table 2). Fig. 7 shows $\delta^{34}\text{S}$ against $\delta^{18}\text{O}$ of dissolved sulphate in Lerma waters, along with data from gypsum samples, regarded as representative of the local origin of gypsum. Fig. 7 also depicts boxes covering the range of values reported in literature for soil sulphate (Rock and Mayer, 2009; Kaown et al., 2009) and sulphate from fertilizers (Vitòria et al., 2004). Samples were clustered in three groups for a $\delta^{34}\text{S}-[\text{SO}_4^{2-}]$ vs. $\delta^{18}\text{O}-[\text{SO}_4^{2-}]$ plot (Fig. 7). The first cluster was constituted by samples collected from a mix of piezometers and springs, which presented $\delta^{34}\text{S}-[\text{SO}_4^{2-}]$ varying from +5.6 to +8.4‰ and $\delta^{18}\text{O}-[\text{SO}_4^{2-}]$ varying from +7.3‰ to +10.5‰. Sulphate concentrations in these samples ranged from 124.5 mg L^{-1} to 297.2 mg L^{-1} , being the lowest in all collected samples. The second group was composed of samples from a piezometer (P12, located near the nodular gypsum stratum, Fig. 1) and a surface water monitoring point (B1). $\delta^{34}\text{S}-[\text{SO}_4^{2-}]$ in these samples ranged from +6.6 to +7.2‰, and $\delta^{18}\text{O}-[\text{SO}_4^{2-}]$ ranged from +12.4 to +12.7‰. Sulphate concentrations ranged from 354.6 mg L^{-1} to 399.8 mg L^{-1} . Finally, samples collected in surface water point B2 presented a characteristic isotopic signature ($\delta^{34}\text{S}-[\text{SO}_4^{2-}]$ from +2.7 to +3.4‰ and $\delta^{18}\text{O}-[\text{SO}_4^{2-}]$ from +13.1 to +13.7‰) and also the highest sulphate concentration (764.5 mg L^{-1} in irrigated season and 502.4 mg L^{-1} in non-irrigated season). No significant differences in the isotopic composition were found between sampling dates, suggesting stability in sources and processes (Baily et al., 2011).

Analysis of gypsum samples resulted in a very similar isotopic composition across samples (Fig. 7). The $\delta^{34}\text{S}$ values ranged from +9.2 to +10‰ and the $\delta^{18}\text{O}$ values ranged from +18.2 to +18.7‰, which are very similar to those reported by Utrilla et al. (1992) for the Lower Miocene near the study zone. Median values of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ were +9.7‰ and +18.5‰ respectively. These values can be considered representative of diffuse gypsum present in the stratum where the samples were collected, as differences between isotopic values of nodular/laminar and interstitial gypsum in a column are minimal (e.g., Huerta et al., 2010).

Typical sources of sulphate in surface and groundwater include (Choi et al., 2011): atmospheric deposition (e.g., acid rain), oxidation of reduced inorganic S compounds (e.g., pyrite), dissolution of sulphate minerals (e.g., gypsum and anhydrite), agricultural fertilizers (e.g., NH_4SO_4 , NPK(S) fertilizers) and mineralization of organic soil sulphur. Lerma Basin waters presented SO_4^{2-} concentrations ranging from 124.5 to 764.5 mg L^{-1} . Atmospheric deposition presents SO_4^{2-} concentrations of approximately 1.7 mg L^{-1} (Choi et al., 2011) and hence cannot solely explain the elevated concentrations in Lerma waters even if evaporation and transpiration are considered. Sulphide oxidation could not be the origin of sulphate in Lerma waters, as indicated by the $\delta^{18}\text{O}-[\text{SO}_4^{2-}]$ vs. $\delta^{18}\text{O}-[\text{H}_2\text{O}]$ plot (not shown). All samples collected in Lerma Basin plotted clearly outside the area defined by Van Stempvoort and Krouse (1994) where sulphate from sulphide oxidation should plot if they are in isotopic equilibrium. In addition, the inexistence of sulphides in the geological materials of the study zone corroborates this fact. Therefore, the three potential sources for sulphate in Lerma waters were soil sulphate, sulphate minerals from the geological background, and fertilizers.

A mixing line between the average value of soil sulphate (centre of the box) and the local Lerma gypsum samples (median of obtained values) is presented with 10% mixing steps, i.e., the isotopic composition presented in this line corresponds to 100% local gypsum sulphate, 90% local gypsum – 10% soil sulphate, and so on. The fertilizers box overlapped almost completely this mixing line, hindering the determination of the origin of sulphate using isotopes. For most of the samples, the mixing line between soil sulphate and gypsum sulphate sufficed to relatively explain the isotopic composition. In these samples, between 40% and 70% of the sulphate origin could be attributed to local gypsum dissolution (the higher the sulphate concentration, the more relative proportion of gypsum dissolution). The only sample outside this pattern was collected in point B2, which presented the highest sulphate concentrations. This suggests a certain degree of influence from sulphate in fertilizers in this sampling location, as decreasing $\delta^{34}\text{S}-[\text{SO}_4^{2-}]$ with increasing SO_4^{2-} concentrations have been related to fertilizers (Hosono et al., 2007). The $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values are close to those present in some of the fertilizers most commonly used in Lerma Basin, i.e., compound NPK and liquid (N32) fertilizers (Vitòria et al., 2004). Quantification of the influence was not possible as there was not a well-defined extreme value for fertilizers. No clear pattern related to other processes (different from mixing) was detected using the isotopic data.

Kume et al. (2010) reported the influence that fertilization management could have on salt loads, as soluble salts are added to soils and water during fertilization applications. However, in Lerma Basin waters the influence of fertilizers on salinization processes was minor and only detected using isotopic data, since the higher sulphate values were obtained in those locations with lower fertilizers application, i.e., the less cultivated Tertiary materials. In addition, several favourable conditions indicate that the seepage of water from the aquifer and the dissolution of Tertiary salts was the major salinization process in Lerma Basin. Between these favourable conditions, it is worthy to mention excess percolation of recharge water (irrigation water), soluble materials (evaporitic

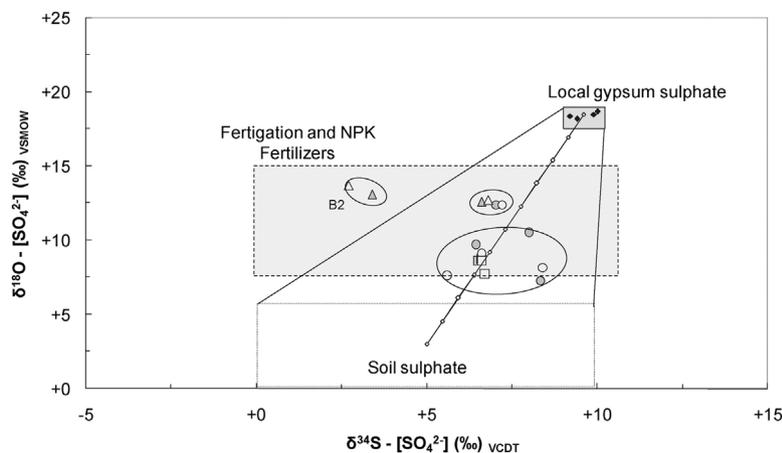


Fig. 7. $\delta^{34}\text{S}$ vs. $\delta^{18}\text{O}$ of dissolved sulphate in Lerma waters. Boxes with typical sulphate isotopic values ranges are depicted. Typical soil sulphate values (Rock and Mayer, 2009; Kaown et al., 2009) and more commonly used fertilizers in the study zone (Vitória et al., 2004). Mixing line between soil sulphate and local gypsum sulphate. GW: groundwater; SpW: spring water; SW: surface water. White symbols: irrigated season. Filled symbols: non-irrigated season.

minerals in the Tertiary materials), and low permeability values at relatively shallow depths, which favour lateral seepage (clay and marls below the Quaternary materials) (Richter and Kreitler, 1991). Moreover, water salinity was already high in the upper reaches of the basin surface waters, since these waters have already circulated over the Tertiary materials (Abrahão et al., 2013), and the contribution of fertilizers in these upper reaches is expected to be negligible due to small contributing agricultural area. Therefore, the major salinization process is the dissolution of Tertiary salts by the water flowing in contact with the Tertiary materials and, consequently, the observed decrease in salinity in the last decade (Merchán et al., 2013) probably responds to a combination of a dilution effect caused by the addition of irrigation water and the successive flushing of soluble salts. Although detected in one sampling location, the role of fertilizers in sulphate contents is masked by the natural conditions of the basin.

3.3. Origin and controlling factors of nitrogen pollution

Nitrate was the predominant form of nitrogen encountered, accounting for 80% of total nitrogen. The concentration of the remaining portion (*i.e.*, the sum of nitrite, ammonia, dissolved organic nitrogen and particulate organic nitrogen) was proportionally higher in samples where nitrate concentration were lower (Fig. 8). This pattern has been widely observed in European waters (Sutton et al., 2011), where nitrate concentrations are higher both in absolute terms and as a proportion of total-N along a gradient from oligotrophic to eutrophic waters. In the Lerma Basin, the proportion of NO_3^- -N in total-N in groundwater was significantly higher than in surface water, which was similar to observations reported at larger scale groundwater–surface water systems (1349 km²; Arauzo et al., 2011). Among different samples, nitrate accounted for 69–98% of all detected nitrogen, with an average of 90% (Fig. 8). Thus, it was considered a reasonable assumption to use nitrate and its isotopic signature to assess the nitrogen pollution.

NO_3^- -N concentration ranged from 12.2 to 52.4 mg L⁻¹, without significant differences between the irrigated season and non-irrigated season. NO_3^- -N averaged 29.2 mg L⁻¹ in groundwater, 34.2 mg L⁻¹ in spring water and 15.4 mg L⁻¹ in surface water, being significantly higher in groundwater/spring water (Table 1). These concentrations are clearly above those feasible to obtain from natural soil N suggesting a minimal influence of this source in the isotopic results (Kendall et al., 2007). $\delta^{15}\text{N}$ -[NO_3^-] ranged from +3.0 to +9.3‰, with a median value of +5.6‰. $\delta^{18}\text{O}$ -[NO_3^-] ranged from +2.5 to +21.5‰, with a median value of +7.0‰ (Table 2). In general,

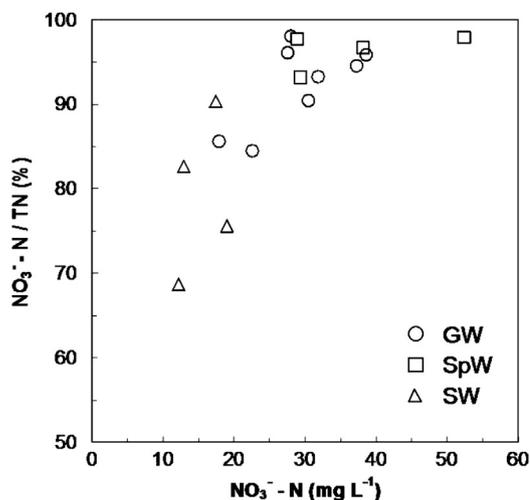


Fig. 8. Proportion of total nitrogen present in the form of nitrate-nitrogen in Lerma Basin waters. GW: groundwater; SpW: spring water; SW: surface water. White symbols: irrigated season. Filled symbols: non-irrigated season.

$\delta^{15}\text{N}$ increased from values of +3.0 to +6.3‰ in groundwater or spring water to +6.3 to +9.3‰ in surface waters. Regarding the relationship between $\delta^{15}\text{N}$ and nitrate concentration, those samples with higher $\delta^{15}\text{N}$ presented lower nitrate concentration; samples over +6‰ presented NO_3^- -N concentration below 25 mg L⁻¹.

Fertilization in Lerma Basin is mainly carried out using different forms of compound fertilizers, liquid fertilizers and urea. Thus, nitrogen is applied to crops in a mixture of nitrate, ammonia and urea-type fertilizers. While the isotopic signature of NO_3^- from synthetic fertilizers is similar in nitrate-type and ammonia/urea-type fertilizers for $\delta^{15}\text{N}$, it is quite different for $\delta^{18}\text{O}$. Synthetic fertilizers present $\delta^{15}\text{N}$ values between -1.7‰ and +3.9‰ (Vitória et al., 2004; Fig. 9), as this nitrogen origin is derived from atmospheric N_2 ($\delta^{15}\text{N} = 0\text{‰}$) through the Haber–Bosch process (Sutton et al., 2011). The $\delta^{15}\text{N}$ of ammonia/urea-type fertilizers is known to slightly increase (2–3‰) in groundwater as a consequence of volatilization (Kendall et al., 2007). However, the oxygen isotopic composition can be quite different in nitrate-type and ammonia/urea-type fertilizers. The first is derived from atmospheric O_2 ($\delta^{18}\text{O} = 23.5\text{‰}$; Horibe et al., 1973) and presents $\delta^{18}\text{O}$ -[NO_3^-] between +18.0‰ and +25.1‰ (Vitória et al., 2004); whereas the ammonia/urea-type fertilizers are oxygen free. Ammonia/urea is nitrified and incorporates atmospheric oxygen

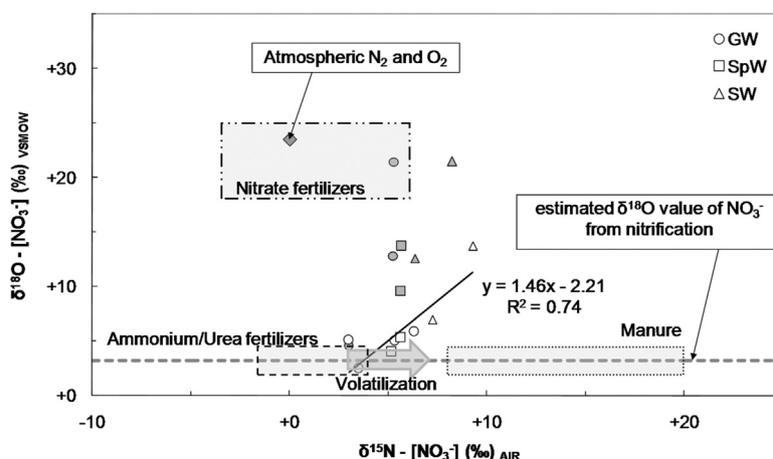


Fig. 9. $\delta^{15}\text{N}$ vs. $\delta^{18}\text{O}$ of nitrate-nitrogen in Lerma waters. Boxes with typical nitrate isotopic values ranges are depicted from Vitòria et al. (2004) and the estimated $\delta^{18}\text{O}$ from nitrification is indicated by the dashed grey line. GW: groundwater; SpW: spring water; SW: surface water. White symbols: irrigated season. Filled symbols: non-irrigated season.

(one third) and water oxygen (two thirds) (e.g., Kendall et al., 2007; Baily et al., 2011). Thus, the $\delta^{18}\text{O}-[\text{NO}_3^-]$ values will vary depending on the local $\delta^{18}\text{O}$ of water. Consequently, the values of $\delta^{18}\text{O}-[\text{NO}_3^-]$ derived from the nitrification of urea/ammonia fertilizers can be estimated using the following equation:

$$\delta^{18}\text{O}-[\text{NO}_3^-] = 1/3(\delta^{18}\text{O}-[\text{O}_2]) + 2/3(\delta^{18}\text{O}-[\text{H}_2\text{O}]) \quad (2)$$

The $\delta^{18}\text{O}-[\text{H}_2\text{O}]$ values of Lerma Basin waters ranged between -7.8 and -6.4% (Fig. 4) and a value of $+23.5\%$ for $\delta^{18}\text{O}-[\text{O}_2]$ (Horibe et al., 1973) was used for the calculation. Thus, at the study site, $\delta^{18}\text{O}-[\text{NO}_3^-]$ values derived from nitrification should range from $+2.6$ to $+3.5\%$ (dashed line in Fig. 9).

This implies that the primary sources of nitrate in Lerma waters were ammonia/urea and nitrate from synthetic fertilizers. The lower contents of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}-[\text{NO}_3^-]$ observed in Lerma waters intersect the line of expected $\delta^{18}\text{O}-[\text{NO}_3^-]$ for *in situ* nitrification of ammonia/urea-type fertilizers which have suffered volatilization (Fig. 9). Deviations of this isotopic signature occurred due to increasing values of $\delta^{15}\text{N}$ and/or $\delta^{18}\text{O}-[\text{NO}_3^-]$. These deviations can be explained by mixing processes; mixing with nitrate from organic sources such as manure was not feasible as any sample presented an isotopic composition towards the manure box (Fig. 9) and, in addition, manure application was reported to be negligible. On the other hand, the nitrate component of mineral fertilizers was detected in several samples, which indicates that nitrate-type synthetic fertilizers are the second source of nitrate in Lerma Basin waters.

Differences were detected in the origin of nitrate across the two sampling surveys. For the irrigated season sampling, a clear origin from ammonia and urea type fertilizers was detected, as most of the samples were located within the values expected for nitrification of this type of fertilizer (white symbols in Fig. 9). However, the origin of nitrate was not clearly inferred for the non-irrigated season (grey symbols in Fig. 9). Samples were located between the expected isotopic composition for ammonia/urea and nitrate type fertilizers, pointing to a mixture of fertilizers. These observations are in line with the fertilization practices developed in the study area. During the irrigated season, the most common crop is maize, which is heavily fertilized, and the most common fertilizers applied to maize are urea and/or N32 liquid fertilizer (1 N atom in NO_3^- form, 1 in NH_4^+ form and 2 in urea form) for side-dressing. Thus, most of the samples are located in a clear area of the $\delta^{15}\text{N}$ vs. $\delta^{18}\text{O}$ plot corresponding to the nitrification of urea and NH_4^+ . However, during the non-irrigated season, winter cereal is dominant in the study

area. Lower fertilization rates are applied and the influence of other crops is relatively higher. Different fertilizer types are applied to this variety of crops, mainly NPK fertilizers, in which the proportion of NO_3^- can be higher than that of ammonia (Otero et al., 2005). As a consequence, in the non-irrigated season, values shifted towards the isotopic composition of nitrate-type fertilizer, and most samples are located on a mixing line between nitrified ammonia/urea fertilizers (slightly volatilized) and nitrate-type fertilizers.

The samples that did not follow the general trend exposed above (mostly surface waters) presented signs of denitrification. Denitrification decreases nitrate concentration and modifies the isotopic composition of remaining NO_3^- , increasing values in both $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ with an approximate relationship between 1:1 and 2:1 (e.g., Kendall et al., 2007). Nitrate concentration in surface waters was significantly lower than in groundwater or spring water (Table 1). This decrease in nitrate concentration can be explained by two processes: dilution with upstream surface water and/or natural attenuation processes (denitrification). Some authors delineated reduction processes from the dilution by tracking changes in ambient chloride to nitrate concentration ratios along the flow path (Thayalakumaran et al., 2008; Craig et al., 2010). However, this approach is of limited use in areas where chloride is not conserved, as occurred in Lerma where significant changes in chloride concentrations were observed in groundwater and surface water (Table 1). Discharge measurements in upstream gullies (median nitrate concentrations ca. 2 mg L^{-1} as these gullies are mostly unaffected by irrigation return flows, Abrahão et al., 2013) indicated that, when there was no recent precipitation, groundwater accounted for more than 90% of the measured outlet flow. This is consistent with observations made prior to irrigation implementation, when the gullies dried up in summer (Abrahão et al., 2011a). In this order of magnitude, dilution alone was not sufficient to be responsible for the observed decrease in nitrate concentration. In addition, dilution does not change isotopic composition and significant changes in isotopic composition were observed in samples with a lower nitrate concentration. Thus, the decrease in nitrate concentration could be due to a combination of dilution with upstream waters bearing low nitrate concentrations and denitrification.

Denitrification processes prove to be highly site dependent (Craig et al., 2010) and are commonly detected in both aquifers and riparian zones with a particular set of characteristics (Thayalakumaran et al., 2008; Ranalli and Macalady, 2010). Aquifer saturated zones with reducing conditions are one of the main sites

in which denitrification has been reported (e.g., [Thayalakumaran et al., 2008](#); [Craig et al., 2010](#)). A non-limiting electron donor is also required, such as sulphurous minerals or organic carbon ([Rivett et al., 2008](#)). TOC in Lerma Basin groundwater averaged 3.8 mg L^{-1} , which is sufficient to deplete oxygen and provide reducing conditions ([Rivett et al., 2008](#)). Eh averaged 223 mV, which is within the range where denitrification is reported to occur. However, denitrification was not found to be feasible in the Lerma Basin aquifer saturated area, as dissolved oxygen concentration averaged 7.3 mg L^{-1} , i.e., aerobic conditions above the threshold required for denitrification. Despite the fact that some studies have detected denitrification through isotopic approaches under aerobic conditions ([Otero et al., 2009](#); [Craig et al., 2010](#)), in the study area presented herein the isotopic results did not demonstrate significant differences between the aquifer and springs in either $\delta^{15}\text{N}$ or $\delta^{18}\text{O}$ -[NO_3^-]. In addition, nitrate concentration did not decrease significantly from the aquifer saturated area to the seepage areas ([Table 1](#)). Therefore, no significant denitrification in the aquifer saturated zone was detected.

A second “hot spot” for denitrification are riparian zones. The effectiveness of a particular zone will depend on several factors (relative location to groundwater sources, hydrogeological properties and vegetation; [Ranalli and Macalady, 2010](#)). Quaternary aquifers in Lerma Basin are underlain by a low permeability layer (depth <4 m in most of the aquifer area), condition recognized in the literature as favourable for natural attenuation ([Hill, 1996](#)). In these areas, groundwater-fed surface pathways are the main denitrification sites, especially when the surface flow occurs diffusively ([Shabaga and Hill, 2010](#)). Springs in Lerma Basin were observed to feed a diffuse pathway over low permeability Tertiary materials until the gullies were reached. The removal of nitrogen by this mechanism is highly dependent on: (i) flow conditions, as the water table dynamics can activate-deactivate different zones of diffuse flow ([Shabaga and Hill, 2010](#)); and (ii) surface water temperature, a factor controlling denitrification rates in streams ([Hansson et al., 2008](#)). Both (i) and (ii) are highly variable throughout the year in the Lerma Basin. Other variables, such as salinity or pH, presented values within a range that will not affect denitrification rates ([Rivett et al., 2008](#)).

Isotopic results demonstrated that the surface waters were slightly but significantly enriched in $\delta^{15}\text{N}$ (+6.3 to +9.3‰) with respect to springs and groundwater (+3.0 to +6.3‰) ([Fig. 9](#)). [Craig et al. \(2010\)](#) reported denitrification in several hotspots of a riparian area with $\delta^{15}\text{N}$ variations of ca. +3‰, supported by $\delta^{18}\text{O}$ variations of ca. +2‰, low NO_3^- concentrations and significant N_2 gas excess in water. [Shabaga and Hill \(2010\)](#) reported a pattern of

NO_3^- concentration decrease and $\delta^{15}\text{N}$ enrichment (from +7 to +8.6‰ to ca. +12.5 to +21.1‰) in flow lines of groundwater-fed surface diffuse flow as a clear indicator of denitrification. Thus, according to $\delta^{15}\text{N}$ values, surface water presented signs of being slightly denitrified with respect to source waters, i.e., ground and spring water.

For the irrigated season samples, the $\delta^{15}\text{N}$ vs. $\delta^{18}\text{O}$ plot presented a linear correlation with a regression slope of 1.46 ($R^2 = 0.74$, $n = 8$; [Fig. 9](#)). This fact supported denitrification to be a nitrate removal mechanism ([Cey et al., 1999](#)), although the value of the slope is higher than the range of those reported in studies where denitrification was clearly identified (between 0.5 and 1.0, [Kendall et al., 2007](#)). The higher slope value is probably due to heterogeneity in the original isotopic composition, since a mixture of nitrate and ammonia/urea-type fertilizers is applied in the study zone. Thus, a clear $\delta^{18}\text{O}$ end-member for isotopic composition does not exist, but rather a mixing line between two end-members. This fact indicates $\delta^{18}\text{O}$ is not of use for denitrification detection in this study case, as the variations observed by the different nitrate sources clearly exceed those that denitrification is expected to cause alone.

In both surface water sampling locations, $\delta^{15}\text{N}$ was ca. 1‰ higher during the irrigated season than during the non-irrigated season ([Fig. 9](#)). Denitrification is suggested to occur more intensively during the irrigated season period (summer), when surface water temperature is favourable for nitrate reduction ([Hansson et al., 2008](#)). For example, a 5 °C increase in temperature can result in a 10-fold increase in denitrification rates ([Rivett et al., 2008](#)). Thus the main denitrification hotspot identified is a surface diffuse pathway, i.e., between the seepage areas and the gullies, occurring during the irrigated season. Similar observations were made in groundwater-fed diffuse surface flow in three riparian zones of Southern Ontario ([Shabaga and Hill, 2010](#)).

Therefore, the upward trends observed in nitrate concentration during the last decade in Lerma Basin ([Merchán et al., 2013](#)) respond to the increasing usage of synthetic fertilizers coupled with the more productive agriculture that irrigation allows. The increase in nitrate concentration observed could be more related to the application of ammonia/urea type fertilizers, since nitrate is often a preferential source for crop growth, especially for arable crops and under high temperatures ([Mengel and Kirkby, 1987](#)). Moreover, nitrate concentrations in the basin outlet support the hypothesis of natural attenuation processes taking place, since they are significantly lower than those observed for groundwater. Thus, even with application of similar fertilizer rates, it is expected that nitrogen pollution can be different in other areas as natural attenuation processes are very site specific.

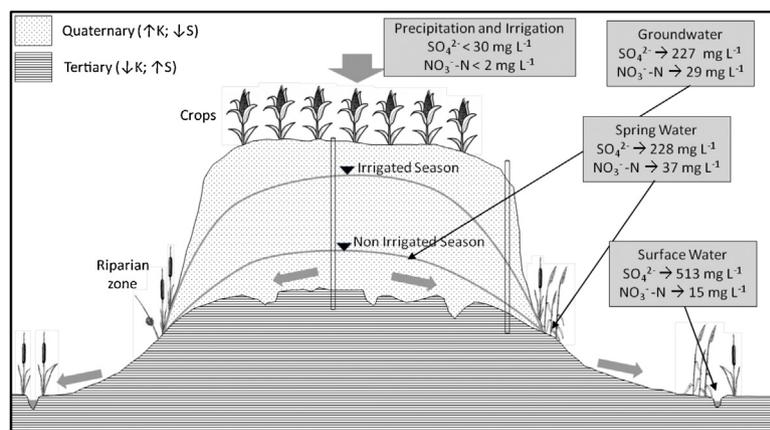


Fig. 10. Cross-section of the conceptual model of Lerma Basin behaviour. Quaternary materials (sandy and loamy matrix gravels) overlay Tertiary materials (marl, clay, mudstone). K: permeability; S: salinity. Grey lines indicate phreatic level in high waters (irrigated season) and low water (non-irrigated season). Average concentrations in SO_4^{2-} and NO_3^- in Lerma Basin waters.

3.4. Conceptual model of the Lerma hydrological system

Fig. 10 presents a simplified conceptual model of sulphate (salinization indicator) and nitrate behaviours in Lerma Basin. Precipitation and irrigation waters with low SO_4^{2-} and NO_3^- infiltrate through Quaternary materials, increasing its SO_4^{2-} and NO_3^- -N concentration to 227 mg L^{-1} and 29 mg L^{-1} , respectively. The sulphate enrichment of groundwater responds to three factors: evapoconcentration, addition of soil sulphate, and dissolution of local gypsum. In the case of nitrate, the increase responds to evapoconcentration and the addition of synthetic fertilizers. Groundwater flows mainly through Quaternary materials until reaching Tertiary materials, where seepage occurs. Water from the sampled springs does not present significantly modified salinity and NO_3^- concentration increased slightly only. Seepage water flows in a diffuse way over the Tertiary materials, increasing considerably SO_4^{2-} concentration to an average of 513 mg L^{-1} and decreasing NO_3^- -N concentration to an average of 15 mg L^{-1} . In this stage, the increase in SO_4^{2-} responds mostly to the dissolution of Tertiary gypsum although the influence of fertilizers was detected. The decrease in nitrate concentration is probably due to a dilution effect with low-nitrate water from upper channels of the basin and to natural attenuation processes in diffuse flow paths over Tertiary materials.

Regarding the differences between irrigated season (summer) and non-irrigated season (winter), they were controlled by both meteorology and agronomy. During winter, it was expected that low flow conditions (absence of irrigation) would result in higher SO_4^{2-} (and other salinity related parameters) concentrations. However, no significant differences were detected between seasons, suggesting a homogenization in the water quality mediated by the aquifers developed in the Quaternary materials. In the case of nitrate, no significant differences were detected either. However, despite the higher flow conditions (as a consequence of irrigation), differences in the isotopic composition suggested a higher degree of denitrification in surface waters during the irrigated season, probably limited by low temperature during the non-irrigated season.

4. Conclusion

In this work, information gathered in a small basin recently transformed to irrigated agriculture has been used to investigate salinization and nitrate pollution in irrigation return flows, which are two widely recognized environmental problems concerning irrigated agriculture. The conclusions obtained in this study must be taken with caveat since they are obtained with scarce data, but they are indicative of the information a detailed isotopic study can provide.

Irrigation water contributed up to 60% of ground and surface water in the Lerma Basin, highlighting the influence of land use in the hydrology of the basin. Evaporation played a minor role in the increase in salinity suffered by incoming water in the basin.

Sulphate was used as the primary solute indicator of salinization processes for two reasons: it increased more substantially from groundwater to surface waters than other anions typically associated with salinization (e.g., chloride), and also allowed for investigation using isotopic methods. Mixing soil sulphate with the local gypsum sulphate sufficed to explain the isotopic composition of most samples, but in the location with the highest sulphate concentration, the influence of fertilizers was detected.

Based on isotopic signatures, the increase in nitrate concentrations was more strongly related to the application of ammonia/urea fertilizers than nitrate fertilizer inputs. Denitrification likely accounted for low nitrate concentrations in the groundwater-fed surface diffuse pathway to the gullies, with higher

activity levels during the summer irrigated season, as temperature limited biological denitrification activity during winter in these weather-exposed sites. A more detailed assessment is needed to confirm this hypothesis.

It is vital that the specific processes causing adverse environmental impacts in agricultural watersheds, such as salinization and increased nutrient exports, be identified and minimized. The contribution of these processes to watershed health is variable and highly dependent on several specific features of the studied area, such as climate, hydrogeological properties, and existing agricultural management practices. An improved understanding of these processes from studies such as ours can allow for better management decisions tailored to the individual needs of these watershed systems.

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