INSTITUTO GEOLÓGICO Y MINERO DE ESPAÑA
DEPARTAMENTO DE CIENCIAS DE LA TIERRA - UNIVERSIDAD DE ZARAGOZA

DOCTORAL THESIS

Hydrological Assessment of a Newly Implemented Irrigated Area in Spain: Salinization and Nitrate Pollution from Irrigation Return Flows

Daniel Merchán Elena
2015




Instituto Geológico y Minero de España

Departamento de Ciencias de la Tierra
Universidad Zaragoza

Hydrological Assessment of a Newly Implemented Irrigated Area in Spain: Salinization and Nitrate Pollution from Irrigation Return Flows

Dissertation presented by
DANIEL MERCHÁN ELENA

in fulfilment of the requirements to obtain a PhD degree from "Universidad de Zaragoza" (*Doctor por la Universidad de Zaragoza)*

Supervisors:

Dr. Jesús Causapé Valenzuela

Drª. María José Gimeno Serrano

Zaragoza, 2015

Esta Tesis Doctoral ha sido elaborada en la modalidad de compendio de publicaciones, y consta de los siguientes trabajos publicados o aceptados para su publicación:

I. Merchán, D., Causapé, J., Abrahão, R., 2013. Impact of irrigation implementation on hydrology and water quality in a small agricultural basin in Spain. *Hydrological Sciences Journal* 58 (7): 1400-1413. DOI: 10.1080/0262667.2013.829576

II. Merchán, D., Otero, N., Soler, A., Causapé, J., 2014. Main sources and processes affecting dissolved sulphates and nitrates in a small irrigated basin (Lerma Basin, Zaragoza, Spain): Isotopic characterization. *Agriculture, Ecosystems and Environment* 195: 127-138. DOI: 10.1016/j.agee.2014.05.011

III. Merchán, D., Auqué, L.F., Acero, P., Gimeno, M.J., Causapé, J., 2015. Geochemical processes controlling water salinization in an irrigated basin in Spain: Identification of natural and anthropogenic influence. *Science of the Total Environment* 502: 330-343. DOI: 10.1016/j.scitotenv.2014.09.041

IV. Merchán, D., Causapé, J., Abrahão, R., García-Garizábal, I. Assessment of a newly implemented irrigated area (Lerma Basin, Spain) over a 10-year period. I: Water Balances and Irrigation Performance. Aceptado en *Agricultural Water Management* el 24 de abril de 2015.

V. Merchán, D., Causapé, J., Abrahão, R., García-Garizábal, I. Assessment of a newly implemented irrigated area (Lerma Basin, Spain) over a 10-year period. II: Salts and Nitrate exported. Aceptado en *Agricultural Water Management* el 24 de abril de 2015.

Instituto Geológico y Minero de España

Departamento de Ciencias de la Tierra
Universidad Zaragoza

INFORME DIRECTORES Y AUTORIZACIÓN PARA PRESENTAR LA TESIS DOCTORAL EN LA MODALIDAD COMPENDIO DE PUBLICACIONES

D. Jesús Causapé Valenzuela, Científico Titular del Instituto Geológico y Minero de España y **Dña. María José Gimeno Serrano**, Profesora Titular del Departamento de Ciencias de la Tierra de la Universidad de Zaragoza,

AUTORIZAN

La presentación en la modalidad de compendio de publicaciones de la siguiente memoria de Tesis Doctoral, titulada **"Hydrological Assessment of a Newly Implemented Irrigated Area in Spain: Salinization and Nitrate Pollution from Irrigation Return Flows"**, presentada por **D. Daniel Merchán Elena** para optar al grado de *Doctor por la Universidad de Zaragoza*, y certifican que ha sido realizada bajo su dirección y se corresponde y adecua al Proyecto de Tesis aprobado por el Departamento de Ciencias de la Tierra de la Universidad de Zaragoza con fecha dos de febrero de 2011 y ratificado por la Comisión de Doctorado con fecha once de febrero de 2011.

Y para que conste a los efectos oportunos expedimos la presente autorización
En Zaragoza, a 12 de mayo de 2015.

Fdo. Dr. Jesús Causapé Valenzuela Fdo. Drª. Mª José Gimeno Serrano

«Siempre que enseñes, enseña a la vez a dudar de lo que enseñes».
José Ortega y Gasset

«Aunque el agua […] pueda emplearse después en riegos, y una parte considerable de la dedicada a la agricultura vuelva a surgir en parajes más bajos…».
Bentabol y Ureta, en «Las aguas de España y Portugal»*, 1900*

A mi familia

Este trabajo ha sido posible gracias a la beca-contrato de formación de personal investigador BES2010-034124, del Ministerio de Economía y Competitividad, con sus ayudas anexas para la realización de estancias breves EEBB-I-2012-03781 y EEBB-I-2013-06260. Los trabajos que aparecen han sido financiados por los proyectos CGL2009-13410-C02-01 y CGL2012-32395, del Ministerio de Economía y Competitividad con participación de fondos FEDER (Unión Europea). El Instituto Geológico y Minero de España, organismo al que se asocia la beca-contrato, ha aportado apoyo institucional y económico a través de su programa de formación de personal investigador.

Agradecimientos

Este trabajo no habría sido posible sin la colaboración y apoyo de multitud de personas, a los que agradezco sus contribuciones. A mi director de tesis, Jesús Causapé Valenzuela, por su apoyo constante, energía, creatividad y meticulosidad, que ha tratado de trasmitirme durante estos años. A mi directora, Mª José Gimeno Serrano, por su tutela científica y palabras de ánimo constantes. A Luis Auqué Sanz, por su «dirección en la sombra», su apoyo, consejo y conocimientos.

A la Comunidad de Regantes nº XI de Bardenas y sus agricultores, porque sin su buena disposición para resolver consultas, su ayuda en temas puntuales, y la posibilidad de consultar sus bases de datos, este trabajo no habría sido posible.

Al personal de la *Unidad Territorial de Zaragoza del Instituto Geológico y Minero de España,* Eduardo Garrido, Javier Lambán, Juan Cruz Larrasoaña, Lupe Piñón, Emilio Pueyo y Samuel Zamora. Especial mención merece Antonio Azcón, por contagiarme su pasión por la hidrogeología, sus incertidumbres políticas y sociales, y sus mil ideas de cómo mejorar el mundo con un café en la mano. Ruth Soto y, en especial, Pilar Clariana han compartido despacho y confidencias, han sido objeto de miles de consultas y siempre las veré como grandes amigas.

Diversas personas del IGME han colaborado en los trabajos que aquí se presentan. El personal de los laboratorios de aguas, en especial Icíar Vázquez, ha analizado gran parte de las muestras. Juan Luís Plata, planificó y ejecutó los estudios geofísicos. Begoña del Moral realizó e interpretó las difracciones de rayos X en muestras de suelos. Por otro lado, Quique Oliver, de la Universidad de Zaragoza, realizó la preparación de muestras de suelos.

A Neus Otero y Albert Soler, por recibirme durante mi estancia en el *Grup de Mineralogia Aplicada i Medi Ambient del Departament de Cristal•lografia, Mineralogia i Dipòsits Minerals, Facultat de Geologia, Universitat de Barcelona*. Dignos de mención por su simpatía y calidad como anfitriones son Raúl Carrey, Carme Audí, Clara Torrentó, Mónica Rosell, Roger Puig y Mercè Olamendi.

A Katarina Kyllmar por recibirme durante mi estancia en el *Department of Soil and Environment (Swedish University of Agricultural Sciences)*, en Upsala. Junto con Katarina, Karin Blombäck, Maria Blomberg, Gören Johansson, Holger Johnsson, Kristina Mårtensson, Kristian Persson y Lovisa Stjernman Forsberg contribuyeron a una estancia muy instructiva. No puedo pasar sin mencionar a Ana Mingot, Helena Jordá, Victor Fernández, y Svenja Wolter que hicieron que el otoño sueco no acabase con mi cordura.

A los coautores de los trabajos publicados que constituyen esta tesis les agradezco sus aportaciones y constructivas correcciones. En concreto, Raphael Abrahão, Patricia Acero e Iker García Garizábal, además de su colaboración científica, han supuesto un importante apoyo. Así mismo, agradezco la oportunidad de colaboración en otros temas relacionados con el impacto ambiental de la agricultura de regadío que han dado lugar a otras publicaciones no recogidas en esta tesis. En concreto quiero mencionar a Maite Arroita, Carmen Lorente, Enrique Navarro y Diane von Gunten.

A Claus Haslauer (Universidad de Tubingen, Alemania) y Thabo Thayalakumaran (Departamento de Medio Ambiente e Industrias Primarias del Gobierno de Australia), que han actuado como revisores internacionales de esta tesis.

A Amaia, por el diseño de la portada y por su apoyo constante desde que nos conocemos.

Son muchos los amigos que me han apoyado durante esta fase y es imposible mencionarlos a todos. Con Bego, Juan y Leandro he compartido inquietudes de doctorandos. Dimas siempre está ahí para lo que lo necesitas. José Antonio lleva a mi lado desde párvulos y ahí sigue. Ale, Antonio, Fernando, Jacob, Lidia, Marisa, Porti y Tato tuvieron el detalle de visitarme en Zaragoza y se han ganado la mención.

Desde mis primeros momentos en Zaragoza me he visto arropado por un grupo de personas con los que he alcanzado una relación muy especial, que hace que volver a Málaga sea mucho más duro de lo que esperaba. Antonio, Carlota, Cristina, Fabi, Irene, Paloma, Tania y Victoria han sido un tremendo apoyo. Con ellos he compartido tardes de deporte y cervezas, así como inquietudes profesionales y personales.

Por último, a mis hermanos Pedro y José María, de los que desde niño me dicen que soy una mezcla, a mi queridísima hermana Rosi por su apoyo incondicional y contagiosa vitalidad; a mi cuñada y cuñado, Mari Carmen y Antonio; a mis sobrinas: Alejandra, Daniela y Mariam, que tanta alegría me aportan; multitud de tíos, tías, primos y primas, que siempre me paran por el pueblo a preguntar cómo me va por el norte y nunca terminan de entender a lo que me he dedicado estos años. Mis padres, Pedro y María del Carmen, que siempre se han desvivido por proporcionarme una buena educación, me han enseñado a ser como soy, a aprovechar el tiempo y a ser consecuente con mis ideas. Tita Paca y tito José, mis padrinos, no podrá leer estos agradecimientos, pero siempre los tengo presentes.

Foreword

The present dissertation, including five published (or accepted for publication) papers in journals indexed in the Science Citations Index (SCI) adjusts to regulation regarding PhD Thesis as a compendium of published papers, approved by Zaragoza's University agreement concerning PhD Dissertations' regulations ("Acuerdo de 20/12/2013 del Consejo de Gobierno de la Universidad de Zaragoza relativo al Reglamento sobre Tesis Doctorales"), requiring four published papers, with at least three in SCI journals. The main body of the dissertation has been written in English, as it is presented under the international mention ("Mención internacional en el título de doctor") and had required two positive reports from experts from non-Spanish scientific institutions.

Document structure

The document has been structured with a general introduction, objectives statement and the justification of the thematic unity of publications (Chapter I) followed by a description of the study site (Chapter II) and of the methodology (Chapter III).

The next section, corresponding to the five central chapters (IV, V, VI, VII y VIII) are the publications and they represent the partial objectives of the work. They are composed by an initial page with publication data (bibliographic reference, impact factor, and journal ranking in the Journal of Citations Report 2013, last available in the moment of submitting this dissertation) followed by the publication itself as it appears in the journal. Each paper has approximately the following sections: introduction, study site, methodology, results and discussion, and conclusions. These five chapters-publications are independent, although they relate each other since they have been developed in the same study zone and with the same global PhD Thesis objective.

Finally, Chapter IX presents the joint discussion, integrating the results of the different publications, and the final conclusions of the PhD Thesis.

ABSTRACT

Irrigated agriculture has many advantages such as increased productivity or reliable harvests, but it is also regarded as the main source of diffuse pollution. The objective of this work was to assess the evolution of the water use and the environmental processes regarding salinization and nitrate pollution after the shift from rainfed to irrigated agriculture in a small hydrological basin.

The Lerma Basin (7.38 km^2, Zaragoza, Spain) was monitored during the hydrological years 2004-2013, covering periods before (2004-2005), during (2006-2008) and after the implementation of irrigation (2009-2013) in half of the basin surface. The main monitoring point was the basin outlet, with discharge and water quality measurements. To increase the knowledge of the involved processes, several studies were carried out, including trends detection and quantification, stable isotopes analysis, hydrogeochemical characterization, assessment of the use of water in irrigation, and quantification of the mass of exported pollutants from the irrigable area.

Irrigation implementation introduced a strong seasonal pattern in the detected trends, with annual values of 3.2 L s^{-1} for flow, -0.38 mS cm^{-1} in electrical conductivity (indicator of water salinity), and 5.4 mg L^{-1} in nitrate concentration, as a consequence of water and nitrogen fertilizers inputs. The annual loads of exported contaminants increased (salts and nitrates, 0.27 Mg ha^{-1} $year^{-1}$, 2.6 kg NO_3^--N ha^{-1} $year^{-1}$). The water balances presented good results, with balance error of 1%, which allowed an adequate estimation of the irrigation performance. Irrigation efficiency reached 76%, while the loss due to evaporation and wind drift from sprinkler irrigation was 14% and drainage fraction reached 10%. Regarding the leaching of pollutants, the transformed area exported 1.89 Mg ha^{-1} $year^{-1}$ of salts and 11.4 kg ha^{-1} $year^{-1}$ of nitrate-nitrogen under unirrigated conditions. With the implementation of irrigation, these amounts increased to 3.51 Mg ha^{-1} $year^{-1}$ of salts and 30.8 kg ha^{-1} $year^{-1}$ of nitrate-nitrogen, values that are in the range of those recorded in other pressurized irrigated areas in the Ebro Valley.

Thus, the implementation of irrigation imposed relevant hydrological changes in the Lerma Basin, increasing aquifer recharge, gully flow and mass of exported pollutants. Several natural and management factors may influence these processes, and their understanding is important in order to achieve a more efficient use of water and fertilizers, and an environmental friendly irrigated agriculture.

RESUMEN
(Spanish abstract)

La agricultura de regadío tiene muchas ventajas, como una alta productividad o cosechas más estables, pero también es considerada como la principal fuente de contaminación difusa. El objetivo de este trabajo fue estudiar la evolución en el uso del agua y los procesos ambientales relativos a la salinización y la contaminación por nitratos tras el cambio de secano a regadío en una pequeña cuenca hidrológica.

La Cuenca de Lerma (7,38 km^2, Zaragoza, España) fue monitorizada durante los años hidrológicos 2004-2013, cubriendo periodos antes (2004-2005), durante (2006-2008) y después de la transformación a regadío (2009-2013) de la mitad de su superficie. El principal punto de control fue la salida de la cuenca, con medidas de caudal y calidad del agua. Para profundizar en el conocimiento de los procesos implicados, se ejecutaron varios estudios, incluyendo detección y cuantificación de tendencias, análisis de isótopos estables, caracterización hidrogeoquímica, evaluación del uso del agua en el regadío y cuantificación de la masa de contaminantes exportados de la zona regable.

La transformación al regadío introdujo una fuerte pauta estacional en las tendencias detectadas, con valores anuales de 3,2 L s^{-1} para el caudal, -0,38 mS cm^{-1} en la conductividad eléctrica del agua (indicador de la salinidad de la misma), y 5,4 mg L^{-1} en la concentración de nitrato, como consecuencia de las entradas de agua y fertilizantes nitrogenados. Las masas anuales de contaminantes exportados aumentaron (sales y nitratos, 0,27 Mg ha^{-1} $año^{-1}$, 2,6 kg $N\text{-}NO_3^-$ ha^{-1} $año^{-1}$). Los balances de agua presentaron buenos resultados, con un error global del 1%, lo que permitió una adecuada estimación de la calidad del riego. La eficiencia de riego alcanzó el 76%, mientras que las pérdidas de eficiencia se debieron a las pérdidas por evaporación y arrastre del riego por aspersión (14%) y al drenaje producido (10%). Respecto al lixiviado de contaminantes, la zona transformada exportó 1,89 Mg ha^{-1} $año^{-1}$ y 11,4 kg ha^{-1} $año^{-1}$ de sales y nitrógeno en forma de nitrato, respectivamente, bajo condiciones de secano. Tras la transformación al regadío, estas cantidades aumentaron a 3,51 Mg ha^{-1} $año^{-1}$ de sales y 30,8 kg ha^{-1} $año^{-1}$ de nitrógeno en forma de nitrato, valores que están en el rango de los registrados para otras zonas bajo riego presurizado en el Valle del Ebro.

Por tanto, la transformación al riego impuso importantes cambios hidrológicos en la Cuenca de Lerma, incrementando la recarga de acuíferos, el caudal en el barranco y la masa de contaminantes exportados. Varios factores naturales y de manejo pueden influenciar estos procesos, y su conocimiento es importante para alcanzar un mejor uso del agua y los fertilizantes, y una agricultura de regadío más sostenible.

INDEX

CHAPTER I

INTRODUCTION

I. INTRODUCTION

1.1. The expansion of irrigated agriculture

More than 1.5 billion ha – about 12% of the world's land area – are used at present for crop production (arable land plus land under permanent crops). Rainfed agriculture is the world's predominant agricultural production system, but increasing climate variability is bringing greater uncertainty in the production levels. Current productivity in rainfed systems is, on average, little more than half of its potential (FAO, 2013). However, world agricultural production has grown between 2 and 4% per year over the last 50 years, while the cultivated area has grown by only 1% annually. More than 40% of the increase in food production has come from irrigated areas.

Irrigated agriculture has many advantages over rainfed agriculture, such as increased productivity, higher diversity of crops, more reliable harvests, or regional economic security (e.g., Duncan et al., 2008). For these reasons, a global increase in irrigated surface has been observed, especially in developing countries, where it doubled between 1962 and 1998 (FAO, 2003a). However, many irrigation systems are currently performing far below their potential, and there is considerable scope for improving the productivity and efficiency of land and water use in agriculture (FAO, 2013).

1.2. Environmental impacts of irrigated agriculture

There is no question about the value of irrigated agriculture but there is an increasing trend to make it accountable for its impacts on the environment as well as to critically evaluate the water use in the agricultural sector compared with other competitive uses (Stockle, 2001).

Agricultural land use is regarded as the main source of diffuse pollution (Novotny, 1999), and it has a wide range of associated environmental impacts such as changes in landscapes and plant and animal communities, and a deterioration of soil, water and air quality (Stoate et al., 2001). In fact, much of the land currently under agriculture is deteriorating due to inappropriate planning, implementation and management (Dougherty and Hall, 1995). Specifically, irrigated agriculture imposes severe pressure on

the environment, as it accounts for the consumption of 70% of global water resources (FAO, 2003b). For instance, water abstraction and regulation for irrigation purposes changes hydrological conditions in dam-regulated rivers (Graf, 2006), or overexploited aquifers (Custodio, 2002). These pressures impact on water resources in qualitative and quantitative ways (e.g., Kurunc et al., 2005).

Apart from the effects on the irrigation water withdrawal location, the irrigation return flows can also cause hydrological changes in the receiving water bodies. This is one of the reasons why organizations such as the US Environmental Protection Agency see irrigated agriculture as the main source of water pollution (US EPA, 1992). Specific problems in waters downstream of the irrigated agricultural areas are related to erosion (García-Ruíz and López-Bermúdez, 2009), salt leaching (Duncan et al., 2008), nitrate leaching (Quemada et al., 2013), phosphorus leaching (Skhiri, 2011), or pesticides (Klaus et al., 2014). In particular, irrigated agriculture possess an enhanced impact in water bodies receiving irrigation return flows, both in surface waters (Barros et al., 2012a, 2012b; Causapé et al., 2004a, 2004b; García-Garizábal et al., 2012, 2014) and in groundwaters (Andrade and Stigter, 2009; Arauzo et al., 2011; Ibrahikmovik et al., 2011; Stigter et al., 2006).

Among the main environmental impacts, the adequate use of water (Causapé, 2009a) and the leaching of salts (Duncan et al., 2008) and nitrate (Quemada et al., 2013) have special interest for their relevance in irrigated areas and are dealt with in the following sections.

1.3. Hydrological alterations in irrigated basins and irrigation efficiency

The progressive water scarcity reported in many areas of the globe implies a great effort in the assessment of the different water uses. Irrigated agriculture is recognised as the main consumer of water resources worldwide (FAO, 2003b) and consequently, several studies have been published about the efficiency of the use of water in irrigated agriculture (e.g., Skhiri and Dechmi, 2012; Soto-García et al., 2013; Van der Kooij et al., 2013).

An additional problem is related to the transformation from rainfed to irrigated land, which is usually implemented in arid to semi-arid areas, as it severely modifies the water balance of a hydrological basin. Irrigation water is usually applied over the crops water requirements, what produces additional aquifer recharge and, therefore, higher base flow in groundwater dependant streams. For instance, Scott et al. (2011) reported the essential role irrigation played over the perennial existence of small lakes in Uzbekistan.

Therefore, the amount of water reaching ground- and surface water is greatly affected by the efficiency of the use of irrigation water. As an example, Jia et al. (2013) reported a decrease on the surface of wetlands after an increase in the efficiency of irrigation systems in China. An increased efficiency would have consequences both on individual farmers –water saving– and on the basin water management authority –modification of effects downstream.

Moreover, irrigation efficiency has influence in the transport of solutes and particles by water, and therefore, it severely affects the leaching of pollutants.

1.4. Salt leaching from irrigated areas

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. Additionally, the application of agrochemicals can influence the water quality by adding solutes and by enhancing the natural weathering (Koh et al., 2007; Kume et al., 2010).

The leaching of salts is a requirement of irrigated agriculture (Corwin et al., 2007; Letey et al., 2011) as the accumulation of salts in soils profiles is deleterious for plants, reducing the productivity and even, in extreme situations, forcing the abandonment of cultivation. However, in many occasion the leaching of salts overpasses this requirement. The implementation of irrigation can mobilize salts long stored in the soil profiles (García-Ruíz and López-Bermúdez, 2009) or present in the subsurface (Richter and Kreitler, 1991).

The actual amount of leached salts depends on several factors such as climate, hydrogeological conditions or irrigation management (Causapé et al., 2004b; García-Garizábal et al., 2012; Isidoro et al., 2006). Eventually, leached salts will reach a water body modifying its salinity. In this sense, salinization of water bodies represents a significant risk in water systems regarding suitability for irrigation (Tanji, 1990), water supply systems and other human uses (Peck and Hatton, 2003) or ecosystems health (Nielsen et al., 2003).

Groundwater salinization by agricultural practices has been widely reported all around the world (e.g., Koh et al., 2007; Stigter et al., 2006; Yuce et al., 2006). In particular, irrigated agriculture represents an enhanced pressure on the hydrological system receiving irrigation return flows and may induce groundwaters and surface waters salinization (e.g., Duncan et al., 2008; Isidoro et al., 2006). In any case, the interaction between ground and surface waters adds complexity to the behaviour of these hydrological systems. On the other hand, salinization in irrigated areas may also be

related to natural ongoing processes which may, to a certain degree, be enhanced by the addition of irrigation water (Isidoro et al., 2006; Tedeschi et al., 2001) or be a direct consequence of the irrigation itself (Stigter et al., 2006), since the dominating salinization processes are very site-specific (Duncan et al., 2008).

As a consequence, the long-term sustainability of agriculture greatly depends on protecting land and water resources from salinity (Thayalakumaran et al., 2007). Thus, a deep knowledge of the local hydrological conditions and processes controlling salinization is required to understand the feasible actions to take in order to mitigate impacts on water resources systems.

1.5. Nitrate leaching from irrigated areas

Nitrogen is applied to crops normally in excessive amounts and then it is leached from the soils during the main rain events, although the proper irrigation water can also produce nitrogen leaching (García-Garizábal et al., 2012; He et al., 2012; Quemada et al., 2013; Tan et al., 2013). Additionally, the availability of irrigation water produces changes in the strategies of farmers, who tend to grow more productive crops and, thus, to increase fertilization rates (Gaydon et al., 2012).

Nitrate pollution is a major concern in agricultural areas since high nitrate concentrations have long been regarded as a threat for human health and ecosystems (Fan and Steinberg, 1996; Höring and Chapman, 2004; Sutton et al., 2011). Nitrate pollution is indeed aggravated by the fact that other nitrogen forms (such as organic N or ammonia) are also present in waters but they are not considered in most cases, neither in legislation (e.g., Nitrates Directive, OJEC, 1991) nor in environmental studies (Durand et al., 2011).

Great increases of nitrate concentration have been linked to irrigated agriculture all around the world in groundwaters (e.g., Stigter et al., 2006; Thayalakumaran et al., 2008) and surface waters (e.g., Lassaletta et al., 2009). 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 the soil types (Arauzo and Valladolid, 2013; Kyllmar et al., 2014), the presence of reducing conditions in aquifers (Rivett et al., 2008; Thayalakumaran et al., 2008) and the irrigation/fertilization management (Schepers et al., 1995, Causapé et al., 2004b). 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.

1.6. Irrigated agriculture environmental impacts in the Ebro Basin (Spain)

In Spain, the increase of irrigated area has been moderate but significant, with 7% more irrigated land between 1990 and 2009 according to the Spanish Ministry of Agriculture, Food and Environment ("Ministerio de Agricultura, Alimentación y Medio Ambiente"). Irrigated agriculture has been a key factor in the agrarian Spanish system (MAAMA, 2014) as it provides more than 50% of the final agrarian production with only 13% of the surface. An irrigated hectare produces, on average, six times more than a rainfed hectare, and generates four times more income.

The Ebro Basin (85,569 km^2, north-east Spain) presents a high level of human interference, with 3.2 million inhabitants, reservoirs volumes of 7,580 hm^3, and more than 680,000 ha dedicated to irrigated agriculture use (CHE, 2009a). The main use of water is for irrigated agriculture, with more than 6,000 hm^3 $year^{-1}$ being extracted. In fact, all other uses together (human consumption, industrial, etc.) do not exceed 1,000 hm^3 $year^{-1}$.

Environmental problems related to irrigated agriculture, such as salinization and nitrate pollution, are openly recognized by the Ebro Basin Hydrological Authority (CHE, 2006, 2009b). In particular, the Arba River, one of the Ebro's tributaries, presented the highest increase in salinity and nitrate concentrations in the Ebro Basin, during the period 1975-2004 (CHE, 2006). This river was also the first surface water body declared as affected by nitrate pollution by the Ebro Basin Hydrological Authority (MMARM, 2011). Consequently, large areas of the Arba Basin were designated as Nitrate Vulnerable Zones in 2008 by the Regional Government (BOA, 2009), according to the Spanish legislation and following the European Council Directive 91/676/EEC (OJEC, 1991) concerning the protection of waters against pollution by nitrates from agricultural sources. The indications and implications of this directive were included in the posterior Water Framework Directive (OJEC, 2000) and Groundwater Directive (OJEU, 2006).

The Lerma Basin is a small hydrological basin (7.38 km^2) draining to the Arba River. The main land use is irrigated agriculture (48%) and it has experienced recently the transformation from rainfed to irrigated agriculture. The environmental monitoring of the basin began two years before the implementation of irrigation. Therefore, it is an extraordinary natural laboratory to study the previously stated problems. The present study expands the knowledge generated in previous works (Abrahão, 2010; Abrahão et al., 2011a, 2011b, 2013) by the use of new approaches and the longer data series provided by the on-going monitoring of the catchment, with the added value of this fact in any hydrological study. The Lerma Basin is deeply described in Chapter 2 of the present dissertation.

1.7. Objectives of the research

1.7.1. PhD Thesis Objective

The general objective of this Thesis was to assess the evolution of the agro-environmental impact of an area over the water resources after its transformation from rainfed to irrigated agriculture. The specific objective is to study the effects on the water use, the salinization and the nitrate pollution, together with increasing the knowledge of the hydrological processes controlling this impact. This objective is consistent with the recommendations of local water authorities (CHE, 2006) which suggest the need for increasing knowledge of water bodies with quality problems in order to create management strategies that will allow improving the control of water resources quantity and quality at the basin scale.

1.7.2. Partial Objectives

The partial objectives, coinciding with those dealt with in the different publications, were:

- To analyse the effects of irrigation implementation on the hydrology of a gully (relationships and trends in flow, water quality and contaminant loads) (Paper I).
- To determine the causes of these dynamics through the assessment of stable isotopes data of both shallow groundwater and surface water (Paper II).
- To identify the geochemical processes controlling the salinization of this gully and to elucidate if they are related to natural or anthropogenic factors (Paper III).
- To assess the evolution of the irrigation performance in an area transformed from rainfed to pressurized irrigated agriculture (Paper IV).
- To assess the evolution of salt and nitrogen pollution induced by this new irrigated area (Paper V).

1.7.3. Thematic unity of the published papers

All the studies, conducted to fulfil the partial objectives of this Thesis, were carried out in the same study zone (Lerma Basin, Zaragoza, Spain) and they aimed, as a whole, to obtain a deeper knowledge of irrigated agriculture environmental impacts on water resources focusing on salinization and nitrate pollution processes.

CHAPTER II

STUDY ZONE

II. STUDY ZONE

2.1. Geographic location

The study zone is the hydrological basin of the upper section of Lerma Gully, placed inside the municipality of Ejea de los Caballeros (Zaragoza province, Aragón Autonomous Community, Spain). It is located on the left bank of the middle Ebro River Valley (which covers a great proportion of the north-eastern area of Spain; Fig. 2-1). The Lerma Gully Basin is located between coordinates X = (654,407 m, 658,587 m) and Y = (4,655,712 m, 4,658,407 m) in the ETRS 1989 projection (UTM Zone 30N). The area of the basin is 7.38 km^2, with about 4.5 km long (from East-Southeast to West-Northwest) and around 2 km wide. Altitudes range from 335 to 495 m above sea level. The Lerma Gully waters drain to the Arba River, one of the main tributaries of the Ebro River.

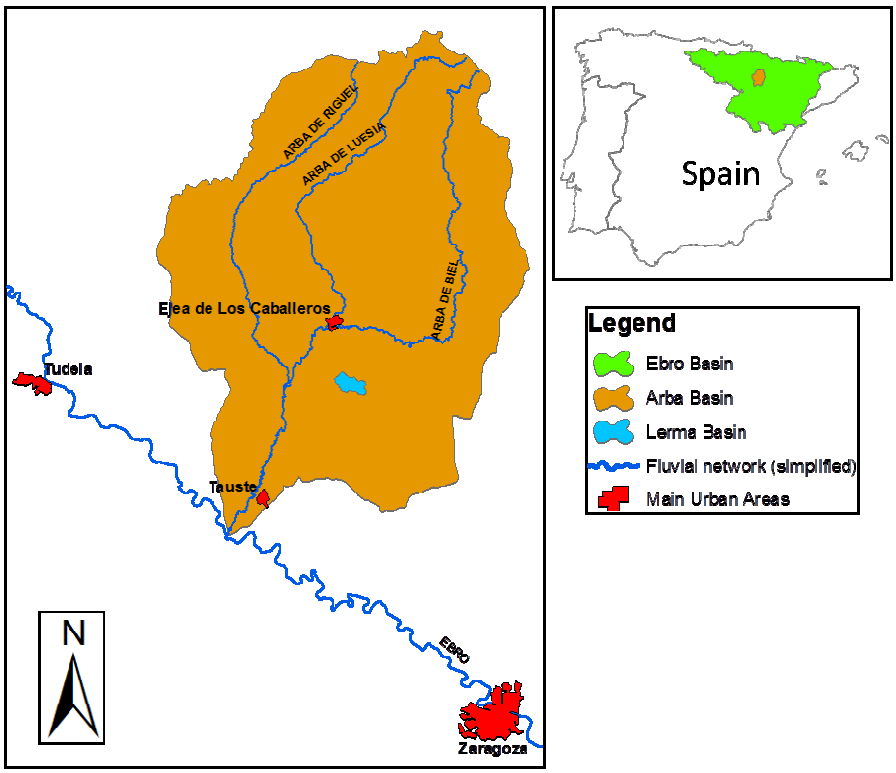

Fig. 2-1. *Geographic location of the Lerma Basin inside Arba and Ebro River Basins, and the main urban areas and rivers (elaborated from data obtained from Confederación Hidrográfica del Ebro, CHE,* www.chebro.es*).*

2.2. Climate

2.2.1. Historic information

Historical information about the climate is available for the municipality of Ejea de los Caballeros, located around 8 km away from the study zone. According to the Spanish National Meteorology Agency (AEMET, 2011), for the period between 1971-2000, the climate in Ejea de los Caballeros has had influence of cold steppe and temperate with a dry season and a hot summer of Köppen classification. In general it is characterized as Continental to Mediterranean, with extreme temperatures and irregular and scarce rain. Average annual temperature is 14 °C, with January and February as the coldest months (average below 5 °C). The hottest months are July and August (average over 23 °C).

Historical annual rainfall in Ejea de los Caballeros is 468 mm. Summers are dry, only wetted by occasional storms. Wind is a characteristic meteor in the study area, with the so-called "cierzo", a northwest-to-southeast wind that follows the topographic low of the Ebro River Valley and can reach speeds up to 90 km h^{-1}.

2.2.2. Climate during the study period

The average annual rainfall for the period 2004-2013 was 382 mm with a high annual variability (coefficient of variation: CV = 31%). A typical year consists of two dry seasons (summer and winter) and two wet seasons (spring and autumn; Fig. 2-2).

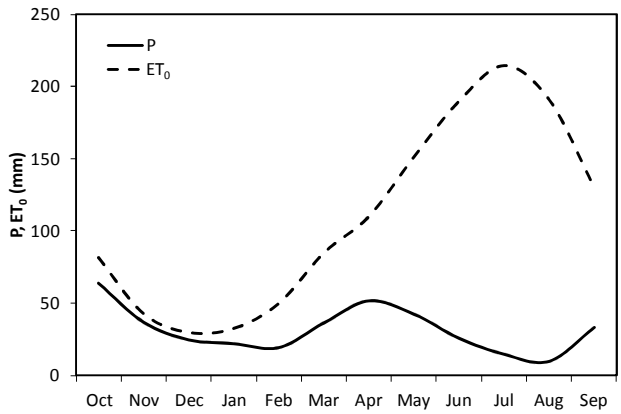

Fig. 2-2. *Monthly average precipitation (P) and reference evapotranspiration (ET_0) during the study period (2004-2013).*

The average reference evapotranspiration (ET_0) calculated by Penman–Monteith method (Allen et al., 1998) was three times higher (1307 mm $year^{-1}$) and much less variable (CV = 6%) than precipitation, and not evenly distributed along the year (Fig. 2-2). 75% of ET_0 occurred between April and September, coinciding with the driest months, which made irrigation a requirement in order to achieve productive agriculture.

2.3. Geology

2.3.1. Geological context

The surface covered by the Lerma Basin is located in the central area of the Tertiary Ebro Basin. The Ebro Basin was endorrheic from the early Oligocene to the Upper Miocene, receiving continental sediments from the surrounding mountain ranges: the Pyrenees in the north, the Iberian Chain in the south and the Catalanides in the southeast. Therefore, the main depositional facies in the Lerma Basin area are of lacustrine origin, such as marls and marly limestones originated in the Castejón Mountains, the higher relief in the study area.

2.3.2. Lerma Basin Geology

The study zone is in the northernmost area of the so-called Hoya de Ejea, located between two ranges of mountains: Pie de Monte Pirenaico (to the north) and Sierras Calcáreas Centrales of the Ebro Depression (to the southeast). Inside the study zone, the main relief corresponds to the Castejón Mountains and it is located in the southeast area (Figure 2-3).

Inside the surface of the Lerma Gully Basin, outcropping materials belong to Tertiary and Quaternary ages. According to mechanical boreholes carried out in the surrounding areas, the Tertiary materials (66% of the basin surface, Fig. 2-3) correspond to Miocene and are composed by about 1000 m of alternating gypsum, clay and silt materials of brown and gray colours, with occasional intercalations of fine limestone layers associated with gypsum and local presence of sandstone paleocanals (ITGE, 1988). The detectable structure in the Tertiary materials is simple, with subhorizontal layers with a maximum dip of 8°, presenting minimal deformation despite of its proximity to the Pyrenean Orogene.

Overlapping the Tertiary, glacis materials (34% of the basin surface, Fig. 2-3, Fig. 2-4) were deposited unconformably at the end of the Pleistocene period. These deposits have their origin in the Castejón Mountains. They are composed by calcareous pebbles and gravels, sand, silt and clay. Pebbles and gravels have generally small size (2-3 cm) and sharp shapes, but occasionally bigger size pebbles are present (up to 0.5 m). These materials present cross beddings and clay, silt and sand intercalations, with some silt-clayey matrix. The depth of these deposits ranges from near 0 m in the proximities of the contact to the Tertiary materials up to 12 m in the centre of the glacis bodies (Plata, 2011).

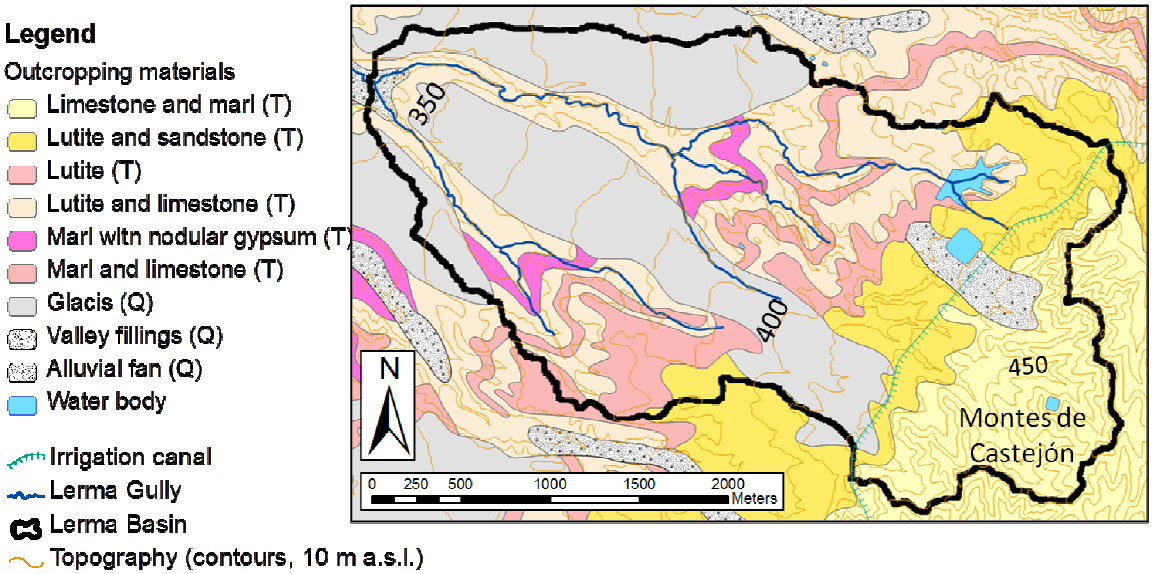

Fig. 2-3. *Outcropping materials of Lerma Basin (elaborated from data obtained at Geological Survey of Spain, IGME,* www.igme.es*).*

The current drainage network has excavated gullies in the glacis so that the Tertiary materials are exposed (Fig. 2-3). These gullies made the different glacis bodies independent. Finally, Holocene valley fillings and low entity alluviums represent the most recent Quaternary materials.

2.3.3. Hydrogeology

The permeability in the Tertiary materials is low and it is associated to the fractures present in the calcareous materials (mainly in the higher part of the basin). Alternating disposition of low thickness limestone levels along with its horizontality provide its scarce hydrogeological possibilities, since permeability in normal direction to stratification is determined by low permeability layers (Custodio and Llamas, 1983), and clay is the main component of the non calcareous levels. In the direction parallel to stratification, the discontinuity in the fractures system makes the existence of significant fluxes hard. Therefore, in this study, Tertiary materials are considered impervious, since possible flow through them is negligible in comparison with other components of the water balance in the basin. Similar approaches were taken in other studies with similar geological context (e.g., Casalí et al., 2008, 2010).

On the other hand, Quaternary is composed by high permeability materials which constitute intergranular porosity aquifers. The different glacis bodies suppose independent perched and free aquifers that provide water for adjacent gullies. The thickness of the Quaternary materials has been estimated with a maximum of 12 m although the common thickness ranges between 1 and 6 m (Plata, 2011). Permeability in

Fig. 2-4. *Detail of the contact between Tertiary and Quaternary materials in an exposed road slope.*

this small-sized aquifers ranges from 1 to 10 m day^{-1} and the effective porosity from 1 to 5% (values obtained from pumping and slug tests performed in the framework of this study, A. Azcón, pers. comm.).

Precipitation and irrigation waters infiltrate through Quaternary materials down to the Tertiary materials where they flow horizontally. The main flow direction in the basin is SE - NW, following the network of gullies, and it is determined mainly by the slope of the outcropping materials. Groundwater seeps to the surface through the contact between Quaternary and Tertiary and it feeds a network of gullies. This network of gullies crosses Lerma Basin from east-southeast to west-northwest (Fig. 2-3).

2.4. Edaphology

Soils developed on the Quaternary materials (Calcixerollic Xerochrepts, Soil Survey Staff, 2014) display loamy textures, with an effective depth of 60–90 cm. Its salinity (electrical conductivity of the saturation extract: EC_e <4 dS m^{-1}) and small risk of erosion (slope <3%) identified these zones as suitable for conversion into irrigated land (Beltrán, 1986), and therefore most of the irrigation surface covers the Quaternary surface.

In contrast, soils developed in the valleys of the Lerma Basin (Typic Xerofluvent, Soil Survey Staff, 2014) have a lower effective depth (between 30 and 45 cm), limited by

limestone or tabular gypsum levels, which provides slow drainage. Higher salinities (EC_e between 4 and 8 dS m^{-1}) and steep slopes (>10%) were the reasons why this Tertiary valleys were classified as not appropriate for irrigation (Beltrán, 1986). 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 minerals in the basin, with tabular and nodular gypsum in a well-defined stratum (Fig. 2-3); gypsum is also present in other lythologies as cement (ITGE, 1988).

2.5. Agronomy

2.5.1. The transformation of the Lerma Basin

Before irrigation implementation, main crops in the study area included wheat and barley, which were seeded in winter and harvested in June or July. Their production relied on meteorological conditions, with good harvest in wet years. During the early 2000's, half of its surface was projected to be transformed in irrigated land with water coming from the Yesa Reservoir, located in a neighbour hydrological basin (Aragón River Basin). An interruption in the rainfed agriculture occurred between 2003 and 2005 as a consequence of irrigation implementation works (new plots distribution, building of ways, main pipe network and ponds installation).

Once the main irrigation network was installed, individual farmers equipped their plots for pressurized irrigation, depending on the date of plot assignation or availability of funds. Consequently, irrigated surface increased gradually between 2006 and 2013 (Fig. 2-5, Table 2-1). The main increase was observed between 2006 and 2008, although the complete transformation was not reached until 2013 (352 ha), the last year included in this study. Maize (44%), winter cereals (19%), sunflower (9%), pea (9%), and tomato (6%) were the main crops in the area (Table 2-1).

2.5.2. Irrigation practice

During spring and summer, Lerma Basin receives water from the Yesa Reservoir (Fig. 2-6) via the Bardenas irrigation channel. These waters present good-quality for irrigation as they come from the Pyrenees (northeast Spain), presenting electrical conductivity (indicative of water salinity) below 0.4 dS m^{-1} and Sodium Adsorption Ratios of c.a. 0.3, what represents very low sodium hazards.

Sprinkler irrigation is the predominant system, accounting for 93% of the irrigated surface. Drip irrigation is used for the rest of the area (mainly for tomatoes and almond trees). Irrigation water rates (average of 5,680 m^3 ha^{-1}) were influenced by the annual

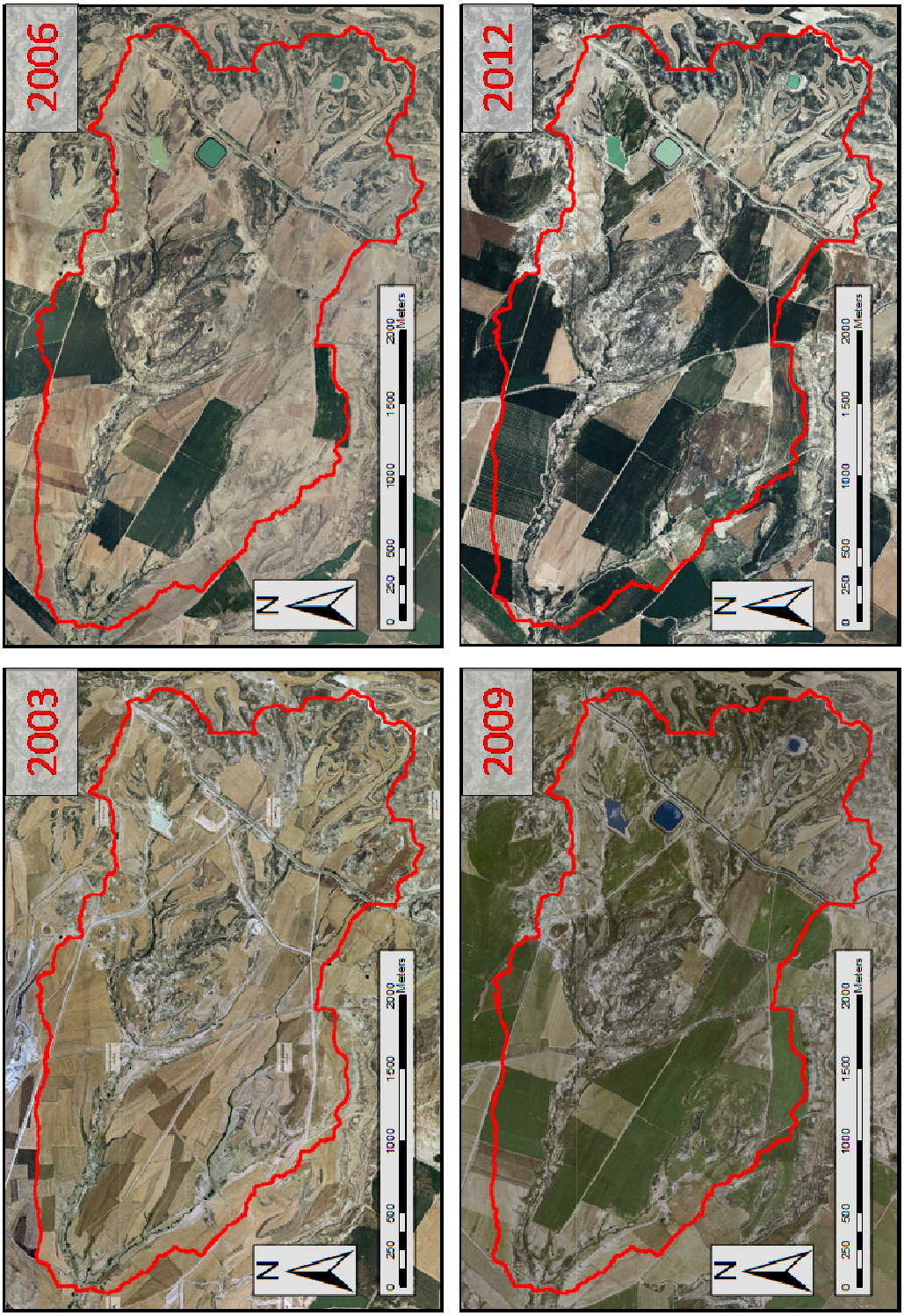

Fig. 2-5. *Successive aerial pictures of the study zone in 2003, 2006, 2009 and 2012 (elaborated from data obtained from Spanish National Geographic Institute, IGN,* www.ign.es*).*

Table 2-1. *Dynamics of the transition into irrigated land for the Lerma Basin.*

		2006	2007	2008	2009	2010	2011	2012	2013	Average[a]
Irrigated area	ha	127	269	316	319	322	331	331	352	-
	%[b]	36.1	76.3	89.6	90.5	91.2	93.8	93.8	100	-
Irrigation system	Sprinkler (%)	91.2	97.9	94.5	90.8	90.6	97.5	88.2	90.8	92.6
	Drip (%)	7.8	2.1	5.5	9.2	9.4	2.5	11.8	9.2	7.4
	m^3 ha^{-1} irrigated	4,860	5,750	5,750	6,200	5,660	5,320	6,630	4,900	5,680
Crops	Maize (%)	64.8	64.3	41.8	49.5	28.2	46.5	44.9	35.9	44.3
	Barley (%)	0.0	17.1	19.0	7.6	10.1	4.6	11.5	15.2	11.6
	Sunflower (%)	6.3	0.0	6.4	15.6	6.7	14.5	12.1	7.2	8.9
	Pea (%)	0.0	0.0	11.8	6.0	21.6	7.9	6.3	6.6	8.7
	Wheat (%)	0.0	10.7	6.6	2.1	13.1	10.9	7.4	3.0	7.2
	Tomatoes (%)	7.8	2.1	5.5	8.1	7.1	0.0	9.2	7.1	5.8
	Broccoli (%)	21.1	2.5	1.7	2.1	1.7	0.0	0.0	6.6	3.1
	Onion (%)	0.0	3.4	2.6	3.5	0.0	0.8	5.2	4.1	2.6
	Leek (%)	0.0	0.0	0.0	0.0	4.1	8.5	0.0	2.4	2.2
	Almond tree (%)	0.0	0.0	0.9	1.1	2.3	2.5	2.6	2.1	1.6
	Vetch (%)	0.0	0.0	0.0	0.0	0.0	3.9	0.8	4.1	1.3
	Raygrass (%)	0.0	0.0	0.0	4.5	5.1	0.0	0.0	0.0	1.3
	Alfalfa (%)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.5	0.9
	Sorghum (%)	0.0	0.0	3.7	0.0	0.0	0.0	0.0	0.0	0.5
	Double cropping (%)	0.0	2.5	27.1	8.7	26.3	14.2	10.9	23.9	15.7

[a] Weighted average considering the transformed area.

[b] Percentage of total irrigable area.

distribution of crops and its water requirements, along with the presence of double cropping (average of 16% of the cultivated surface, Table 2-1). Irrigation applied to maize, winter cereal and vegetables averaged 740, 160 and 552 mm year^{-1}, respectively. The irrigation volume applied to crops varied depending on water availability in the different years, but the total amount of irrigation for the entire basin increased progressively, stabilizing approximately at 2 hm^3 year^{-1}.

Fig. 2-6. *Yesa reservoir, origin of irrigation water of Lerma Basin (picture downloaded from www.turisbox.com).*

2.5.3. Nitrogen fertilization

Nitrogen fertilization applied to each crop was rather variable depending on the expected productions and weather conditions, among other factors. Fertilization of maize represented an average of 352 kg N ha^{-1} year^{-1}. The general agronomic management during the irrigated period consisted on sowing fertilization with compound fertilizers (NPK, mainly 8-15-15 and 15-15-15), followed by multiple applications of liquid fertilizers (32% N: 16% urea and 16% ammonium nitrate). Winter cereals (wheat and barley) received 143 kg N ha^{-1} year^{-1} distributed between the first applications in compound fertilizers a few days before sowing, and the remainder in the form of urea in early spring. Fertilization of tomato was characterized by frequent applications of small rates throughout the cycle, with the aim of overcoming the different nutritional requirements of each vegetative stage. Compound fertilizers and liquid fertilizers (fertigation through drip irrigation) were mainly used, with a contribution up to 124 kg N ha^{-1} year^{-1}. Finally, sunflower received an average of 104 kg N ha^{-1} year^{-1} through two applications, the first before sowing and a side-dressing in early June.

The remaining crops constituted a minority in the Lerma Basin, in part associated with double cropping of a plot in the same year. The main associations were peas with either maize or sunflower, and winter cereal with sunflower, maize or other summer crop.

When a winter cereal was followed by maize cultivation in the same year and plot (Fig. 2-7), N fertilization reached 410 kg N ha^{-1} $year^{-1}$. The application of organic fertilizers such as manure or pig slurry was minimal, not used systematically and only in a few plots (farmers surveys).

Fig. 2-7. *A typical example of double cropping with recently sowed maize over the residues after winter cereal harvest.*

2.6. Environmental issues in the Lerma Basin

As mentioned in Chapter 1, environmental problems related to irrigated agriculture, such as salinization and nitrate pollution, are openly recognized by the Ebro Basin Authority (CHE, 2006, 2009b). Specifically, Arba River, the tributary of the Ebro River which receives 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, the Arba River was the first surface water body declared as polluted by nitrate in the entire Ebro Basin (MMARM, 2011).

For this reason, all the agricultural area inside the municipality of Ejea de los Caballeros included in the land registry as irrigated (including the irrigated surface of the Lerma Basin) were designated as vulnerable area to nitrate pollution in 2008 (BOA, 2009), according to Spanish legislation following the European Council Directive 91/676/EEC (OJEC, 1991) concerning the protection of waters against pollution by nitrates from

agricultural sources. Additionally, an increase in the knowledge on water bodies suffering severe water quality problems has been considered paramount by the Ebro Basin Water Authority (CHE, 2006).

In the study presented here, the agro-environmental monitoring of water use, salinization and nitrate pollution processes were investigated for the period 2004-2013. Other environmental problems of irrigated agriculture have been studied in the Lerma Basin but are not included in this work. For instance, Lorente et al. (2014), Abrahão et al. (2013), and Skhiri and Dechmi (2012) studied pesticides, heavy metals and phosphorous problems, respectively.

CHAPTER III

METHODOLOGY

III. METHODOLOGY

In this section, the methodologies used in this PhD Thesis are presented. For brevity's sake a general overview of the different methods is summarized here and the complete information can be found in the specific papers.

3.1. Meteorological data (all the papers)

Meteorological data for the study zone were obtained from four agro-climatic stations belonging to the Irrigation Integrated Advisory Service (Servicio Integrado de Asesoramiento al Regante) network (Fig. 3-1) (http://servicios.aragon.es/oresa), from the Agriculture, Livestock and Environment Department (Departamento de Agricultura, Ganadería y Medio Ambiente) of Aragón Government.

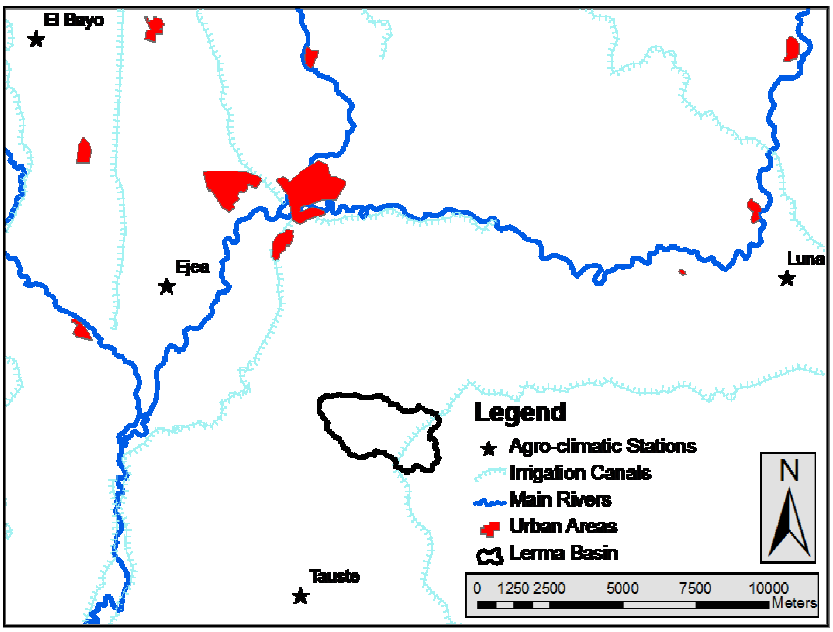

Fig. 3-1. *Location of agro-climatic stations in the surrounding areas of Lerma Basin.*

The stations included in this network provided daily precipitation, wind speed, relative humidity and reference evapotranspiration. To obtain data for the study zone, the data from the four closest stations were interpolated using the inverse distance squared

method (Isaaks and Srivastava, 1989). The stations used were El Bayo, Ejea, Luna and Tauste, located between 4 and 18 km away from the study zone (Fig. 3-1).

3.2. Agriculture management

3.2.1. Irrigation data (all the papers)

Irrigation data for each plot in the study area were estimated from data obtained from the Irrigation Authority responsible for the irrigation in the area ("Comunidad de Regantes nº XI, del Canal de Bardenas, Sector XII"). The Irrigation Authority provided the daily requirements of irrigation time made by the farmers and the yearly used amount of water, measured using flow meters in every hydrant present in the study zone. In addition, information was provided about the typical irrigation management for the different crops present in the area.

3.2.2. Fertilization practices and rates (papers II, III, V)

During the years 2007, 2008 and 2012 surveys were conducted (by phone and face-to-face enquiries) with all the farmers from the Lerma Basin. These surveys included data about the type of fertilizers used, the rate and timing of fertilization and any other practice regarding fertilization management. Additionally, the irrigation authority and the farmer's advisory service (Agrarian Cooperative "Virgen de la Oliva") provided abundant information about fertilization management of the crops present in the area.

3.3. Lerma Gully's discharge data (papers I, IV and V)

In 2005, a gauging station (Fig. 3-2) was installed at a defined section (rectangular thin-plate weir), and since then water level has been registered every 10 min with an electronic limnigraph (Thalimedes, OTT, Germany). In 2010, the analogical system was replaced by a digital one, composed by a pressure transducer (PX437, Omega Engineering Inc., USA) coupled to an *ad hoc* designed data-logger with capabilities of data transmission (Tafyesa, Spain).

The recorded water height data (h; m) were transformed to flow (Q; $m^3\ s^{-1}$) using gauge rating curves, obtained using the WinFlume software (Whal, 2000), as follows:

$$Q = 1.73\ (h + 0.00347)^{1.624} \qquad \text{for } h \leq 0.5 \qquad \text{[Eq. 1]}$$

$$Q = 10.28\ (h + 0.01125)^{1.725} \qquad \text{for } h > 0.5 \qquad \text{[Eq. 2]}$$

The correspondence between water heights and flow was cross-checked by several manual gauging methods, such as the velocity–area method using a wading rod, dilution gauging, and the use of a portable V-notch weir.

Fig. 3-2. *Gauging station in the Lerma Gully.*

3.4. Exported contaminant loads estimation (papers I and V)

The monitoring of Lerma Gully water quality began in October 2003 at the beginning of the work for its transformation (two years before irrigation started). Manual water sampling was performed at a monthly frequency between October 2003 and September 2005. In October 2005, automatic sampling equipment (3700 Portable Sampler, Teledyne ISCO, USA) was installed. The automatic sampler was programmed to collect a sample per day. In 2010, high resolution water quality monitoring devices were installed (Fig. 3-3). An electrical conductivimeter (ST 3254, B&C Electronics, Italy) and a nitrate measuring probe (Nitratax, Hach-Lange, Germany) were coupled to an *ad hoc* designed data-logger and transmitter (Tafyesa, Spain).

Manually or automatically collected samples were taken to the laboratory where the electrical conductivity corrected to 25 °C (EC; mS cm^{-1}) and nitrate concentration (NO_3^-; mg L^{-1}) were determined using an Orion-5 Star conductivitimeter and a colorimetry Autoanalizer 3 system, respectively.

Seventeen water samples were selected within the range of variation of EC in Lerma Gully, for which the alkalinity (mostly bicarbonate concentration, HCO_3^-; mg L^{-1}) and dry

residue (DR; mg L^{-1}) were determined. From these concentrations, the total dissolved solids (TDS; mg L^{-1}) was calculated (Custodio and Llamas, 1983):

$$TDS = DR + {}^{1}/_{2}\ HCO_3^- \qquad \text{[Eq. 3]}$$

The EC (mS cm^{-1}) was converted into TDS (mg L^{-1}) for each collected sample and measured EC through:

$$TDS = 712.22\ EC - 104.83 \qquad R^2 = 0.99 \qquad n = 17 \qquad p < 0.01 \qquad \text{[Eq. 4]}$$

Once EC was converted to TDS, the use of both TDS and NO_3^- combined with flow allowed the calculation of the exported load of salts; and the exported load of nitrate.

Fig. 3-3. *Details of EC-meter and Nitratax equipments installed in the gully.*

3.5. Lerma Basin ground-, spring and surface water monitoring

3.5.1. Sampling procedures (papers II, III)

Samples of the Lerma Basin waters were collected for complete chemical analysis in 2011, February the 10th and July the 27th, and in 2012, January the 10th and July the 31st, representing two non-irrigated and two irrigated seasons, and two low water and two high water seasons, respectively. Samples were collected at least one week after the last precipitation event to avoid dilution and mixing effects.

Sixty three water samples were collected from the Lerma Basin throughout the study period: groundwaters (GW, 31 samples), spring waters (SpW, 8) and surface waters (SW, 24). Additionally, samples of precipitation (P, 11) and irrigation waters (I, 6) were collected between 2007 and 2012.

The piezometers were drilled in 2008 in the Quaternary materials to a depth between 6 and 8 m, where 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. The screened interval was the whole piezometer. Piezometers were used for both measuring the depth of the water table and taking groundwater samples.

Groundwater samples were collected using a dispensable bailer whereas spring or surface water samples were collected manually. Field parameters (electrical conductivity corrected to 25 °C [EC], temperature [T], pH, redox potential relative to the standard hydrogen electrode [Eh], dissolved oxygen [DO] and alkalinity) were measured *in situ* just after sample collection, with previously calibrated instruments. EC-meter CRISON CM35, and pH/Eh-meter CRISON T25 were used for EC, T, pH and Eh. Alkalinity was measured using a HACH alkalinity test kit.

Fig. 3-4. *Piezometers drilling and depth to groundwater monitoring.*

3.5.2. Analytical procedures (papers II and III)

The filtered samples were analyzed within a month of collection. Chemical parameters (Cl^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}, Na^+, K^+, Ca^{2+}, Mg^{2+}, NO_3^-, NO_2^-, NH_4^+, 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 NO_3^-, NO_2^- and Kjeldahl N concentrations. Cations 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 H_2SO_4 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 infrared emission using TOC-V analyzer Shimadzu.

The charge balance was cross-checked to ensure adequate analysis quality (Weight, 2008):

$$Charge\ balance\ (\%) = 200 \frac{\sum meq\ cation - \sum meq\ anion}{\sum meq\ cation + \sum meq\ anion} \quad \text{[Eq. 5]}$$

3.5.3. Isotopic Study (paper II)

In a sub set of sixteen samples (eight samples in two sampling campaigns, July 27th 2011 and January 10th 2012), stable isotopes analysis were performed. Results were reported in δ notation, i.e., the deviation from an international standard. Analysis included δD and $\delta^{18}O$-[H_2O]; $\delta^{34}S$ and $\delta^{18}O$-[SO_4^{2-}]; $\delta^{15}N$ and $\delta^{18}O$-[NO_3^-]) and they were used to determinate the origins and processes affecting sulphate and nitrate contents in the Lerma Basin ground-, spring and surface waters. International standards used were VSMOW (Vienna Standard Mean Ocean Water), for δD and $\delta^{18}O$; AIR (atmospheric N_2), for $\delta^{15}N$; V-CDT (Vienna Canyon Diablo Troillite) for $\delta^{34}S$.

3.5.4. Geochemical modelling (paper III)

The USGS software PHREEQC (Parkhurst and Appelo, 1999) with its database *phreeqc.dat* was used for the geochemical modelling. Speciation-solubility calculations were performed to obtain the saturation indexes of the different water samples with respect to the mineral phases of interest (calcite, dolomite, gypsum and halite). CO_2(g) partial pressures were also computed based on the alkalinity and pH of the samples (Appelo and Postma, 2005). Additionally, an inverse modelling approach was applied between selected water samples considered representative of the variety observed. This approach allowed estimating the net geochemical reactions between samples assumed to be connected by a flow line. Finally, a forward modelling approach was applied using feasible chemical reactions to reproduce the evolution of the system. All the information provided by these geochemical modelling exercises was used to discard or confirm the hypotheses of the different processes inferred throughout the study.

3.5.5. X-ray diffraction (paper III)

Mineralogical determinations were performed in soil samples by X-ray Diffraction. After removing the fraction > 2 mm, around 5 g of dry sample were ground in an agate mortar and pestle, and then sieved through 63 µm. X-ray diffraction was performed in a XPERT PRO MPD equipment (PANanalytical), and the data were processed using the software HighScore 3.0.4 (PANalanytical).

3.6. Water and pollutants balances (papers IV and V)

Daily water balances in the irrigable area of Lerma Basin were carried out for the period 2004-2013. Balances were performed for the 55 irrigated plots included in the Lerma Basin along with the irrigable area as a whole. Calculations were automated by the usage of EMR 2.0 (Irrigation Land Environmental Tool –EMR–, from its Spanish abbreviation; Causapé, 2009b).

Soil water balances were based in the following equation:

$$(P + I) - (ET_a + D_{SWB} + EWDL) = \Delta S \qquad \text{[Eq. 6]}$$

Where P is precipitation, I is irrigation, ET_a is the actual evapotranspiration, D_{SWB} is the drainage from the soil water balance, EWDL are the losses by evaporation and wind drift and ΔS is soil storage. The detailed calculations involved in the methodology for soil water balance are presented in Paper IV and they are not reproduced here.

The irrigable area water balance was based in the general equation:

Inputs − Outputs − Storage = Balance error

$$(P + I + IWF) - (ET_a + LG + EWDL) - (\Delta S + \Delta A) = Balance\ Error \qquad \text{[Eq. 7]}$$

Where IWF is the incoming water flows from unirrigated area, LG is the discharge in the Lerma Gully and ΔA is the aquifers storage.

For water balances purposes, since the beginning of the study (October 1st, 2003) until when the gauging station was operational (August, 2005), the flow of the Lerma Gully was estimated from precipitation data and based on a runoff coefficient of 10.1% and the form of the recession curves, which was obtained during the period when the gauging station was available and the first irrigation season had not started (October 2005 to March 2006).

The IWF was composed by the runoff generated on the non-irrigated area, together with the channel filtrations and several breakages of pipes that produced increases in the discharge. For the unirrigated area the runoff coefficient aforementioned was also applied to estimate the incoming water flows. Irrigation channel filtrations were estimated through chemical gauging in several locations and seasons. For the piping breakages, a high resolution hydrograph was obtained and treated to estimate the amount of water provided in the breakage.

The annual water storage in the aquifer was estimated based on the aquifer area (251 ha), the saturated thickness in three representative piezometers located in each

independent groundwater body, and an effective porosity of 5%. Since the piezometers were not installed until March 2008, the storage in the aquifer could only be estimated for the hydrological years 2009-2013.

3.6.1. Irrigation performance indicators (paper IV)

Net hydric needs (HNn), indices evaluating the irrigation efficiency (IE), irrigation drainage fraction (IDF), and water deficit (WD) were utilized to analyze irrigation quality. These indices were calculated for each field and during crop cycles from data provided by water balances in the soil, according to the criteria proposed by Causapé (2009b).

HNn estimates the volume of irrigation water necessary to avoid crop yield losses due to water stress. IE quantifies the percentage of irrigation that has been used to either meet the water requirements of the crops or to be stored as soil water. IDF quantifies the percentage of irrigation lost in drainage and is influenced by the irrigation volume applied and the soil water content when irrigation occurs. Finally, WD evaluates the extent to which the water requirements of crops have not been met.

High quality irrigation is experienced when WD and IDF are close to zero and IE approaches 100%. It must be noted that there are irrigation events not intended to meet water requirements, but to optimize humidity in the soil for specific agronomic activities (e.g., seed irrigation, tillage, testing irrigation equipment). Conversely, it may be necessary to apply excessive irrigation under certain circumstances to promote the leaching of salts with the subsequent generation of drainage and irrigation efficiency loss (Tanji and Kielen, 2002; Corwin et al., 2007). Furthermore, controlled deficit irrigation techniques might be applied to cause an intended water deficit (e.g., Farré and Faci, 2006, 2009).

3.6.2. Salts and Nitrate contamination indexes (paper V)

After applying salt and nitrate concentration to all the components in the water balance, salt and nitrate contamination index were estimated from the mass of salts or nitrate exported from the irrigated area as an indicator of the conditions of the area. They were used to assess the evolution of agro-environmental impact in the Lerma Basin taking into account natural or agronomic factors. It was also used as a comparative indicator of the impact in different irrigated areas.

3.7. Non-parametric statistics in hydrology research

Data from hydrological variables have uncommon characteristics, including positive skewness and seasonal patterns. Water resources data analysis methods should recognize these characteristics and take them into account to obtain adequate

knowledge of the studied system (Helsel and Hirsch, 2002). As a consequence, non-normality of the data was a common fact indicating the necessity of using non-parametric statistical tests, which has been recommended instead of the conversion of data sets to normality (Helsel and Hirsch, 2002). The use of parametric tests on data sets with a strong seasonal component or correlated variables can result in false positives (Bouza-Deaño et al., 2008).

3.7.1. Correlation Matrix (paper I)

The correlation matrix was used to understand the relationships between the different variables studied in the Lerma Gully waters. The non-parametric, rank-based, resistant-to-outliers Kendall's tau (Helsel and Hirsch, 2002) was computed for each pair of variables.

3.7.2. Trends analysis (papers I, IV and V)

Trends detection and estimation was based on the Mann-Kendall test (Mann, 1945, Kendall, 1975) and Sen's slope estimator (Sen, 1968), non-parametric methods widely applied to hydrological and environmental data (e.g., Stålnacke et al., 2003; CHE, 2006; Battle-Aguilar et al., 2007). The Mann-Kendall test has the advantages of not assuming any distribution for the data and having similar utility as the parametric methods (Battle-Aguilar et al., 2007). Different levels of significance were applied and the Microsoft Excel spreadsheet MAKESENS was used for the computation of the tests.

3.7.3. Statistical comparisons (papers II, III)

Statistical comparisons for the different studied variables were performed between ground-, spring and surface water. In particular, one-way ANOVA post hoc and Kruskal-Wallis tests were used. The level of significance was set to 5% and the statistical package Statgraphics (Statpoint Technologies, 2009) was used for the computation of these tests.

3.7.4. Multivariate statistics (paper III)

Principal components analysis and hierarchical cluster analysis were used in order to increase the knowledge of the Lerma Basin ground-, spring and surface waters, quantificate their similarity and infere the controlling water quality processes. Both methods have wide application in hydrology research (e.g., Acero et al., 2013; Lorite-Herrera et al., 2008). The statistical package Statgraphics (Statpoint Technologies, 2009) was used for the computation of these tests.

CHAPTER IV

RELATIONSHIPS AND TRENDS IN HYDROLOGICAL VARIABLES

PAPER I

Merchán, D., Causapé, J., Abrahão, R., 2013. Impact of irrigation implementation on hydrology and water quality in a small agricultural basin in Spain. *Hydrological Sciences Journal* 58(7): 1400-1413.

Impact factor: 1.252 (JCR 2013).
Quartile and category: Q2 (39/79), Water Resources.

D. Merchán took part in the planning of the study, performed the statistical analysis, data interpretation and writing, with assistance from all co-authors.

1400 *Hydrological Sciences Journal – Journal des Sciences Hydrologiques*, 58 (7) 2013
http://dx.doi.org/10.1080/02626667.2013.829576

Impact of irrigation implementation on hydrology and water quality in a small agricultural basin in Spain

D. Merchán[1], J. Causapé[1] and R. Abrahão[2]

[1]*Geological Survey of Spain – IGME, C/ Manuel Lasala no. 44, 9°B, Zaragoza, 50006, Spain*
d.merchan@igme.es

[2]*Federal University of Paraíba – UFPB, Cidade Universitária, João Pessoa, Paraíba, 58051-900, Brazil*

Received 2 August 2012; accepted 10 January 2013; open for discussion until 1 April 2014

Editor Z.W. Kundzewicz

Citation Merchán, D., Causapé, J., and Abrahão, R., 2013. Impact of irrigation implementation on hydrology and water quality in a small agricultural basin in Spain. *Hydrological Sciences Journal*, 58 (7), 1400–1413.

Abstract Irrigation practice has increased considerably recently and will continue to increase to feed a growing population and provide better life standards worldwide. Numerous studies deal with the hydrological impacts of irrigation, but little is known about the temporal evolution of the affected variables. This work assesses the effects on a gully after irrigation was implemented in its hydrological basin (7.38 km^2). Flow, electrical conductivity, nitrate concentration and exported loads of salts and nitrates were recorded in Lerma gully (Zaragoza, Spain) for eight hydrological years (2004–2011), covering the periods before, during and after implementation of irrigation. Non-parametric statistical analysis was applied to understand relationships and trends. The results showed the correlation of irrigation with flow and the load of salts and nitrates exported, although no significant relationship with precipitation was detected. The implementation of irrigation introduced annual trends in flow (3.2 L s^{-1}, +23%), salinity (–0.38 mS cm^{-1}, –9%), and nitrate concentration (5.4 mg L^{-1}, +8%) in the gully. In addition, the annual loads of contaminants exported increased (salts and nitrates, 27.3 Mg km^{-2} year^{-1}, +19%, and 263 kg NO_3^--N km^{-2} year^{-1}, +27%, respectively). The trends presented a strong seasonal pattern, with higher and more significant trends for the irrigation season. The changes observed were different from those of larger irrigation districts or regional basins, due to the differences in land use and irrigation management. It is important to understand these changes in order to achieve an adequate management of the environment and water resources.

Key words irrigation; trend; salinity; nitrate; contaminant loads; land use

Impact de la mise en œuvre de l'irrigation sur l'hydrologie et la qualité de l'eau dans un petit bassin versant agricole en Espagne

Résumé Récemment, l'utilisation de l'irrigation a considérablement augmenté, et elle va continuer à augmenter pour nourrir une population croissante et fournir un meilleur niveau de de vie à travers le monde. De nombreuses études traitent des impacts hydrologiques de l'irrigation, mais on connait peu de choses sur l'évolution temporelle des variables affectées. Ce travail évalue les effets sur une ravine, après que l'irrigation ait été mise en œuvre sur son bassin hydrologique (7,38 km^2). A cette fin, le débit, la conductivité électrique, la concentration en nitrates et les charges exportées de sels et de nitrates ont été enregistrées sur la ravine de Lerma (Saragosse, Espagne) pendant huit années hydrologiques (2004–2011), allant de la période antérieures à la période postérieure à la mise en œuvre de l'irrigation. Nous avons réalisé une analyse statistique non paramétrique pour comprendre les relations et les tendances. Les résultats ont montré une corrélation entre l'irrigation d'une part, et le débit et les charges exportées de sels et de nitrates d'autre part, mais aucune relation significative avec les précipitations n'a été détectée. La mise en œuvre de l'irrigation a provoqué une évolution du débit (3,2 L s^{-1}, +23%), de la salinité (–0,38 mS cm^{-1}, –9%), et de la concentration en nitrates (5,4 mg L^{-1}, +8%) dans la ravine. En outre, la charge annuelle de polluants exportée a augmenté (27,3 Mg km^{-2} an^{-1}, +19%, pour les sels, et 263 kg NO_3-N km^{-2} an^{-1}, +27%, pour les nitrates). Les tendances présentent une forte saisonnalité, et sont plus fortes et significatives pour la saison d'irrigation. Les changements observés sont différents de ceux de districts d'irrigation plus étendus ou de bassins régionaux, cela étant dû aux différences dans l'utilisation des terres et dans la gestion de l'irrigation. Il est important de comprendre ces changements afin de parvenir à une gestion adéquate de l'environnement et des ressources en eau.

Mots clefs irrigation; tendance; salinité; nitrates; charges de contaminants; utilisation des terres

1 INTRODUCTION

There are many advantages to irrigated agriculture, such as increased production, reliable harvests and regional economic security (Duncan *et al.* 2008). As a consequence, a global increase in irrigated areas has been observed, especially in developing countries where, between 1962 and 1998, irrigated area doubled (Food and Agriculture Organization (FAO 2003a). In Spain, the increase is moderate but significant, with 7% more irrigated area between 1990 and 2009 according to the Spanish environment ministry (*Ministerio de Medio Ambiente y Medio Rural y Marino*; MMARM).

However, irrigation imposes sever pressure on the environment, as it accounts for the consumption of 70% of global water resources (FAO 2003b). Water abstraction for irrigation purposes changes hydrological conditions in dam-regulated rivers (Graf 2006), or overexploited aquifers (Custodio 2002). These pressures impact on water resources not only in a quantitative way, but also qualitatively (Kurunc *et al.* 2005).

The impacts are not only found at the irrigation water withdrawal location, as irrigation return flows can cause hydrological changes in the receiving water bodies. For this reason, organizations such as the US Environmental Protection Agency see irrigated agriculture as the main source of water pollution (US EPA 1992), particularly due to the leaching of salts (Duncan *et al.* 2008) and nitrate (Arauzo *et al.* 2011, Sánchez-Pérez *et al.* 2003), among other pollutants (pesticides, phosphates, etc.).

Several studies exist on the hydrological changes caused by irrigated agriculture. However, these studies were carried out either at such a large scale that the influence of irrigation was masked by other factors (water abstraction, industrial uses, etc.; CHE (2006), or in areas where irrigation had already been implemented (e.g. García-Garizábal and Causapé 2010, Qin *et al.* 2011) without considering the dynamics of irrigation implementation.

The impacts of irrigation are major issues in the development of sustainable basin management strategies. Irrigation affects land use and, therefore, causes hydrological changes in the basin. The responses of the basin to these changes need to be understood (Zhang *et al.* 2011). Despite such an interest, to the best of our knowledge, the study area of this work is the first in which alteration induced by the transformation from rainfed to irrigated agriculture has been assessed, and this was achieved through the monitoring of the hydrological basin during the transition. The research team has studied changes in this study area for approximately ten years and several papers have been published (Abrahão *et al.* 2011a, 2011b, 2011c, Peréz *et al.* 2011). A non-parametric approach is used herein to deal with issues not treated in previous research, such as trends in flow, water quality parameters and exported loads of both salts and nitrates, imposed by irrigation.

Within this framework, the aim of this work is to analyse the effects of a newly-implemented irrigated area on the hydrology of a gully, evaluating relationships between variables, and trends in flow, water quality, and contaminant loads. This objective is consistent with the recommendations of local water authorities (CHE 2006) that suggest the need for increasing knowledge of water bodies with quality problems, in order to create management strategies that will allow to control the quantity and quality of water resources at the basin scale.

2 STUDY AREA AND BACKGROUND

The study area is Lerma gully and its hydrological basin (7.38 km^2), which is located on the left bank of the middle Ebro River Valley, in northeast Spain (Fig. 1). The Ebro basin presents a high level of human interference, with reservoir volumes of 7580 hm^3, and more than 680 000 ha dedicated to irrigated agriculture and other domestic and industrial uses (CHE 2009a). The main use of water is for irrigated agriculture, with more than 6000 hm^3 $year^{-1}$ being extracted. All other uses together do not exceed 1000 hm^3 $year^{-1}$. Environmental problems related to irrigated agriculture, such as salinization and nitrate pollution, are openly recognized by the Ebro Basin Authority (e.g. CHE 2006, 2009b). In particular, the Arba River, one of the Ebro's tributaries and receiver of Lerma gully waters, is the river that presented the highest increase in salinity and nitrate concentrations in the Ebro basin during the period 1975–2004 (CHE 2006). In addition, the Arba River is the only surface water body declared as affected by nitrate pollution by the Ebro Basin Authority (MMARM 2011). Consequently, large areas of the Arba basin, including the Lerma basin, were designated as Nitrate Vulnerable Zones in 2008 by the Regional Government (CAA 2009), according to Spanish legislation and following the European Council Directive 91/676/EEC EC (1991) concerning the protection of waters against pollution by nitrates from agricultural sources.

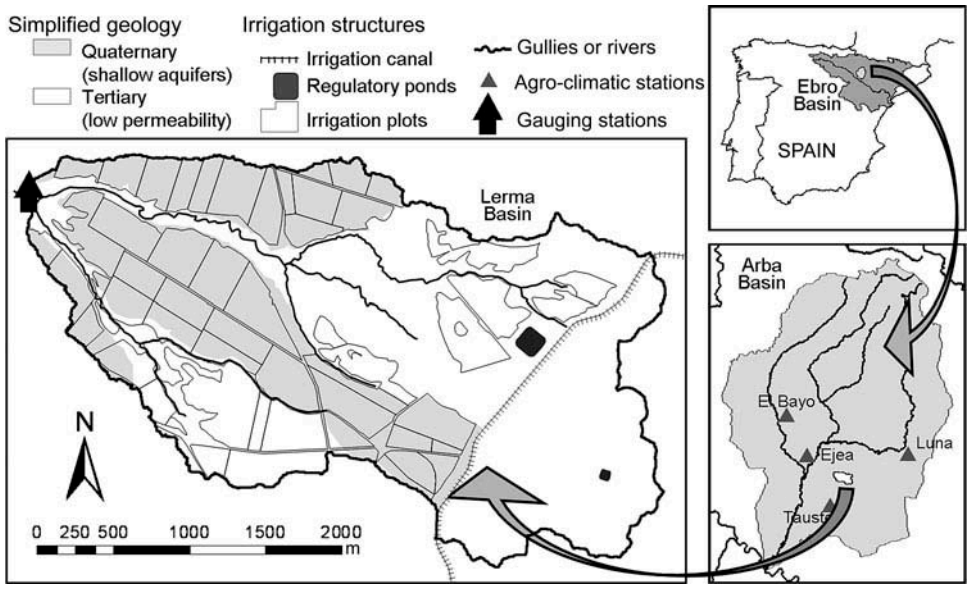

Fig. 1 Location of the Lerma basin within the Arba and Ebro basins (Spain), showing the simplified geology; the irrigation canal, ponds and plots; and the agro-climatic and gauging stations.

The Lerma gully has been monitored for eight hydrological years (2004–2011), covering the transformation of approximately half of its surface (48%) into irrigated land. Previous to our monitoring of Lerma basin, rainfed agriculture was the main land use. In 2003 the implementation of irrigation began with the construction of regulatory pounds and the installation of pipes. The area was not cultivated during this initial construction period (2004–2005). After the main irrigation network was installed, individual farmers equipped their plots for pressurized irrigation, depending on the date of plot assignation or availability of funds. Consequently, the actual irrigated area increased progressively (from 36% in 2006 to 76% in 2007 and 90% in 2008). Since 2009, more than 95% of the projected irrigable area has actually been irrigated.

This region is therefore a valuable location for the evaluation of hydrological changes in terms of environmental issues (flow changes, salts and nitrate pollution) occurring before, during and after implementation of irrigation in the upper sections of hydrological basins (stream order <3, according to Strahler 1952).

2.1 Climate

According to the Spanish national agency of meteorology (AEMET 2010), the study area has a semi-arid Mediterranean climate, with an annual average temperature of 14°C. The coldest months are January and February with monthly mean temperatures lower than 5°C, and the warmer months are July and August, experiencing mean temperatures higher than 23°C, although the maximum temperature can reach 40°C. Historical annual precipitation is 468 mm, with two dry (winter and summer) and two wet (spring and autumn) seasons.

Mean annual rainfall during the study period (1 October 2003–30 September 2011) was 402 ± 113 mm year^{-1} (average ± standard deviation), according to the agro-climatic stations of the integrated irrigation advisory service (*Sociedad Aragonesa de Gestión Agroambiental*; SARGA (2011). A humid hydrological year (2004: 632 mm year^{-1}) and a dry year (2005: 227 mm year^{-1}) were recorded during the implementation period. Under irrigation conditions (2006–2011), mean annual precipitation was closer to average years (ranging between 350 and 444 mm year^{-1}). The average reference evapotranspiration (ET_0), calculated by the Penman-Monteith method (Allen *et al.* 1998), was 1301 ± 61 mm year^{-1}, i.e. three times greater than precipitation, and its coefficient of variation (5%) was less than that of precipitation (28%), which made irrigation essential to achieve productive agriculture.

2.2 Geology

Two geological units are present in the Lerma basin (Fig. 1). Quaternary glacis composed of layers of

gravel with a loamy matrix and of maximum thickness 10 m (ITGE 1988) extend over 34% of its area. Soils with good drainage conditions, low salinity and little risk of erosion are found on the Quaternary materials (Calcixerollics Xerochrepts; Soil Survey Staff 1992), which makes these soils preferable for irrigation (Beltrán 1986). The Quaternary glacis overlay Tertiary materials. The Tertiary lutites and marls are interbedded with thin limestone and gypsum layers (ITGE 1988), and generate slow-drainage soils (Typic Xerofluvent; Soil Survey Staff 1992) of high salinity and steeper slopes, which make these areas less suitable for irrigation (Beltrán 1986).

The Quaternary materials provide perched aquifers over the low-permeability Tertiary materials. These aquifers are recharged by both precipitation and irrigation water, and drained by springs which feed a network of gullies. The network of gullies crosses Lerma basin from east-southeast to west-northwest. The low permeability of the Tertiary materials ensures a suitable control of the water balance (Casalí *et al.* 2008, 2010).

2.3 Agronomy

Agriculture was the main land use in Lerma basin, covering 48% of the total basin area. Major crops were similar to those in the middle Ebro Valley: maize (46%), winter cereal (19%), vegetables (15%), sunflowers (9%) and others. Sprinkler irrigation was the main system used (>90%), although drip irrigation was also present, mainly for vegetables. Good-quality irrigation water (electrical conductivity ~0.35 mS cm^{-1}; nitrate concentration ~2 mg L^{-1}) came from reservoirs located in a neighbouring basin that are fed with water from the Pyrenees Mountains (northeast Spain). According to Abrahão (2010), irrigation applied to main crops of maize, winter cereal and vegetables averaged 740, 160 and 552 mm $year^{-1}$, respectively. The irrigation volume applied to crops varied depending on water availability in the different years, but the total amount of irrigation for the entire basin increased progressively, stabilizing at approx. 2 hm^3 $year^{-1}$. Regarding nitrogen fertilization, the main applications were conducted for maize (380 kg N ha^{-1} $year^{-1}$), winter cereal (164 kg N ha^{-1} $year^{-1}$) and vegetables (mainly tomatoes, 182 kg N ha^{-1} $year^{-1}$). The fertilizers used depended on the crops and included compound fertilizers, urea and liquid fertilizers (Abrahão *et al.* 2011b).

3 METHODOLOGY

3.1 Data collection

Daily precipitation data (P) were obtained from the agro-climatic stations of the integrated irrigation advisory service (SARGA). Data for Lerma basin were obtained by applying the inverse distance squared method (Isaaks and Srivastava 1989) with data from four stations (El Bayo, Ejea, Luna and Tauste) located between 6 and 18 km away (Fig. 1). Daily irrigation data (I) measured by flow meters in each plot were provided by the local irrigation authority.

Monitoring of Lerma gully began in October 2003, with the beginning of the work for its transformation (two years before irrigation started). Manual water sampling was performed at a monthly frequency between October 2003 and September 2005. In October 2005, automatic sampling equipment (ISCO 3700) was installed. The automatic sampler was programmed to collect one sample per day. At the same time, a gauging station was installed at a defined section (rectangular thin-plate weir), and water level was registered every 10 min with an electronic limnigraph (Thalimedes, OTT).

The recorded water height data (h; m) were transformed to flow (Q; m^3 s^{-1}) using gauge rating curves, obtained using the WinFlume software (Whal 2000), as follows:

$$Q = 1.73(h + 0.00347)^{1.624} \text{ for } h \leq 0.5 \quad (1)$$

$$Q = 10.28(h + 0.01125)^{1.725} \text{ for } h > 0.5 \quad (2)$$

The correspondence between water heights and flow was cross-checked by several manual gauging methods, such as the velocity–area method using a wading rod, dilution gauging, and the use of a portable V-notch weir.

Between October 2003 and September 2005 (before installation of the gauging station), flow was estimated using the relationship between flow and precipitation (runoff coefficient of 10.1%) and the form of recession curves during the period when the gauging station was available but the first irrigation season had not commenced (October 2005–March 2006).

Manually or automatically collected samples were taken to the laboratory where the electrical conductivity corrected to 25°C (EC; mS cm^{-1}) and nitrate concentration (NO_3^-; mg L^{-1}) were determined using

an Orion-5 Star conductivity meter and a colorimetry Autoanalizer 3 system, respectively.

Seventeen (17) water samples were selected within the range of variation of EC in Lerma gully, for which the concentration of bicarbonate (HCO_3^-; mg L^{-1}) and dry residue (DR; mg L^{-1}) were determined. From these concentrations, the total dissolved solids (TDS; mg L^{-1}) were calculated by (Custodio and Llamas 1983):

$$\mathrm{TDS} = \mathrm{DR} + {}^1\!/_2\mathrm{HCO}_3^- \tag{3}$$

The EC (mS cm^{-1}) was converted into TDS (mg L^{-1}) for each collected sample through:

$$\begin{aligned} &\mathrm{TDS} = 712.22\mathrm{EC} - 104.83 \\ &R^2 = 0.99 \quad n = 17 \quad p < 0.01 \end{aligned} \tag{4}$$

Once EC was converted to TDS, the use of both TDS and NO_3^- combined with flow allowed the calculation of: (a) the exported load of salts (SL; Mg km^{-2} $year^{-1}$); and (b) the exported load of nitrate (NL; kg NO_3^--N km^{-2} $year^{-1}$).

3.2 Statistical analysis

Data from hydrological variables have common characteristics, including positive skewness and seasonal patterns. Water resources data analysis methods should recognize these and take them into account to obtain adequate knowledge of the studied system (Helsel and Hirsch 2002).

Rain events cause positive skewness in data, which affects data reliability. In Lerma gully, rain events caused daily discharge volumes to be similar to that of a whole month, modifying considerably the average flow (Fig. 2) and loads of pollutants. The use of medians instead of averages as measures of central tendency reduced the influence of short intense rain events, and permitted a better assessment of irrigation impact (Fig. 2), as medians are known to be more resistant to outliers (Helsel and Hirsch 2002). Consequently, monthly data series were created from the studied variables (P, I, Q, EC, NO_3^-, SL and NL), by taking medians from daily values in those months for which more than one sampling occasion was available (October 2005–September 2011).

The obtained monthly data series were tested for normality (Chi-square and Shapiro-Wilks tests; Statgraphics Plus 5.1). The non-normality of the data series indicated the need to use non-parametric statistical tests, which is recommended instead of the conversion of data sets to normality, and use of parametric tests (Helsel and Hirsch 2002). The use of parametric tests on data sets with a strong seasonal component or correlated variables can result in false positives (Bouza-Deaño *et al.* 2008).

3.2.1 Correlation analysis A correlation matrix was obtained through a rank-based procedure from the P, I, Q, EC, NO_3^-, SL and NL monthly data. Kendall's tau (Helsel and Hirsch 2002) was computed for each pair of variables (called x and y); Kendall's tau is a non-parametric, rank-based, resistant-to-outliers test that measures all monotonic correlations in the data set. Tau (τ) is obtained by sorting the pairs with increasing x and computing:

$$\tau = \frac{(A - B)}{n(n-1)/2} \tag{5}$$

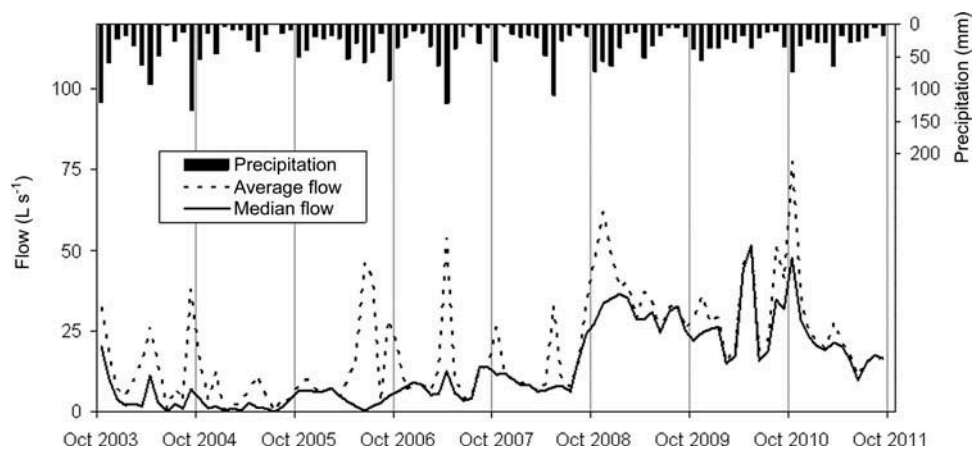

Fig. 2 Monthly precipitation, average flow and median flow in the Lerma basin during hydrological years 2004–2011.

where n is the number of data pairs; A is the number of $y_i < y_j$ for all $i < j$; and B is the number of $y_i > y_j$ for $i < j$; for all $I = 1, \ldots, (n-1)$ and $j = (i+1), \ldots, n$. The correlation matrix allowed the understanding of inter-relationships between the studied variables.

3.2.2 Trend analysis Trend analysis was performed for the variables P, Q, EC, NO_3^-, SL and NL, and detection and estimation of trends was based on the Mann-Kendall test (Mann 1945, Kendall 1975), referred to herein as the M-K test, which is widely applied to trends in hydrological and environmental data (e.g. Stålnacke *et al.* 2003, CHE 2006, Battle *et al.* 2007). The M-K test has the advantages of not assuming any distribution for the data and having similar power to parametric methods (Battle *et al.* 2007). The M-K test determines whether or not a trend is present with an indicator based on the calculation of differences between pairs of successive data (Battle *et al.* 2007):

$$S = \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \operatorname{sgn}(C_j - C_i) \tag{6}$$

where:

$$\operatorname{sgn}(C_j - C_i) = \left\{ \begin{array}{lll} 1 & \text{if} & C_j - C_i > 0 \\ 0 & \text{if} & C_j - C_i = 0 \\ -1 & \text{if} & C_j - C_i < 0 \end{array} \right\} \tag{7}$$

and C_i and C_j are the values at different times i and j; with $j > i$ and n the size of the data set. If there is no trend, S is close to zero; thus the trend will be significant when S differs statistically from zero.

Trend estimation is based on the calculation of Sen's slope estimator (Sen 1968) and is obtained by computing the slopes (b_{ij}) for all pairs of successive data:

$$b_{ij} = \frac{C_j - C_i}{t_j - t_i} \tag{8}$$

where C_i and C_j are values of the variable at time t_i and t_j, respectively. Finally, the value of Sen's slope estimator is median of the slope:

$$b = \operatorname{median}\left(b_{ij}\right) \tag{9}$$

As irrigation and fertilization management are seasonal stresses, the Seasonal Kendall test (S-K test; Helsel and Hirsch 2002) was applied to obtain a better understanding of seasonal patterns. The S-K test is a non-parametric test that computes the M-K test for each season (months in our study), and results are combined to obtain an annual trend. This seasonal approach has been used in several hydrological studies (e.g. Lassaleta *et al.* 2009, Lespinas *et al.* 2010, Morán-Tejeda *et al.* 2011).

In addition, the M-K test was applied to different periods within the data set. Tests were performed for the non-irrigated period (2004–2005) and for the irrigated period (2006–2011). Moreover, trends were computed for the transition period (2006–2008), when the irrigation surface was increasing, and the last three years (2009–2011), in which neither irrigation surface nor irrigation volume changed significantly and the irrigated area could be considered as consolidated. No seasonal approach was applied to the different sections of the data set as the S-K test requires a minimal amount of data not reached by the different sections.

Finally, for all estimated trends, a percentage trend value was calculated by dividing the estimated trend by the average value of the variable throughout the period in which the trend was computed.

4 RESULTS AND DISCUSSION

A data summary for the eight hydrological years (2004–2011) of monitoring at Lerma gully is presented in Table 1. Precipitation was the only water input during the non-irrigated stage (2004–2005), contributing 56–59% of the total water entering the basin when irrigation was consolidated. Intermediate values were observed during the period in which irrigation was being implemented. Irrigation volume increased progressively from 2006 and stabilized in 2008, with an annual value of approximately 2 hm^3, when most of the projected surface was actually irrigated.

Water flow in Lerma gully was highly dependent on precipitation during the non-irrigated period and increased after irrigation implementation (Table 1, Fig. 3). Annual flow ranged from 1.1 L s^{-1} (interquartile range, IQR: 3.9 L s^{-1}) in the non-irrigated year, 2005, to 30.8 L s^{-1} (IQR: 9.5 L s^{-1}) in the irrigated year, 2009. Under non-irrigated conditions, Lerma gully was observed to dry up in those seasons when precipitation was scarce. After implementation of irrigation, water flow in the gully evolved from intermittent to perennial (Fig. 3). Scott *et al.* (2011) have reported how some ephemeral lakes

Table 1 Precipitation (*P*) and irrigation (*I*) volumes in the Lerma basin; median [inter-quartile range] for flow (*Q*), electrical conductivity (EC) and nitrate concentration (NO_3^-) in Lerma gully; and salt (SL) and nitrate (NL) exported load; for the hydrological years 2004–2011.

Year	*P* (hm^3)	*I* (hm^3)	*Q* ($L\ s^{-1}$)	EC ($mS\ cm^{-1}$)	NO_3^- ($mg\ L^{-1}$)	SL ($Mg\ km^{-2}$)	NL ($kg\ NO_3^-\text{-}N\ km^{-2}$)
2004	4.65	0.00	2.9 [13.9]	5.2 [2.0]	42 [17]	235	561
2005	1.74	0.00	1.1 [3.9]	6.0 [0.7]	78 [25]	98	403
2006	3.39	0.62	4.3 [4.7]	3.7 [1.1]	23 [15]	154	329
2007	2.94	1.59	7.6 [6.1]	4.2 [1.2]	56 [32]	128	568
2008	2.69	2.00	9.4 [5.7]	4.3 [0.4]	86 [22]	176	1068
2009	2.88	2.01	30.8 [9.5]	4.0 [1.6]	87 [12]	404	2707
2010	2.57	2.03	26.5 [17.5]	3.1 [0.4]	71 [20]	259	1936
2011	2.70	2.07	19.6 [8.0]	3.0 [0.4]	85 [15]	198	1763

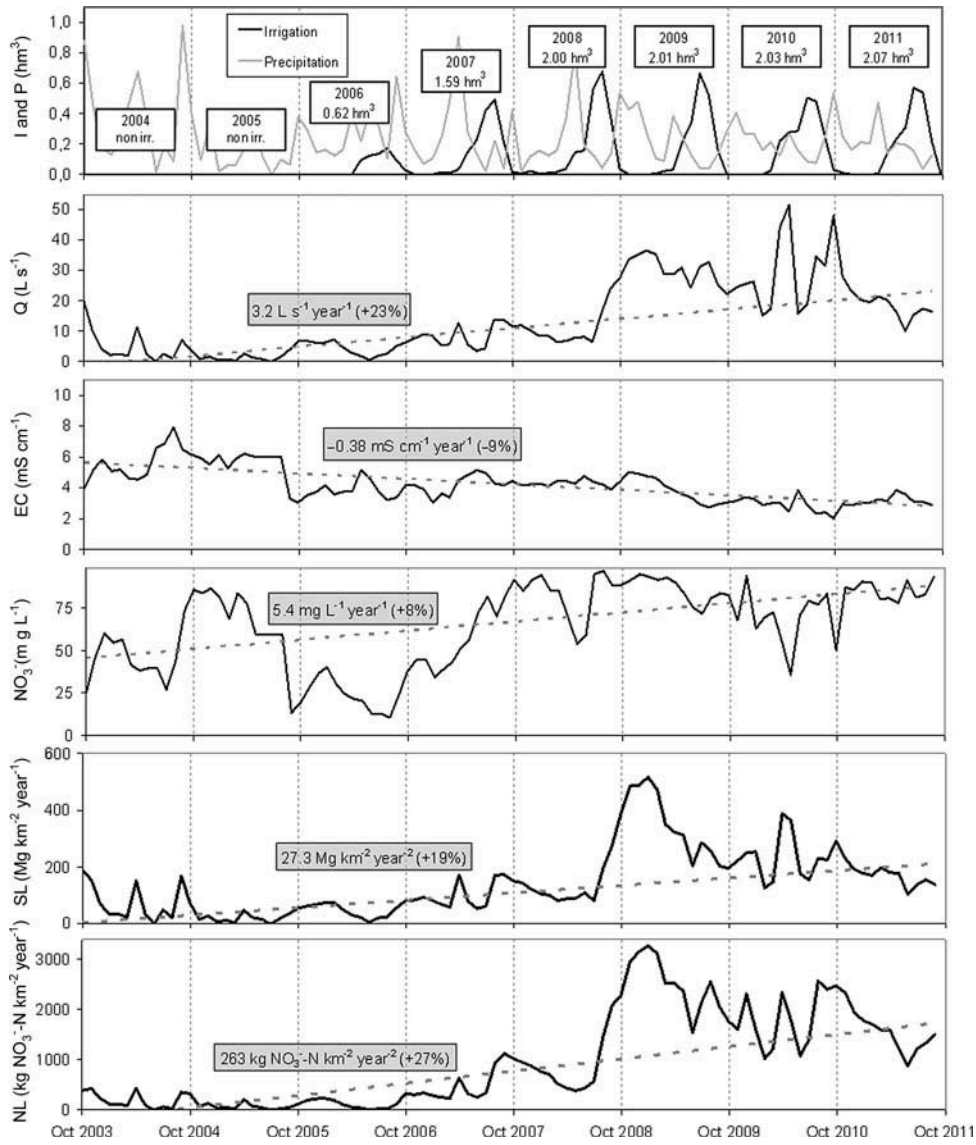

Fig. 3 Monthly precipitation (*P*) and irrigation volume (*I*), flow (*Q*), electrical conductivity (EC), nitrate concentration (NO_3^-), salt load (SL) and nitrate load (NL) at Lerma gully during the hydrological years 2004–2011. Trends (Sen's slope) are shown as broken grey lines.

became perennial as a result of irrigation return flows in the higher reaches of the Aral Sea basin.

Electrical conductivity varied widely, from 6.0 mS cm^{-1} (IQR: 0.7 mS cm^{-1}) in the dry non-irrigated year of 2005 to 3.0 mS cm^{-1} (IQR: 0.4 mS cm^{-1}) in 2011, after six years of irrigation. Intermediate values were observed during the transition to irrigation. Electrical conductivity values during the non-irrigation period are indicative of the high natural salinity of Lerma basin (Beltrán 1986), while lower values at the end of the study period are due to dilution with less-saline irrigation water, and to the flushing of accumulated salts from the surface and upper soil horizons (McNeil and Cox 2007) by irrigation return flows (flow increased while electrical conductivity decreased, Table 1 and Fig. 3).

Nitrate concentrations varied from 23 mg L^{-1} (IQR: 15 mg L^{-1}) during the first irrigated year (2006) to 87 mg L^{-1} (IQR: 12 mg L^{-1}) in the fourth year after irrigation began (2009). Despite no fertilizer applications during 2004 and 2005, nitrate concentrations were 42 mg L^{-1} (IQR: 17 mg L^{-1}) and 78 mg L^{-1} (IQR: 25 mg L^{-1}), respectively. This nitrate concentration is probably a response to fertilizers applied prior to the irrigation implementation, when the basin land use was rainfed agriculture (Irrigation Authority, personal communication), as nitrate leaching in any given year is often dependent on conditions in previous years (Burt *et al.* 2010).

The behaviour of the exported loads of contaminants (both salts and nitrate) was conditioned by the variations observed in flow, although minor differences were attributed to the different processes affecting these solutes. As suggested for flow, exported loads of salts and nitrate were highly dependent on climatic conditions during the non-irrigated period, and increased during the irrigation period. Kyllmar *et al*. (2006) reported that natural factors, such as soil characteristics, hydrogeology and climate, seem to determine the main level of nutrient loads in non-irrigated basins, whereas agricultural management influences the variation in loads around this main level. However, in Lerma basin, irrigation implementation has modified both the main level and the pattern of variation associated with agricultural management (Fig. 3).

4.1 Correlation of variables

The application of the Kendall correlation revealed that precipitation did not present significant correlation with the remaining variables (Table 2).

Table 2 Kendall correlation coefficient between monthly values of precipitation (*P*), irrigation (*I*), flow (*Q*), electrical conductivity (EC), nitrate concentration (NO_3^-), salt load (SL) and nitrate load (NL) in the study period. Medians were used to obtain the correlation coefficient, except in the case of *P* and *I*, for which accumulated monthly values were used. Only significant correlations are presented ($p < 0.05$).

	P	*I*	*Q*	EC	NO_3^-	SL	NL
P	1.00	-	-	-	-	-	-
I	-	1.00	0.26	−0.29	-	0.25	0.28
Q	-	-	1.00	−0.48	-	0.84	0.86
EC	-	-	-	1.00	-	−0.36	−0.41
NO_3^-	-	-	-	-	1.00	0.36	0.46
SL	-	-	-	-	-	1.00	0.85
NL	-	-	-	-	-	-	1.00

Irrigation volume was significantly correlated ($p < 0.05$) with all variables except nitrate concentration, showing its influence on the gully's hydrology. The non-correlation of nitrate concentration can be explained by the complexity of the nitrate dynamics, with many influences apart from those of irrigation, such as previous soil conditions and fertilizer management (Burt *et al.* 2010). In fact, no correlation was detected between nitrate concentration and flow in Lerma gully. Irrigation was negatively correlated with EC (–0.29) and positively correlated with *Q*, SL and NL (correlations between 0.25 and 0.28).

A negative correlation coefficient was found between *Q* and EC (–0.48), as a result of the dilution effect (addition of irrigation water). Correlations between *Q* and both SL and NL were the highest (0.84 and 0.86, respectively), showing the important influence of flow on exported loads of contaminants. Antonopoulos *et al.* (2001) also reported a high relationship between discharge and loads, and a low or no relationship between discharge and concentrations. No correlation was found between EC and NO_3^-, indicating that different processes affect each kind of pollution. In fact, EC *vs* SL and NO_3^- *vs* NL presented correlation values of –0.36 and 0.46, respectively. This means that months with higher salt loads were associated with lower salinity in the gully, and months with a higher nitrate load presented higher nitrate concentrations.

Flow presented a greater influence on the exported load of pollutants than water quality, as the correlation coefficients between flow and loads were higher than those between loads and water quality parameters. Similar conclusions on the major importance of flow in exported loads were obtained by

Barros *et al*. (2012), following different approaches in irrigated areas with similar climatic and soil conditions.

4.2 Trend analysis

4.2.1 Seasonal trends Seasonal patterns were observed in the trends of the studied variables (Fig. 4). The S-K test detected significant trends (at least $p < 0.1$) for all months in Q, for nine months in EC (mainly in spring and summer), and for three months (summer) in NO_3^- (Fig. 4). Monthly trends were positive for flow and ranged from 2.2 to 4.6 L s^{-1} $year^{-1}$, with the highest trend for the most irrigated month (August). These trends were equivalent to a relative annual increase in flow from 19 to 31%. However, monthly trends in EC were found to be negative (Fig. 4). Trends for EC ranged from –0.26 to –0.66 mS cm^{-1} $year^{-1}$ (–6 to –16%). Higher and more significant trends were detected for the spring/summer period, i.e. the more irrigated months. Trends detected in nitrate concentration ranged from 4.2 to 6.2 mg L^{-1} $year^{-1}$ (6% to 10%), and were found in June, August and September.

The increasing trends in Q and decreasing trends in EC are responses to water addition as irrigation, as trends in precipitation were not significant during the study period, neither in monthly nor annual values ($p > 0.1$ for all cases). Those months with higher irrigation presented stronger trends. In addition, trends were also detected in months with no irrigation, which can be explained by the effect that shallow aquifers have on the hydrology of the basin (retardation and attenuation of hydrological response). Similar results of seasonal trend patterns were reported for the Arba River and several points of the Ebro basin (Spain) between 1976 and 2004 for flow and dissolved solids (CHE 2006). Those results were linked to irrigated agriculture over large areas of the Ebro basin.

Trends detected in NO_3^- responded to the addition of nitrogen fertilizers coupled with irrigation activity. In the case of NO_3^-, significant trends are only detected for some of the months of the irrigation season, with the highest trend, in June, probably influenced by side-dressing fertilization of maize (Causapé *et al.* 2004), that being the main crop present in the basin. Out of the irrigation season, no monthly trends were detected.

Trends were also detected in the exported load of contaminants. In nine months there was a significant increase in SL, ranging from 21.5 to 36.0 Mg km^{-2} $year^{-2}$ (16% to 34%), while 11 months presented

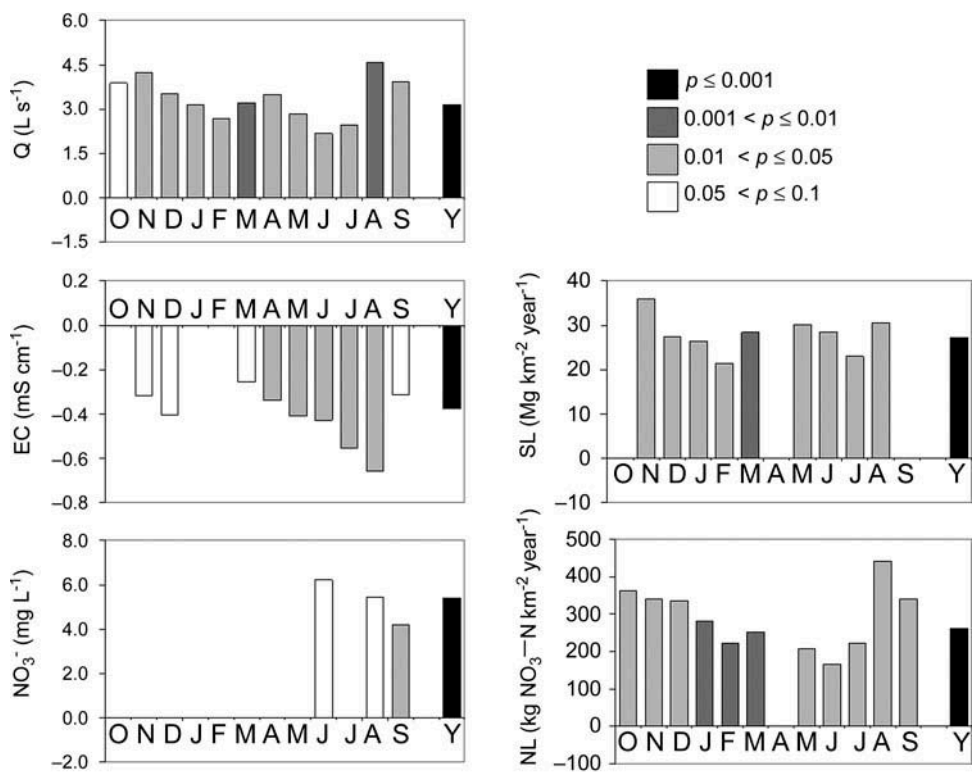

Fig. 4 Monthly (O–S) and annual (Y) trends detected with the S-K test for flow (Q), electrical conductivity (EC), nitrate concentration (NO_3^-), salt load (SL) and nitrate load (NL) at Lerma gully during the hydrological years 2004–2011.

a significant trend in NL, ranging from 165 to 442 kg NO_3^--N km^{-2} year^{-2} (25% to 40%). Trend patterns for SL and NL were mainly conditioned by trends in flow (positive trends for most of the months) with slight differences depending on the particular behaviour of each solute. It is interesting to note that, although trends in nitrate concentration were only detected for three months, trends in nitrate loads were detected in 11 months. As mentioned in Section 4.1, nitrate loads were influenced more by water flow than by nitrate concentration, and, therefore, the trends detected in water flow for all months are consistent with the occurrence of trends in NL in almost all months. This fact is important, as management decisions are usually taken considering only concentrations, as indicated by the EC Nitrate Directive (91/676/EEC). Several studies agree that loads, instead of concentration, must be considered in regulations if an adequate assessment of the agricultural impacts regarding nitrogen is to be performed (e.g. Causapé *et al.* 2004, Arauzo *et al.* 2011). In addition, shallow aquifers play an important role in the seasonal impact of irrigation in the study area. The attenuation and retardation of the hydrological response prevents the pollutant loads from reaching receiving body waters in the season when vulnerability is maximum (summer low waters), and loads are distributed throughout the year.

4.2.2 Trends in different periods The trend results under different conditions (non-irrigated, 2004–2005, transformation to irrigation, 2006–2008; and consolidation of irrigation, 2009–2011) are presented in Table 3. For non-irrigated conditions, decreasing trends were detected for *Q*, SL and NL. No trends were detected in the water quality parameters. Trends in the non-irrigated period are related to the decrease in precipitation between 2004 (634 mm) and 2005 (237 mm), as trends were detected in parameters influenced by this variable, i.e. flow, salts load and nitrogen load.

The trend in flow during the irrigated period was 3.8 L s^{-1} year^{-1}, but important differences were observed between the transformation and the consolidation periods, 2.1 and –5.8 L s^{-1} year^{-1}, respectively. The sudden increase in flow observed between 2008 and 2009 (Fig. 3) is responsible for this unusual trend pattern.

A different behaviour was observed between EC and NO_3^- during the irrigation period, when trends were assessed for the different stages of irrigation implementation. Both EC and NO_3^- increased during the transition period; however, EC decreased during the consolidation period while NO_3^- remained stable (Table 3). The EC pattern can be explained by means of both a dilution effect and soil salt leaching caused by irrigation water entering the system. For the first years, EC increased as soluble salts stored in soils and geological materials were leached. After the successive washing out of these salts, EC is now decreasing and is expected to decrease until a new equilibrium in salinization processes is reached. According to Thayalakumaran *et al.* (2007), the time that elapses until new equilibrium states are reached in salt balances varies from less than a year (root zone) to

Table 3 Annual trends detected by the Mann-Kendall test ($p < 0.01$) and quantified by Sen's slope for flow (*Q*), electrical conductivity (EC), nitrate concentration (NO_3^-), salt load (SL) and nitrate load (NL) in Lerma gully during the non-irrigated period (2004–2005) and the irrigated period (2006–2011). The irrigated period is subdivided into the transition (2006–2008) and consolidation (2009–2011) periods.

Variables	Non-irrigated (2004–2005)	Irrigated (2006–2011)	
		Transition (2006–2008)	Consolidation (2009–2011)
Q (L s^{-1} year^{-1})	−1.8	-	3.8
		2.1	−5.8
EC (mS cm^{-1} year^{-1})	-		−0.21
		0.26	−0.44
NO_3^- (mg L^{-1} year^{-1})	-		9.4
		28.1	-
SL (Mg km^{-2} year^{-2})	−28.6		29.3
		29.6	−84.7
NL (kg NO_3^--N km^{-2} year^{-2})	−95		323
		248	−512

thousands of years (regional basin), and will depend on climate. After reviewing several modelling studies, Thayalakumaran *et al.* (2007) suggest that the time required for a small arid basin to reach a new equilibrium in its salt balance is between a hundred and a thousand years.

Nitrate concentration patterns can be explained by the increased use of fertilizers while the irrigation area and volume were increasing, as no fertilizer was applied during 2004–2005. Previous to our monitoring of Lerma gully, the use of fertilizers in rainfed agriculture was a common practice, but was interrupted for a couple of years when work for transformation to irrigation began. The previous fertilization and climatic conditions explain the high nitrate values obtained during the non-irrigated period, which are comparable to those of the irrigated period, especially in the dry year 2005 (precipitation: 237 mm, NO_3^-: 78 mg L^{-1}). High nitrate concentrations have also been reported for dry years by Reynolds and Edwards (1995) and Burt *et al*. (2010) for upland streams and long-term nitrate concentration time series, respectively. By 2006, most of the nitrate stored in the soils and aquifer during rainfed conditions should have been released. At this moment, which coincides with the beginning of irrigation, minimal values in nitrate concentration were recorded. The progressive increase in fertilizer application coupled with irrigation increased the nitrate concentration in the gully. After expansion of irrigation, the amounts of water and fertilizer applied became stable; the hydrological system appears to have reached a new equilibrium regarding nitrate concentration, although it presents a degree of variation as a consequence of the seasonality in irrigation, fertilization and climate. Thus, nitrogen dynamics seem to have a delay in response to input changes at the upper basin scale (river orders <3). This is probably due to water-transit times in soils and groundwater. This delay is, as expected, lower than what was observed at regional basin scales (river orders >7), where delays can reach more than 10 years (Stålnacke *et al.* 2003).

The aforementioned processes affecting flow, salinity and nitrate concentration have consequences for the exported loads of contaminants. Both SL and NL increased during transition and then decreased during consolidation (as a consequence of decrease in flow). However, SL decrease during consolidation was relatively higher than that of NL (Table 3). While SL decreased as a result of both lower flow and EC, NL was only affected by the lower flow, as NO_3^- remained stable during the consolidation period.

4.2.3 Trends for the entire study period The seasonal Kendall (S-K) test provides an annual trend value taking into account all seasons (Fig. 4). As seen in Fig. 4, the overall trend was very significant for all the variables ($p < 0.001$), even in cases where few seasonal trends were detected as significant. This fact can be explained by the particular case of NO_3^-: although seasonal tests did not detect significant trends for most months (Fig. 4), all the apparent trends were in the same direction, i.e. increasing nitrate concentration with time. These monthly statistics were aggregated when the annual trends were computed (Helsel and Hirsch 2002), and thus the annual trends were significant.

Over the entire study period, the S-K test detected significant trends in Q (3.2 L s^{-1} $year^{-1}$, +23% of annual increase), EC (–0.38 mS cm^{-1} $year^{-1}$, –9%), and NO_3^- (5.4 mg L^{-1} $year^{-1}$, +8%). In addition, positive trends were detected in SL (27.3 Mg km^{-2} $year^{-2}$, +19%) and NL (263 kg NO_3^--N km^{-2} $year^{-2}$, +27%). No trend in precipitation was detected, as occurred in the seasonal test (monthly trends), pointing to irrigation as the factor controlling changes in the gully's hydrology.

The scale of Lerma basin conditioned the prevailing hydrological processes, which were different from those studied in other basins. Thus flow and salinity trends were different from those detected by CHE (2006) at most of the Ebro basin gauging stations for the hydrological years 1976–2004. A decrease in Ebro River flow and an increase in salinity were detected in the aforementioned study, especially in the lower part of the basin. Trends at the Ebro basin scale were explained by the implementation of irrigation in large areas of the basin, including large areas with saline soils. While in Lerma basin the only effect assessed was the incorporation of irrigation return flows, for the whole Ebro basin the effect of abstraction to provide water for irrigation and other uses resulted in less water reaching the rivers, thus decreasing flows and increasing salinity. Decreasing trends have also been reported for flow in other large-scale basins where the irrigated surface had significantly increased (e.g. Great Ruaha River, Tanzania; Kashaigili 2008).

The Arba River presented interesting differences to Lerma gully regarding the trends detected in Q and EC. Contrary to the situation in the Ebro basin, in both the Arba and Lerma basins the water used for irrigation originated from neighbouring basins. However, trends in flow were positive for Lerma basin and negative for Arba basin. In addition, trends in salinity were negative in Lerma basin and positive

in Arba basin (CHE 2006). These differences can be explained because the trends detected for the Arba River are a response to an increase in water-use efficiency as a consequence of modernization of irrigation systems and re-use of irrigation return flows (Causapé 2009a, 2009b). In other areas, trends in river water salinity have been related to the proportion of the basin cleared for rainfed agriculture. The greater the area cleared, the higher the trend observed in water salinity, with no trends detected in those river basins without transformation to agriculture (Peck and Hatton 2003). Thus, both rainfed and irrigated agriculture transformation cause increasing trends in streamwater salinity.

Regarding nitrate concentration, Lassaleta *et al.* (2009) also reported significant trends for the period 1981–2005 in four out of 10 sub-basins in the Ebro basin that have experienced change from rainfed to irrigated land over an average of 2.4% of their basin areas, which are minor changes relative to what occurred in Lerma basin (48%). Nitrate concentration trends quantified for the Ebro basin (CHE 2006) were positive (0.91 mg L^{-1} $year^{-1}$ in the Arba River and 0.09–0.21 mg L^{-1} $year^{-1}$ at Ebro River gauging stations), but much lower than those in Lerma gully (5.6 mg L^{-1} $year^{-1}$). These results agree with those of Howden and Burt (2008), who found that detected trends tended to decrease from the headwaters to main rivers in two basins with areas of 208 and 414 km^2 in the south of the UK.

Observed differences between basins are complex to account for, as many influencing factors exist, even if we assume that irrigation has a major role. The main factors are the proportion of irrigated surface (Ebro basin, 9.2%; Arba basin, 25.1%; and Lerma basin, 48%), the rate of land-use change, and the management of irrigation water. Estimated trends were higher in the Lerma basin, as, unlike the Arba or Ebro basins, a high proportion of its surface (48%) was subject to land-use change in a short period of time (2006–2008), which could have a large impact on nitrate concentrations in the short term (Burt 2001).

Trends for loads of pollutants exported were positive and mainly depended on flow conditions, with minor differences as a consequence of the decreasing trend in salinity and the increasing trend in nitrate concentration. According to CHE (2009b), trends in SL and NL in most Ebro basin gauging stations were non-significant or negative. In most cases, as in the Lerma basin, trends in exported loads were conditioned by trends in water flow.

Thus, the impacts of the transformation to irrigation on the hydrology of receiving water bodies will depend on the characteristics of the irrigation project (water withdrawn from the same or a neighbouring basin), climate, hydrological properties of the basin (soils properties, presence of groundwater systems) and agricultural management (rate of fertilizer applications, recent or consolidated irrigation areas). Other uses apart from irrigation add complexity to the assessment of these impacts.

5 CONCLUSIONS

The hydrological dynamics of the Lerma basin have been altered by the incorporation of irrigation return flows. Although rain events imposed great variability on the hydrological response, the effect of irrigation could be isolated to a reasonable degree by the use of non-parametric statistics. No significant relationships were found between precipitation and other hydrological variables of interest. However, significant relationships were found between irrigation volumes and flow and exported loads of salt and nitrate, highlighting irrigation as a controlling factor of the observed changes. Implementation of irrigation imposed significant trends on hydrological variables: (a) increase in flow at Lerma gully, detected both monthly and annually; (b) decrease in salinity and increase of nitrate concentration, mainly in summer months; and (c) increase in exported loads of salts and nitrate, as a consequence of the increase in flow. The detected trends in Q and EC were rather different to those reported in the literature for other irrigation basins, where other processes or land uses interacted with the effects of irrigation. The NO_3^- trend was consistent with that detected at higher scales but with decreasing values downstream, as the influence of other land uses gained relative importance for water quality. Changes in flow mainly controlled the exported mass of pollutants. It is important to continue collecting data in the study area in order to assess the medium- to long-term implications of irrigation implementation.

The results of this study have shown the hydrological changes imposed on a stream as a consequence of the implementation of irrigation in its hydrological basin. The data set generated can also be used for testing hydrological models that simulate the impacts of land-use changes, such as implementation of irrigation. These impacts depend on the characteristics of the irrigation project, the hydrology of

the basin and the irrigation and fertilization management, among other factors, which should be taken into account in order to achieve the adequate management of water resources.

Acknowledgements Thanks are extended to the Irrigation Authority XI of Bardenas Irrigation Scheme, for facilitating data and providing help in several field-related issues.

Funding This work was performed within the framework of project CGL2009-13410-C02-01 and benefited from grant BES2010-034124, both from the Spanish Ministry of Science and Innovation.

REFERENCES

Abrahão, R., 2010. *Impactos ambientales del riego: La transformación de la cuenca de Lerma (Zaragoza, España)*. Thesis (PhD), Universidad de Zaragoza, Spain.

Abrahão, R., *et al*., 2011a. Implementing irrigation: water balances and irrigation quality in the Lerma basin (Spain). *Agricultural Water Management*, 102, 97–104.

Abrahão, R., *et al*., 2011b. Implementing irrigation: salt and nitrate exported from the Lerma basin (Spain). *Agricultural Water Management*, 102, 105–112.

Abrahão, R., *et al*., 2011c. Influence of irrigation on the occurrence of organic and inorganic pollutants in soil, water and sediments of a Spanish agrarian basin (Lerma). *Spanish Journal of Agricultural Research*, 9 (1), 124–134.

AEMET (Agencia Estatal de Meteorología), 2010. Datos climatologicos (in Spanish). Spain: Gobierno de España, Ministerio de Agricultura, Alimentación y Medio Ambiente. Available from: www.aemet.es [Accessed 25 October 2010].

Allen, R.G., *et al*., 1998. Crop evapo-transpiration: guidelines for computing crop water requirements. Rome: United Nations Food and Agriculture Organization, Irrigation and Drainage Paper no. 56.

Antonopoulos, V.Z., Papamichail, D.M., and Mitsiou, K.A., 2001. Statistical and trend analysis of water quality and quantity data for the Strymon River in Greece. *Hydrology and Earth System Sciences*, 5 (4), 679–691.

Arauzo, M., Valladolid, M., and Martínez-Bastida, J.J., 2011. Spatio-temporal dynamics of nitrogen in river–alluvial aquifer systems affected by diffuse pollution from agricultural sources: implications for the implementation of the Nitrates Directive. *Journal of Hydrology*, 402, 155–168.

Barros, R., Isidoro, D., and Aragüés, R., 2012. Three study decades on irrigation performance and salt concentrations and loads in the irrigation return flows of La Violada irrigation district (Spain). *Agriculture, Ecosystems and Environment*, 151, 44–52.

Battle Aguilar, J., *et al*., 2007. Identification of groundwater quality trends in a chalk aquifer threatened by intensive agriculture in Belgium. *Hydrogeology Journal*, 15, 1615–1627.

Beltrán, A., 1986. Estudio de suelos de la zona regable de Bardenas, II. Sectores: VIII, XI, X, XII y XIII. Spain: Instituto Nacional de Reforma y Desarrollo Agrario, Ministerio de Agricultura, Pesca y Alimentación (in Spanish).

Bouza-Deaño, R., Ternero-Rodríguez, M. and Fernández-Espinosa, A.J., 2008. Trend study and assessment of surface water quality in the Ebro River (Spain). *Journal of Hydrology*, 361, 227–239.

Burt, T.P., 2001. Integrated management of sensitive catchment systems. *Catena*, 42, 275–290.

Burt, T.P., *et al*., 2010. Long-term monitoring of river water nitrate: how much data do we need? *Journal of Environmental Monitoring*, 12, 71–79.

CAA (Consejero de Agricultura y Alimentación), 2009. Orden de 11 de diciembre de 2008, del Consejero de Agricultura y Alimentación, por la que se designan y modifican las zonas vulnerables a la contaminación de las aguas por nitratos procedentes de fuentes agrarias en la Comunidad Autónoma de Aragón (in Spanish). Spain: Consejero de Agricultura y Alimentación, Boletín Oficial de Aragón, 1, 2 January 2009.

Casalí, J., *et al*., 2008. Runoff, erosion, and water quality of agricultural watersheds in central Navarre (Spain). *Agricultural Water Management*, 95, 1111–1128.

Casalí, J., *et al*., 2010. Sediment production and water quality of watersheds with contrasting land use in Navarre (Spain). *Agricultural Water Management*, 97, 1683–1694.

Causapé, J., 2009a. Agro-environmental evaluation of irrigation land, I. Water use in Bardenas irrigation district (Spain). *Agricultural Water Management*, 96, 179–187.

Causapé, J., 2009b. Agro-environmental evaluation of irrigation land, II. Pollution induced by Bardenas irrigation district (Spain). *Agricultural Water Management*, 96, 188–194.

Causapé, J., Quílez, D. and Aragüés, R., 2004. Assessment of irrigation and environmental quality at the hydrological basin level-II. Salt and nitrate loads in irrigation return flows. *Agricultural Water Management*, 70, 211–228.

CHE (Confederación Hidrográfica del Ebro), 2006. Control de los retornos de las actividades agrarias de la cuenca del Ebro: evaluación de tendencias en la calidad del agua, control experimental de los retornos y propuesta de red de control (in Spanish). Available from: www.chebro.es [Accessed 25 May 2012].

CHE, 2009a. Situación actual de la cuenca (in Spanish). Available from: www.chebro.es [Accessed 25 May 2012].

CHE, 2009b. Análisis de tendencias de masas exportadas en la Cuenca del Ebro (in Spanish). Available from: www.chebro.es [Accessed 25 May 2012].

Custodio, E., 2002. Aquifer overexploitation: what does it mean? *Hydrogeology Journal*, 10, 254–277.

Custodio, E. and Llamas, M., 1983. *Hidrología subterránea*. Barcelona: Ediciones Omega.

Duncan, R.A., *et al*., 2008. Management of salt mobilisation in the irrigated landscape—a review of selected irrigation regions. *Journal of Hydrology*, 351, 238–252.

EC (European Communities), 1991. Council Directive 91/676/EEC of 12 December 1991 concerning the protection of waters against pollution caused by nitrates from agricultural sources. Official Journal of the European Communities L375, volume 34, 31 December 1991.

FAO (Food and Agriculture Organization), 2003a. Unlocking the water potential of agriculture. Rome: United Nations FAO.

FAO, 2003b. World agriculture towards 2015/2030. A FAO perpective. Rome: United Nations FAO.

García-Garizábal, I. and Causapé, J., 2010. Influence of irrigation water management on the quantity and quality of irrigation return flows. *Journal of Hydrology*, 385, 36–43.

Graf, W.L., 2006. Downstream hydrologic and geomorphic effects of large dams on American rivers. *Geomorphology*, 79, 336–360.

Helsel, D.R. and Hirsch, R.M., 2002. *Statistical methods in water resources*. *Techniques of water resources investigations*, Book 4, Chapter A3. Reston, VA: US Geological Survey.

Howden, N.J.K. and Burt, T.P., 2008. Temporal and spatial analysis of nitrate concentrations from the Frome and Piddle catchments in Dorset (UK) for water years 1978 to 2007: evidence for nitrate breakthrough? *Science of the Total Environment*, 407, 507–526.

Isaaks, E. and Srivastava, R.M., 1989. *An introduction to applied geostatistics*. Nueva York: Oxford University.

ITGE (Instituto Tecnológico Geominero de España), 1988. Mapa Geológico de España, Ejea de los Caballeros (map) no. 284 27-12. Madrid: ITGE.

Kashaigili, J.J., 2008. Impacts of land-use and land-cover changes on flow regimes of the Usangu wetland and the Great Ruaha River, Tanzania. *Physics and Chemistry of the Earth*, 33, 640–647.

Kendall, M.G., 1975. *Rank correlation methods*. London: Griffin.

Kurunc, A., Yurekli, K., and Okman, C., 2005. Effects of Kilickaya Dam on concentration and load values of water quality constituents in Kelkit stream in Turkey. *Journal of Hydrology*, 317, 17–30.

Kyllmar, K., *et al*., 2006. Nutrient discharge from small agricultural catchments in Sweden. Characterisation and trends. *Agriculture, Ecosystems and Environment*, 115, 15–26.

Lassaleta, L., *et al*., 2009. Agriculture-induced increase in nitrate concentration in stream waters of a large Mediterranean catchment over 25 years (1981–2005). *Science of The Total Environment*, 407, 6034–6043.

Lespinas, F., Ludwig, W., and Heussner, S., 2010. Impact of recent climate change on the hydrology of coastal Mediterranean rivers in southern France. *Climatic Change*, 99, 425–456.

Mann, H.B., 1945. Nonparametric tests against trend. *Econometrica*, 13, 245–259.

McNeil, V.H. and Cox, E.M., 2007. Defining the climatic signal in stream salinity trends using the Interdecadal Pacific Oscillation and its rate of change. *Hydrology and Earth System Sciences*, 11, 1295–1307.

MMARM (Ministerio de Medio Ambiente y Medio Rural y Marino), 2010. ESYRCE: Encuesta sobre Superficies y Rendimientos de Cultivos. Informe de los regadíos de España (in Spanish). Madrid: MMARM Secretaría General Técnica, Subsecretaría. Available from: www.marm.es [Accessed 7 December 2011].

MMARM, 2011. Resolución de 24 de marzo de 2011 de la Dirección General del Agua, por la que se determinan las aguas afectadas por la contaminación, o en riesgo de estarlo, por aportación de nitratos de origen agrario en las cuencas hidrográficas intercomunitarias (in Spanish). Available from: www.marm.es [Accessed 7 December 2011].

Morán-Tejeda, E., *et al*., 2011. River regimes and recent hydrological changes in Duero basin (Spain). *Journal of Hydrology*, 404, 241–258.

Peck, A.J. and Hatton, T., 2003. Salinity and the discharge of salts from catchments in Australia. *Journal of Hydrology*, 272, 191–202.

Pérez, A., *et al*., 2011. Simulating the transition of a semi-arid rained catchment towards irrigation agriculture. *Journal of Hydrology*, 409, 663–681.

Qin, D., *et al*., 2011. Assessing impact of irrigation water on groundwater recharge and quality in arid environments using CFCs, tritium and stable isotopes, in the Zhangye Basin, Northwest China. *Journal of Hydrology*, 405, 194–208.

Reynolds, B. and Edwards, A., 1995. Factors influencing dissolved nitrogen concentrations and loadings in upland streams of the UK. *Agricultural Water Management*, 27, 181–202.

Sánchez-Pérez, J.M., *et al*., 2003. The influence of nitrate leaching through unsaturated soil on groundwater pollution in an agricultural area of the Basque country: a case study. *Science of the Total Environment*, 317, 173–187.

SARGA (Sociedad Aragonesa de Gestión Agroambiental), 2011. Datos meteorologicos (Meteorological data, in Spanish). Aragón, Spain: Gobierno de Aragón, Departamento de Agricultura, Ganadería y Medio Ambiente, Sociedad Aragonesa de Gestión Agroambiental. Available from: http://servicios.aragon.es/oresa [Accessed December 2011].

Scott, J., *et al*., 2011. The influence of irrigation water on the hydrology and lake water budgets of two small arid-climate lakes in Khorezm, Uzbekistan. *Journal of Hydrology*, 410, 114–125.

Sen, P.K., 1968. Estimates of the regression coefficient based on Kendall's tau. *Journal of the American Statistics Association*, 63, 1379–1389.

Soil Survey Staff, 1992. *Keys to soil taxonomy*. Blacksburg, VA: Pocahontas Press/US Department of Agriculture, Soil Conservations Service, Soil Management Support Services, SMSS Technical Monograph no. 19.

Strahler, A.N., 1952. Hypsometric (area–altitude) analysis of erosional topography. *Bulletin of the Geological Society of America*, 63, 1117–1142.

Stålnacke, P., *et al*., 2003. Trends in nutrients concentrations in Latvian rivers and the response to the dramatic change in agriculture. *Journal of Hydrology*, 283, 184–205.

Thayalakumaran, T., Bethune, M.G., and McMahon, T.A., 2007. Achieving a salt balance?—Should it be a management objective? *Agricultural Water Management*, 92, 1–12.

US EPA (US Environment Protection Agency), 1992. *Managing nonpoint source pollution*. Washingon, DC: US EPA, Office of Water.

Whal, T., 2000. *Winflume user's manual*. US Department of Agriculture. Available from: www.usbr.gov/wrrl/winflume.

Zhang, Y., *et al*., 2011. Analysis of impacts of climate variability and human activity on streamflow for a river basin in northeast China. *Journal of Hydrology*, 410, 239–247.

CHAPTER V

ISOTOPIC STUDY

PAPER II

Merchán, D., Otero, N., Soler, A., Causapé, J., 2014. Main sources and processes affecting dissolved sulphates and nitrates in a small irrigated basin (Lerma Basin, Zaragoza, Spain): Isotopic characterization. *Agriculture, Ecosystems and Environment* 195: 127-138.

Impact factor: 3.203 (JCR 2013).
Quartile and category: Q1 (1/56), Agriculture, Multidisciplinary; Q2 (38/140), Ecology; Q1 (38/215), Environmental Sciences.

D. Merchán took part in the planning of the study together with the second author, leaded the sampling campaigns and conducted samples preparation, and performed the data interpretation and writing, with assistance from all co-authors.

Agriculture, Ecosystems and Environment 195 (2014) 127–138

Contents lists available at ScienceDirect

Agriculture, Ecosystems and Environment

journal homepage: www.elsevier.com/locate/agee

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

D. Merchán[a,*], N. Otero[b], A. Soler[b], J. Causapé[a]

[a] Geological Survey of Spain – IGME, C/ Manuel Lasala n° 44, 9° B, 50006 Zaragoza, Spain
[b] Grup de Mineralogia Aplicada i Medi Ambient, Departament de Cristal·lografia, Mineralogia i Dipòsits Minerals, Facultat de Geologia, Universitat de Barcelona, C/ Martí i Franquès s/n, 08028 Barcelona, Spain

ARTICLE INFO

Article history:
Received 7 September 2013
Received in revised form 19 May 2014
Accepted 21 May 2014

Keywords:
Environmental impact
Multi-isotopic
Salinization
Synthetic fertilizers
Denitrification

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

* Corresponding author. Tel.: +34 976 555 282; fax: +34 976 553 358.
E-mail address: d.merchan@igme.es (D. Merchán).

http://dx.doi.org/10.1016/j.agee.2014.05.011
0167-8809/

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 $\delta^{34}S$ 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.*

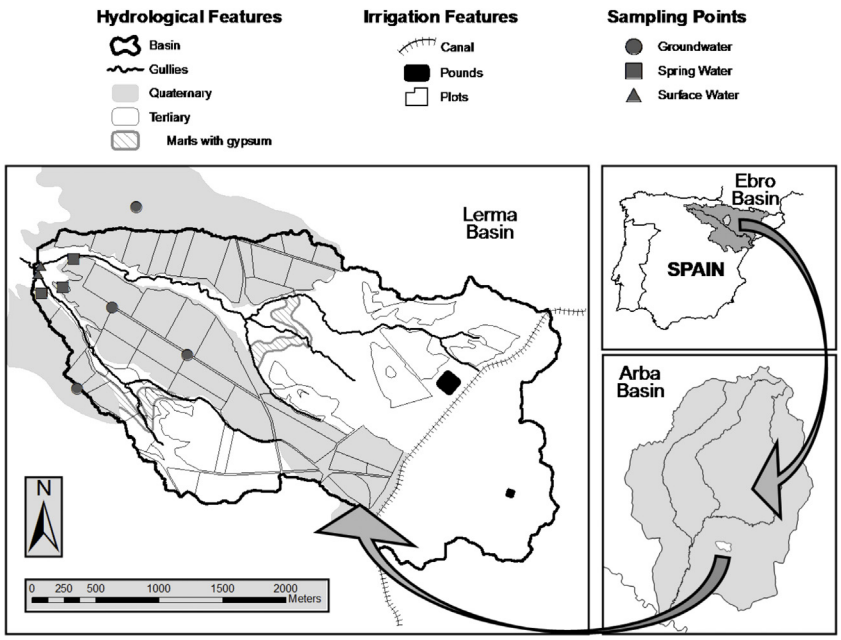

Fig. 1. Location map of Lerma Basin inside Arba and Ebro Basins, hydrological and irrigation features. Ground, spring and surface water monitoring points are depicted.

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^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}, Na^+, K^+, Ca^{2+}, Mg^{2+}, silica, NO_3^-, NO_2^-, NH_4^+, 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 NO_3^-, NO_2^- 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 H_2SO_4 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 ($\delta^{15}N$ and $\delta^{18}O$-[NO_3^-]), the sulphur and oxygen isotopic composition of dissolved sulphate ($\delta^{34}S$ and $\delta^{18}O$-[SO_4^{2-}]) and the deuterium and oxygen isotopic composition of water (δD and $\delta^{18}O$-[H_2O]). For $\delta^{15}N$ and $\delta^{18}O$-[NO_3^-], isotopic analyses were performed according to the anion exchange method proposed by Silva et al. (2000). For $\delta^{34}S$ and $\delta^{18}O$-[SO_4^{2-}], dissolved sulphate was precipitated as $BaSO_4$ by adding $BaCl_2 \cdot H_2O$ after acidification with HCl and ebullition to prevent $BaCO_3$ 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 H_2 gas with a Pt catalyst, and between O-water and CO_2 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 δD and δ^{18}O, AIR (atmospheric N_2) for δ^{15}N, V-CDT (Vienna Canyon Diablo Troillite) for δ^{34}S. The reproducibility (1σ) was calculated using international and internal laboratory standards systematically interspersed in the analytical batches: ±0.3‰ for δ^{15}N-[NO_3^-]; ±0.3‰ for δ^{34}S-[SO_4^{2-}]; ±1.5‰ for δD-[H_2O]; ±0.5‰ for δ^{18}O-[NO_3^-], δ^{18}O-[SO_4^{2-}] and δ^{18}O-[H_2O]. 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^-, SO_4^{2-} and Ca^{2+} in surface water were significantly higher than in groundwater. In the case of NO_3^-, 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 SO_4^{2-} (116%) followed by Cl^- (86%). A negative correlation was found between SO_4^{2-} and NO_3^- (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 SO_4^{2-} and NO_3^- (*e.g.*, Nakano et al., 2008). According to the Piper classification, the majority

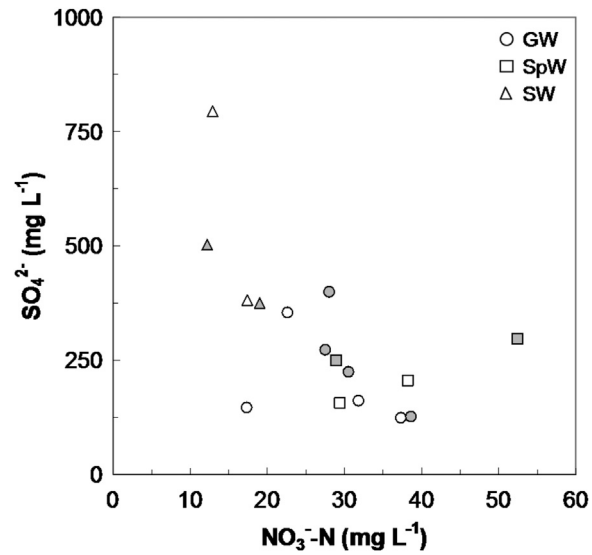

Fig. 2. Bivariate plot of NO_3^--N against SO_4^{2-} concentrations. GW: groundwater; SpW: spring water; SW: surface water. White symbols represent samples collected during the irrigated season whereas filled symbols represent samples collected during the non-irrigated season. No significant relationship was detected between the solutes.

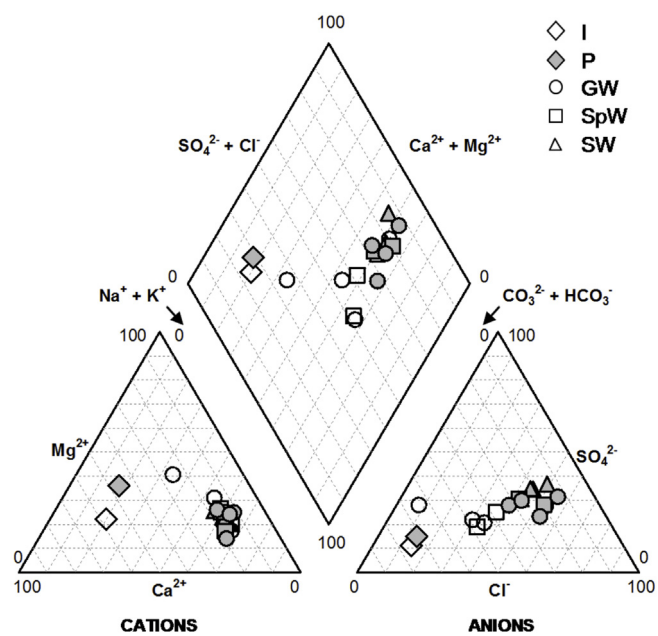

Fig. 3. Piper diagram of irrigation (I), precipitation (P), ground (GW), spring (SpW) and surface (SW) waters collected in Lerma Basin during the irrigated season (white symbols) and the non-irrigated season (filled symbols).

of Lerma Basin waters are Na^+-(Cl^-, SO_4^{2-}) type (Fig. 3). Some samples tended to (Ca^{2+}, Mg^{2+})-HCO_3^- water types, showing the influence of precipitation and irrigation waters, which are (Ca^{2+}, Mg^{2+})-HCO_3^- types.

3.1. The influence of irrigation water on Lerma Basin

δD-[H_2O] ranged between −56.7 and −45.0‰, with a median value of −49.3‰. δ^{18}O-[H_2O] 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 δD-[H_2O] and δ^{18}O-[H_2O]. The local meteoric water line (LMWL, $\delta D = 7.6 \cdot \delta^{18}O + 4.8$; Fig. 4),

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

	Site Units	EC mS cm^{-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)															
GW	P4	1.19	7.6	7.1	211	348	125	126	49	32	233	4.2	2.9	37.3	39.4
	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)															
GW	P4	1.10	7.8	9.4	225	186	127	134	50	22	197	3.1	2.4	38.6	40.3
	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
Significatively 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
Significatively 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 $\delta^{18}O$ 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

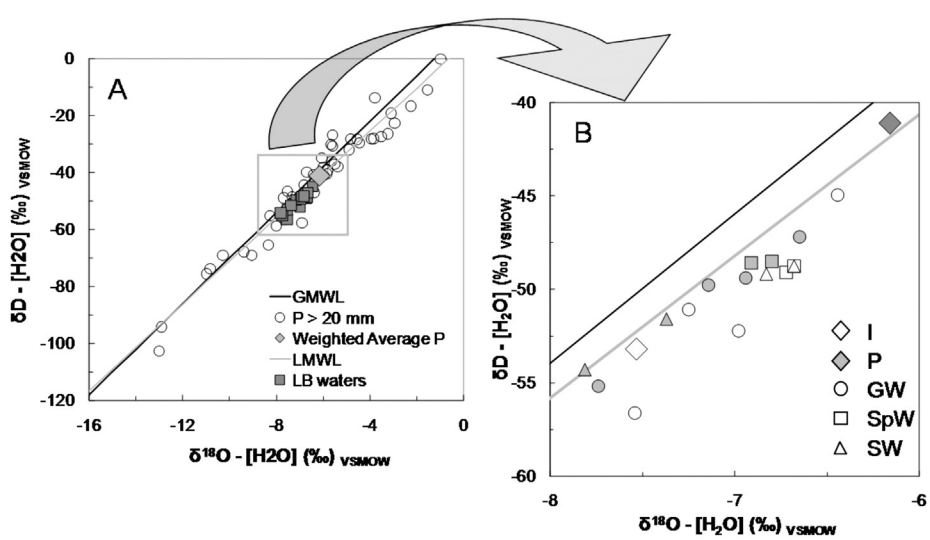

Fig. 4. (A) $\delta^{18}O$ *vs.* δD of the Global Meteoric Water Line (GMWL; Craig, 1961), precipitation events of more than 20 mm in Zaragoza (white circles), weighted average precipitation (grey diamond shapes), the Local Meteoric Water Line of Zaragoza (LMWL, IAEA/WMO, 2006), and samples collected 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.

		H_2O		SO_4^{2-}		NO_3^-	
	Site	δ^2H	$\delta^{18}O$	$\delta^{34}S$	$\delta^{18}O$	$\delta^{15}N$	$\delta^{18}O$
	Units	‰	‰	‰	‰	‰	‰
	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
Significatively 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
Significatively 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 $\delta^{18}O$-[H_2O] (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

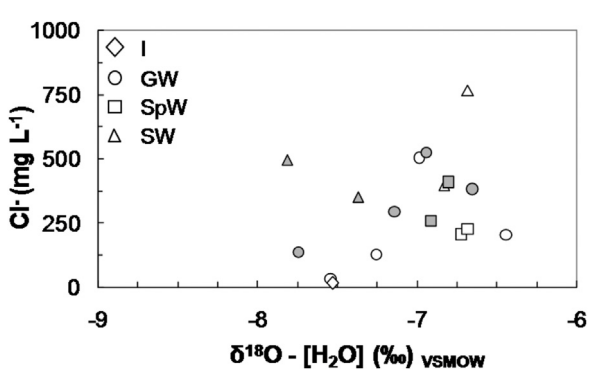

Fig. 5. $\delta^{18}O$-[H_2O] *vs.* chloride concentration in irrigation (I), ground (GW), spring (SpW) and surface (SW) waters during the irrigated (white symbols) and non-irrigated season (filled symbols). No correlation was detected between these two variables.

(<0.2 $\delta^{18}O$ 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 $\delta^{18}O$ in precipitation events (>20 mm) were −41.1‰ and −6.2‰, respectively. In a δD *vs.* $\delta^{18}O$ 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 ($\delta D_P = -41.1$‰ and $\delta^{18}O_P = -6.2$‰), irrigation water ($\delta D_I = -53.2$‰ and $\delta^{18}O_I = -7.5$‰) and an estimation of Lerma Basin waters ($\delta D_{LB} = -49.3$‰ and $\delta^{18}O_{LB} = -6.9$‰, 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 $\delta^{18}O$ 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.

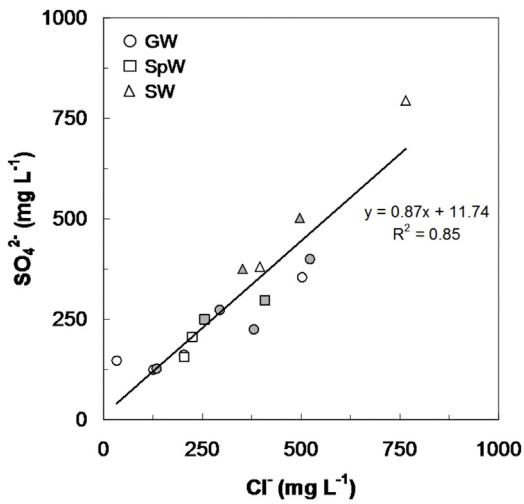

Fig. 6. Bivariate plot of Cl^- *vs.* SO_4^{2-} concentrations in ground (GW), spring (SpW) and surface (SW) waters of the Lerma Basin during the irrigated season (white symbols) and non-irrigated season (filled symbols). Best-fit line and correlation estimates.

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.

$\delta^{34}S$-[SO_4^{2-}] ranged from +2.7 to +8.4‰, with a median value of +6.6‰. $\delta^{18}O$-[SO_4^{2-}] ranged from +7.3 to +13.7‰, with a median value of +9.4‰ (Table 2). Fig. 7 shows $\delta^{34}S$ against $\delta^{18}O$ 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 $\delta^{34}S$-[SO_4^{2-}] *vs.* $\delta^{18}O$-[SO_4^{2-}] plot (Fig. 7). The first cluster was constituted by samples collected from a mix of piezometers and springs, which presented $\delta^{34}S$-[SO_4^{2-}] varying from +5.6 to +8.4‰ and $\delta^{18}O$-[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). $\delta^{34}S$-[SO_4^{2-}] in these samples ranged from +6.6 to +7.2‰, and $\delta^{18}O$-[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 ($\delta^{34}S$-[SO_4^{2-}] from +2.7 to +3.4‰ and $\delta^{18}O$-[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 $\delta^{34}S$ values ranged from +9.2 to +10‰ and the $\delta^{18}O$ 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 $\delta^{34}S$ and $\delta^{18}O$ 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 $\delta^{18}O$-[SO_4^{2-}] *vs.* $\delta^{18}O$-[H_2O] 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 $\delta^{34}S$-[SO_4^{2-}] with increasing SO_4^{2-} concentrations have been related to fertilizers (Hosono et al., 2007). The $\delta^{34}S$ and $\delta^{18}O$ 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

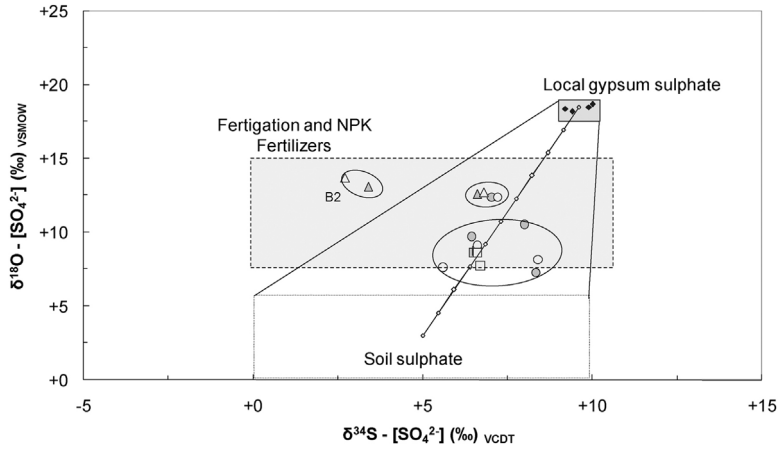

Fig. 7. δ^{34}S *vs.* δ^{18}O of dissolved sulphate in Lerma waters. Boxes with typical sulphate isotopic values ranges are depicted. Typical soil sulphate values (Rock and Mayer, 2009; Kaown et al., 2009) and more commonly used fertilizers in the study zone (Vitòria et al., 2004). Mixing line between 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 were 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 km^2; 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). δ^{15}N-[NO_3^-] ranged from +3.0 to +9.3‰, with a median value of +5.6‰. δ^{18}O-[NO_3^-] ranged from +2.5 to +21.5‰, with a median value of +7.0‰ (Table 2). In general,

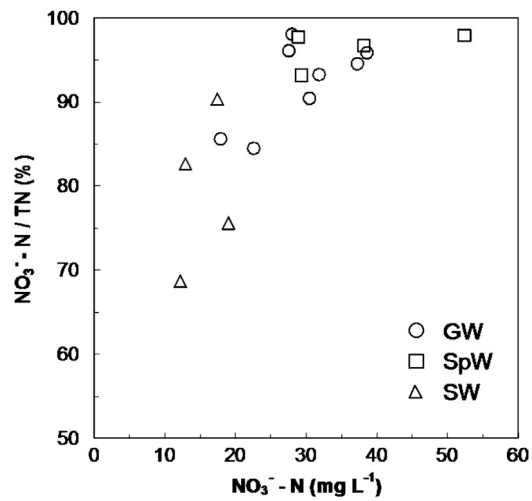

Fig. 8. Proportion of total nitrogen present in the form of nitrate-nitrogen in Lerma Basin waters. GW: groundwater; SpW: spring water; SW: surface water. White symbols: irrigated season. Filled symbols: non-irrigated season.

δ^{15}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 δ^{15}N and nitrate concentration, those samples with higher δ^{15}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 δ^{15}N, it is quite different for δ^{18}O. Synthetic fertilizers present δ^{15}N values between −1.7‰ and +3.9‰ (Vitòria et al., 2004; Fig. 9), as this nitrogen origin is derived from atmospheric N_2 (δ^{15}N = 0‰) through the Haber–Bosch process (Sutton et al., 2011). The δ^{15}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 (δ^{18}O = 23.5‰; Horibe et al., 1973) and presents δ^{18}O-[NO_3^-] between +18.0‰ and +25.1‰ (Vitòria et al., 2004); whereas the ammonia/urea-type fertilizers are oxygen free. Ammonia/urea is nitrified and incorporates atmospheric oxygen

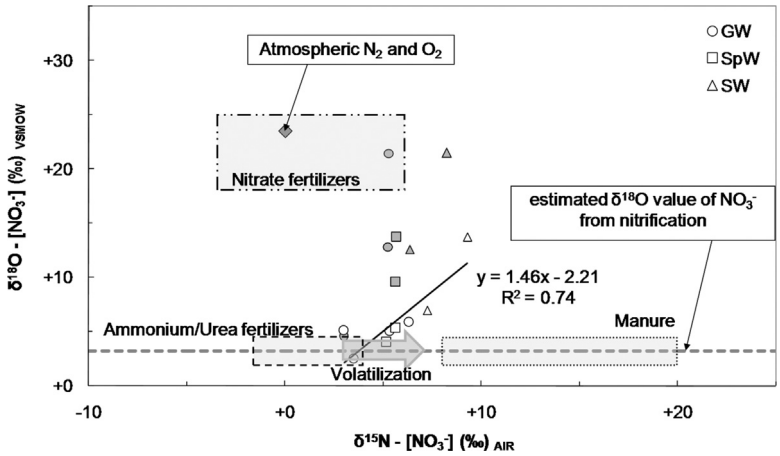

Fig. 9. δ^{15}N *vs.* δ^{18}O of nitrate-nitrogen in Lerma waters. Boxes with typical nitrate isotopic values ranges are depicted from Vitòria et al. (2004) and the estimated δ^{18}O from nitrification is indicated by the dashed grey line. GW: groundwater; SpW: spring water; SW: surface water. White 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 δ^{18}O-[NO_3^-] values will vary depending on the local δ^{18}O of water. Consequently, the values of δ^{18}O-[NO_3^-] derived from the nitrification of urea/ammonia fertilizers can be estimated using the following equation:

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

The δ^{18}O-[H_2O] values of Lerma Basin waters ranged between −7.8 and −6.4‰ (Fig. 4) and a value of +23.5‰ for δ^{18}O-[O_2] (Horibe et al., 1973) was used for the calculation. Thus, at the study site, δ^{18}O-[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 δ^{15}N and δ^{18}O-[NO_3^-] observed in Lerma waters intersect the line of expected δ^{18}O-[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 δ^{15}N and/or δ^{18}O-[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 δ^{15}N *vs.* δ^{18}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 δ^{15}N and δ^{18}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 $\delta^{15}N$ or $\delta^{18}O$-[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 $\delta^{15}N$ (+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 $\delta^{15}N$ variations of *ca.* +3‰, supported by $\delta^{18}O$ 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 $\delta^{15}N$ 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 $\delta^{15}N$ 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 $\delta^{15}N$ *vs.* $\delta^{18}O$ 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 $\delta^{18}O$ end-member for isotopic composition does not exist, but rather a mixing line between two end-members. This fact indicates $\delta^{18}O$ 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, $\delta^{15}N$ 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.

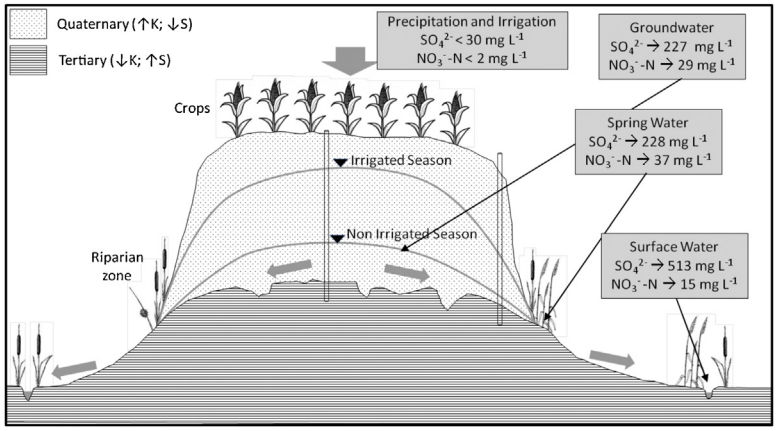

Fig. 10. Cross-section of the conceptual model of Lerma Basin behaviour. Quaternary materials (sandy and loamy matrix gravels) overlay Tertiary materials (marl, clay, mudstone). K: permeability; S: salinity. Grey lines indicate phreatic level in high waters (irrigated season) and low water (non-irrigated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

Acknowledgements

This research was supported by the Spanish Ministry of Science and Innovation projects CGL2009-13410-C02-01 and CGL2011-29975-C04-01, and by project 2014SGR 1456 of the Catalan Government. The authors would like to thank the Centres Científics I Tècnològics of the Universitat de Barcelona. Thanks are also extended to the farmers, for providing information about agriculture management, and to the Water Community, for providing support in different field-related tasks. D. Merchán acknowledges the support of the Spanish Ministry of Economy and Competitiveness through research grant BES2010-034124. We also appreciate the thoughtful comments of two anonymous reviewers, which greatly increased the quality of the manuscript.

References

Abrahão, R., Causapé, J., García-Garizábal, I., Merchán, D., 2011a. Implementing irrigation: water balances and irrigation quality in the Lerma basin (Spain). Agric. Water Manage. 102, 97–104.
Abrahão, R., Causapé, J., García-Garizábal, I., Merchán, D., 2011b. Implementing irrigation: salt and nitrate exported from the Lerma basin (Spain). Agric. Water Manage. 102, 105–112.
Abrahão, R., Causapé, J., Moreno-Mateos, D., Comín, F., 2013. Nitrate and salt water contamination associated with the transition of an agrarian basin into an irrigated area. Water Environ. Res. 85 (2), 105–112.
Arauzo, M., Valladolid, M., Martínez-Bastida, J.J., 2011. Spatio-temporal dynamics of nitrogen in river-alluvial aquifer systems affected by diffuse pollution from agricultural sources: implications for the implementation of the Nitrates Directive. J. Hydrol. 411, 155–168.
Baily, A., Rock, L., Watson, C.J., Fenton, O., 2011. Spatial and temporal variations in groundwater nitrate at an intensive dairy farm in south-east Ireland: insights from stable isotope data. Agric. Ecosyst. Environ. 144, 308–318.
Beltrán, A., 1986. Estudio de suelos de la zona regable de Bardenas. II. Sectores: VIII, XII, X, XII y XIII. Instituto Nacional de Reforma y Desarrollo Agrario, Ministerio de Agricultura, Pesca y Alimentación, Spain.
BOA, 2009. Orden de 11 de diciembre de 2008, del Consejero de Agricultura y Alimentación, por la que se designan y modifican las zonas vulnerables a la contaminación de las aguas por nitratos procedentes de fuentes agrarias en la Comunidad Autónoma de Aragón. Boletín Oficial de Aragón 1, de 02 de Enero de 2009 (in Spanish). www.boa.aragon.es (accessed 25.05.12).
Causapé, J., Quílez, D., Aragüés, R., 2004. Assessment of irrigation and environmental quality at the hydrological basin level I. Irrigation quality. Agric. Water Manage. 70, 195–209.
Cey, E.E., Rudolph, D.L., Aravena, R., Parkin, G., 1999. Role of the riparian zone in controlling the distribution and fate of agricultural nitrogen near a small stream in Southern Ontario. J. Contam. Hydrol. 37, 45–67.
CHE, 2006. Control de los retornos de las actividades agrarias de la cuenca del Ebro: evaluación de tendencias en la calidad del agua, control experimental de los retornos y propuesta de red de control. Confederación Hidrográfica del Ebro, 284 pp. (in Spanish). www.chebro.es (accessed 25.05.12).
Choi, B.-Y., Yun, S.-T., Mayer, B., Kim, K.-H., 2011. Sources and biogeochemical behaviour of nitrate and sulfate in an alluvial aquifer: hydrochemical and stable isotopes approaches. Appl. Geochem. 26, 1249–1260.
Craig, H., 1961. Standards for reporting concentrations of deuterium and oxygen-18 in natural waters. Science 133, 1833–1834.
Craig, L., Bahr, J.M., Roden, E.E., 2010. Localized zones of denitrification in a floodplain aquifer in southern Wisconsin, USA. Hydrogeol. J. 18, 1867–1879.
Dansgaard, W., 1964. Stable isotopes in precipitation. Tellus 16, 436–438.

Duncan, R.A., Bethune, M.G., Thayalakumaran, T., Christen, E.W., McMahon, T.A., 2008. Management of salt mobilisation in the irrigated landscape – a review of selected irrigation regions. J. Hydrol. 351, 238–252.
Elmi, A.A., Madramootoo, C., Egeh, M., Hameo, C., 2004. Water and fertilizer nitrogen management to minimize nitrate pollution from a cropped soil in southwestern Quebec, Canada. Water Air Soil Pollut. 151, 117–134.
Epstein, S., Mayeda, T., 1953. Variation of O^{18} content of waters from natural sources. Geochim. Cosmochim. Acta 4 (5), 213–224.
Fan, A.M., Steinberg, V.E., 1996. Health implications of nitrate and nitrite in drinking water: an update on methemoglobinemia occurrence and reproductive and developmental toxicity. Regul. Toxicol. Pharm. 23 (1), 35–43.
García-Garizabal, I., Causapé, J., Abrahão, R., 2012. Nitrate contamination and its relationship with flood irrigation management. J. Hydrol. 442–443, 15–22.
Han, D., Song, X., Currell, M.J., Cao, G., Zhang, Y., Kang, Y., 2011. A survey of groundwater levels and hydrogeochemistry in irrigated fields in the Karamay Agricultural Development Area, northwest China: implications for soil and groundwater salinity resulting from surface water transfer for irrigation. J. Hydrol. 405, 217–234.
Hansson, K., Wallin, M., Djodjic, F., Lindgren, G., 2008. The FyrisNP model Version 3.1 – a tool for catchment-scale modelling of source apportioned gross and net transport of nitrogen and phosphorus in rivers. Technical description. Dept. of Aquatic Science and Assessment, Swedish University of Agricultural Sciences.
Hill, A.R., 1996. Nitrate removal in stream riparian zones. J. Environ. Qual. 25, 743–755.
Houhou, J., Lartiges, B.S., France-Lanord, C., Guilmette, C., Poix, S., Mustin, C., 2010. Isotopic tracing of clear water sources in an urban sewer: a combined water and dissolved sulfate stable isotope approach. Water Res. 44, 256–266.
Horibe, Y., Shigehara, K., Takakuwa, Y., 1973. Isotope separation factors of carbon dioxide–water systems and isotopic composition of atmospheric oxygen. J. Geophys. Res. 78, 2625–2629.
Hosono, T., Nakano, T., Igeta, A., Tayasu, I., Tanaka, T., Yachi, S., 2007. Impact of fertilizer on a small watershed of Lake Biwa: use of sulfur and strontium isotopes in environmental diagnosis. Sci. Total Environ. 384, 342–354.
Huerta, P., Armenteros, I., Recio, C., Blanco, J.A., 2010. Palaeogroundwater evolution in playa-lake environments: sedimentary facies and stable isotope record (Paleogene, Almazán basin, Spain). Palaeogeogr. Palaeoclimatol. Palaeoecol. 286 (3–4), 135–148.
IAEA/WMO, 2006. Global Network of Isotopes in Precipitation. The GNIP Database, http://www.iaea.org/water
ITGE, 1988. Mapa Geológico de España, Ejea de los Caballeros (map). No. 284 27-12. Instituto Tecnológico Geominero de España, Madrid.
Kaown, D., Koh, D.-C., Mayer, B., Lee, K.-K., 2009. Identification of nitrate and sulfate sources in groundwater using dual stable isotope approaches for an agricultural area with different land use (Chuncheon, mid-eastern Korea). Agric. Ecosyst. Environ. 132, 223–231.
Kehew, A.E., 2001. Applied Chemical Hydrogeology. Prentice Hall, Inc., New Jersey, pp. 368.
Kendall, C., Elliott, E.M., Wankel, S.D., 2007. Tracing anthropogenic inputs of nitrogen to ecosystems. In: Michener, R.H., Lajtha, K. (Eds.), Stable Isotopes in Ecology and Environmental Science. , 2nd ed. Blackwell Publishing, Malden, MA, USA, pp. 375–449 (Chapter 12).
Koh, D.-C., Ko, K.-S., Kim, Y., Lee, S.-G., Chang, H.-W., 2007. Effect of agricultural land use on the chemistry of groundwater from basaltic aquifers, Jeju Island, South Korea. Hydrogeol. J. 15, 727–743.
Krouse, H.R., 1980. Sulphur isotopes in our environment. In: Fritz, P., Fontes, J.C. (Eds.), Handbook of Environmental Isotopes Geochemistry. Elsevier, Amsterdam, pp. 435–471.
Kume, T., Akca, E., Nakano, T., Kapur, S., Watanabe, T., 2010. Seasonal changes of fertilizers impacts on agricultural drainage in a salinized area in Adana, Turkey. Sci. Total Environ. 408, 3319–3326.
Mengel, K., Kirkby, E.A., 1987. Principles of Plant Nutrition, 4th ed. International Potash Institute, Bern, Switzerland.
Merchán, D., Causapé, J., Abrahao, R., 2013. Impact of irrigation implementation on hydrology and water quality in a small agricultural basin in Spain. Hydrol. Sci. J. 58 (7), 1–14.
MMARM, 2011. Resolución de 24 de marzo de 2011 de la Dirección General del Agua, por la que se determinan las aguas afectadas por la contaminación, o en riesgo de estarlo, por aportación de nitratos de origen agrario en las cuencas hidrográficas intercomunitarias. Ministerio de Medio Ambiente, Medio Rural y Marino (in Spanish). www.marm.es (accessed 07.12.11).
Nakano, T., Tayasu, I., Yamada, Y., Hosono, T., Igeta, A., Hyodo, F., Ando, A., Saitoh, Y., Tanaka, T., Wada, E., Yachi, S., 2008. Effect of agriculture on water quality of Lake Biwa tributaries, Japan. Sci. Total Environ. 389, 132–148.
Nielsen, D.L., Brock, M.A., Rees, G.N., Baldwin, D.S., 2003. Effects of increasing salinity on freshwater ecosystems in Australia. Aust. J. Bot. 51, 655–665.
Novotny, V., 1999. Diffuse pollution from agriculture – a worldwide outlook. Water Sci. Technol. 39 (3), 1–13.
OJEC, 1991. Directive 1991/676/CEE concerning the protection of waters against pollution caused by nitrates from agricultural sources. Off. J. Eur. Communities.
OJEC, 2000. Directive 2000/60/EC of the European Parliament and of the council of 23 October 2000 establishing a framework for community action in the field of water policy. Off. J. Eur. Communities.
Otero, N., Vitòria, L., Soler, A., Canals, A., 2005. Fertiliser characterization: major, trace and rare earth elements. Appl. Geochem. 20, 1473–1488.
Otero, N., Torrentó, C., Soler, A., Menció, A., Mas-Pla, J., 2009. Monitoring groundwater nitrate attenuation in a regional system coupling hydrogeology with multi-isotopic methods: the case of Plana de Vic (Osona, Spain). Agric. Ecosyst. Environ. 133, 103–113.
Portugal, E., Izquierdo, G., Truesdell, A., Álvarez, J., 2005. The geochemistry and isotope hydrology of the Southern Mexicali Valley in the area of the Cerro Prieto, Baja California (Mexico) geothermal field. J. Hydrol. 313, 132–148.
Ranalli, A.J., Macalady, D.L., 2010. The importance of the riparian zone and in-stream processes in nitrate attenuation in undisturbed and agricultural watersheds – a review of the scientific literature. J. Hydrol. 389, 406–415.
Richter, B.C., Kreitler, C.W., 1991. Identification of Sources of Ground-Water Salinization Using Geochemical Techniques. U.S. Environmental Protection Agency, Ada, Oklahoma.
Rivett, M.O., Buss, S.R., Morgan, P., Smith, J.W.N., Bemment, C.D., 2008. Nitrate attenuation in groundwater: a review of biogeochemical controlling processes. Water Res. 42, 4215–4232.
Rock, L., Mayer, B., 2009. Identifying the influence of geology, land use, and anthropogenic activities on riverine sulfate on a watershed scale by combining hydrometric, chemical and isotopic approaches. Chem. Geol. 262, 121–130.
Schepers, J.S., Varvel, G.E., Watts, D.G., 1995. Nitrogen and water management strategies to reduce nitrate leaching under irrigated maize. J. Contam. Hydrol. 20, 227–239.
Sebilo, M., Billen, G., Grably, M., Mariotti, A., 2003. Isotopic composition of nitrate-nitrogen as a marker of riparian and benthic denitrification at the scale of the whole Seine River system. Biogeochemistry 63, 35–51.
Shabaga, J.A., Hill, A.R., 2010. Groundwater-fed surface flow path hydrodynamics and nitrate removal in three riparian zones in southern Ontario, Canada. J. Hydrol. 388, 52–64.
Silva, S.R., Kendall, C., Wilkison, D.H., Ziegler, A.C., Chang, C.C.Y., Avanzino, R.J., 2000. A new method for collection of nitrate from fresh water and the analysis of nitrogen and oxygen isotope ratios. J. Hydrol. 228, 22–36.
Spanish National Agency of Meteorology, 2012. Datos Climatológicos. Agencia Estatal de Meteorología. Ministerio de Agricultura, Alimentación y Medio Ambiente. Gobierno de España (in Spanish). Available in: www.aemet.es (accessed 25.10.10).
Soil Survey Staff, 1992. Keys to Soil Taxonomy. Pocahontas Press, Blacksburg, United States.
Statpoint Technologies, 2009. Statgraphics Centurion XVI. User Manual. StatPoint Technologies Inc, 297 p.
Sutton, M.A., Howard, C.M., Erisman, J.W., Billen, G., Bleeker, A., Grennfelt, P., van Grisven, H., Grizzetti, B., 2011. The European Nitrogen Assessment: Sources, Effects and Policy Perspectives. Cambridge University Press, Cambridge.
Thayalakumaran, T., Bethune, M.G., McMahon, T.A., 2007. Achieving a salt balance—should it be a management objective? Agric. Water Manage. 92, 1–12.
Thayalakumaran, T., Bristow, K.L., Charlesworth, P.B., Fass, T., 2008. Geochemical conditions in groundwater systems: implications for the attenuation of agricultural nitrate. Agric. Water Manage. 95, 103–115.
Tichomirowa, M., Heidel, C., Junghans, M., Haubrich, F., Matschullat, J., 2010. Sulfate and strontium water source identification by O, S and Sr isotopes and their temporal changes (1997–2008) in the region of Freiberg, central-eastern Germany. Chem. Geol. 276, 104–118.
Utrilla, R., Pierre, C., Orti, F., Pueyo, J.J., 1992. Oxygen and sulphur isotope compositions as indicators of the origin of Mesozoic and Cenozoic evaporates from Spain. Chem. Geol. (Isot. Geosci. Sect.) 102, 229–244.
Van Stempvoort, D.R., Krouse, H.R., 1994. Controls of $d^{18}O$ in sulfate: review of experimental data and application to specific environments. In: Alpers, C.N., Blowes, D.W. (Eds.), Environmental Geochemistry of Sulfide Oxidation. Am. Chem. Soc. Symp. Ser., vol. 550, pp. 446–480.
Vitòria, L., Otero, N., Soler, A., Canals, À., 2004. Fertilizer characterization: isotopic data (N, S, O, C, and Sr). Environ. Sci. Technol. 38, 3254–3262.

CHAPTER VI

HYDROGEOCHEMISTRY

PAPER III

Merchán, D., Auqué, L.F., Acero, P., Gimeno, M.J., Causapé, J., 2014. Geochemical processes controlling water salinization in an irrigated basin in Spain: Identification of natural or anthropogenic influence. *Science of the Total Environment* 502: 330-343.

Impact factor: 3.163 (JCR 2013).
Quartile and category: Q1 (40/215), Environmental Sciences.

D. Merchán took part in the planning of the study, leaded the sampling campaigns and conducted samples preparation, and performed the statistical analysis, geochemical models, data interpretation and writing, with assistance from all co-authors.

Science of the Total Environment 502 (2015) 330–343

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Geochemical processes controlling water salinization in an irrigated basin in Spain: Identification of natural and anthropogenic influence

D. Merchán [a,*], L.F. Auqué [b], P. Acero [b], M.J. Gimeno [b], J. Causapé [a]

[a] Geological Survey of Spain — IGME, C/Manuel Lasala 44 9B, 50006 Zaragoza, Spain
[b] University of Zaragoza — Department of Earth Sciences (Geochemical Modelling Group), C/Pedro Cerbuna 12, 50009 Zaragoza, Spain

HIGHLIGHTS

- Salinization in Lerma Basin was controlled by the dissolution of soluble salts.
- Water salinization and nitrate pollution were found to be independent processes.
- High NO_3, fresh groundwater evolved to lower NO_3, higher salinity surface water.
- Inverse and direct geochemical modeling confirmed the hypotheses.
- Salinization was a natural ongoing process slightly enhanced by land use.

ARTICLE INFO

Article history:
Received 12 May 2014
Received in revised form 10 September 2014
Accepted 12 September 2014
Available online 28 September 2014

Editor: Eddy Y. Zeng

Keywords:
Mineral dissolution
Cation exchange reactions
Nitrate pollution
Multivariate analysis
Geochemical modeling

ABSTRACT

Salinization of water bodies represents a significant risk in water systems. The salinization of waters in a small irrigated hydrological basin is studied herein through an integrated hydrogeochemical study including multivariate statistical analyses and geochemical modeling. The study zone has two well differentiated geologic materials: (i) Quaternary sediments of low salinity and high permeability and (ii) Tertiary sediments of high salinity and very low permeability. In this work, soil samples were collected and leaching experiments conducted on them in the laboratory. In addition, water samples were collected from precipitation, irrigation, groundwater, spring and surface waters. The waters show an increase in salinity from precipitation and irrigation water to ground- and, finally, surface water. The enrichment in salinity is related to the dissolution of soluble mineral present mainly in the Tertiary materials. Cation exchange, precipitation of calcite and, probably, incongruent dissolution of dolomite, have been inferred from the hydrochemical data set. Multivariate statistical analysis provided information about the structure of the data, differentiating the group of surface waters from the groundwaters and the salinization from the nitrate pollution processes. The available information was included in geochemical models in which hypothesis of consistency and thermodynamic feasibility were checked. The assessment of the collected information pointed to a natural control on salinization processes in the Lerma Basin with minimal influence of anthropogenic factors.

1. Introduction

Salinization of water bodies represents a significant risk in water systems regarding suitability for irrigation (Tanji, 1990), other human uses (Peck and Hatton, 2003) or ecosystem health (Nielsen et al., 2003). There are many processes which can cause water salinization. For instance, the main sources of groundwater salinization in the US are natural saline groundwater, sea-water intrusion, halite dissolution, oil- and gas-field activities, saline seep, road salting and agricultural techniques (Richter and Kreitler, 1991).

Groundwater salinization by agricultural practices has been widely reported all around the world (e.g., Koh et al., 2007; Stigter et al., 2006; Yuce et al., 2006). Specifically, irrigated agriculture represents an enhanced pressure on the hydrological system receiving irrigation return flows, with in general higher salinization rates under irrigated areas in comparison with rainfed areas (Johansson et al., 2009). Some examples of the reported processes that increase water salinity include the recirculation of irrigation water (Stigter et al., 2006), the application of agrochemicals (Kume et al., 2007), or the enhanced weathering of existing materials in the area (Kim et al., 2005; Koh et al., 2007). In some cases, natural salinization processes of water bodies are enhanced by irrigated agriculture, either by the transport of solutes in the water (Johansson et al., 2009) or by the depletion of aquifers and consequent concentration of salts (Chaudhuri et al., 2014). Irrigated agriculture may

* Corresponding author.
E-mail addresses: d.merchan@igme.es, eremad@hotmail.com (D. Merchán).

http://dx.doi.org/10.1016/j.scitotenv.2014.09.041
0048-9697/

induce salinization not only in groundwater, but also in surface waters (e.g., Duncan et al., 2008; Isidoro et al., 2006). In any case, the interaction between ground and surface waters adds complexity to the behavior of these hydrological systems. However, salinization in irrigated areas may be related to natural ongoing processes which may be, to a certain degree, enhanced by the addition of irrigation water (Carreira et al., 2014; Chaudhuri and Ale, 2014; Isidoro et al., 2006; Tedeschi et al., 2001) or a direct consequence of the irrigation itself (Stigter et al., 2006), since the dominating salinization processes are very site-specific (Duncan et al., 2008). For instance, irrigation water enhances salinization processes in areas with available salts in the geological substrate, which are mobilized by the extra available water. In other cases, the continuous use of groundwater for irrigation may cause salinization due to the evapotranspiration that the groundwater body is suffering in successive pumping–irrigation–recharge cycles.

Thus, a deep knowledge of the local hydrogeological conditions and processes controlling salinization is required to understand the feasible actions to take in order to mitigate impacts on water resource systems. In line with this idea, two of the most useful tools to increase the knowledge of complex systems with several variables are multivariate statistical analyses (Hair et al., 1999) and geochemical modeling (e.g., Edmunds, 2009; Zhu and Anderson, 2002). Applications reported in the literature include the use of multivariate analysis to understand the main factor explaining the chemical evolution of waters in regional alluvial aquifers (Acero et al., 2013; Lorite-Herrera et al., 2008). For geochemical modeling, some examples of application are the use of inverse modeling approaches to elucidate the net geochemical reactions occurring in a water flow line from irrigation water to drainage water (Causapé et al., 2004a; García-Garizábal et al., 2014) or the use of direct modeling approaches to reproduce observed patterns in groundwater and to develop simulations in which different hypotheses can be tested (Kim et al., 2005; Stigter et al., 2006). However, both approaches are seldom applied to the same study area, which could improve the knowledge on the processes controlling the hydrological system.

In this context, the objective of the present study is to identify the main geochemical processes related to the salinization of waters in a headwater agricultural basin through the use of both multivariate statistical analysis and geochemical modeling. Specifically, the main aim is to elucidate if the processes controlling salinization of Lerma Basin waters (Merchán et al., 2013, 2014) are related to natural or to anthropogenic factors.

2. Study site description

The Lerma Basin is a small hydrological basin (7.38 km^2, Fig. 1), with 48% of its surface area under irrigation. It is located inside the municipality of Ejea de los Caballeros (Zaragoza, Spain) and is representative, regarding geology, hydrology and agronomy, of a wide range of land–water connected environments in the region (Causapé et al., 2004b).

According to the Spanish National Agency of Meteorology (AEMET, 2014), the climate in the area is Continental to Mediterranean, characterized by extreme temperatures and irregular and scarce precipitations. Temperatures may vary from below zero during winter to as high as 40 °C during summer, with an average temperature of 14 °C. Average annual precipitation during the hydrological years 2004–2011 was around 402 mm and concentrated in spring and autumn (Merchán et al., 2013). Summer and winter are generally dry, only wetted by occasional storms.

The geology in the Lerma Basin is represented by Tertiary and Quaternary materials (Fig. 1). The Tertiary materials appear as a bottom layer (66% of its surface) several hundreds of meters thick, composed of alternating gypsum, clay and silt materials of brown and gray colors, with occasional intercalations of fine limestone layers associated with gypsum (Causapé et al, 2004a; ITGE, 1988). This unit is locally covered by a Quaternary glacis (34% of the surface) up to 10 m thick, dominated by detrital sediments composed of gravels with some Tertiary limestone clasts, alternating with sands, silts and clays (ITGE, 1988). Tertiary materials are exposed due to the erosive effect of a network of gullies developed over the glacis.

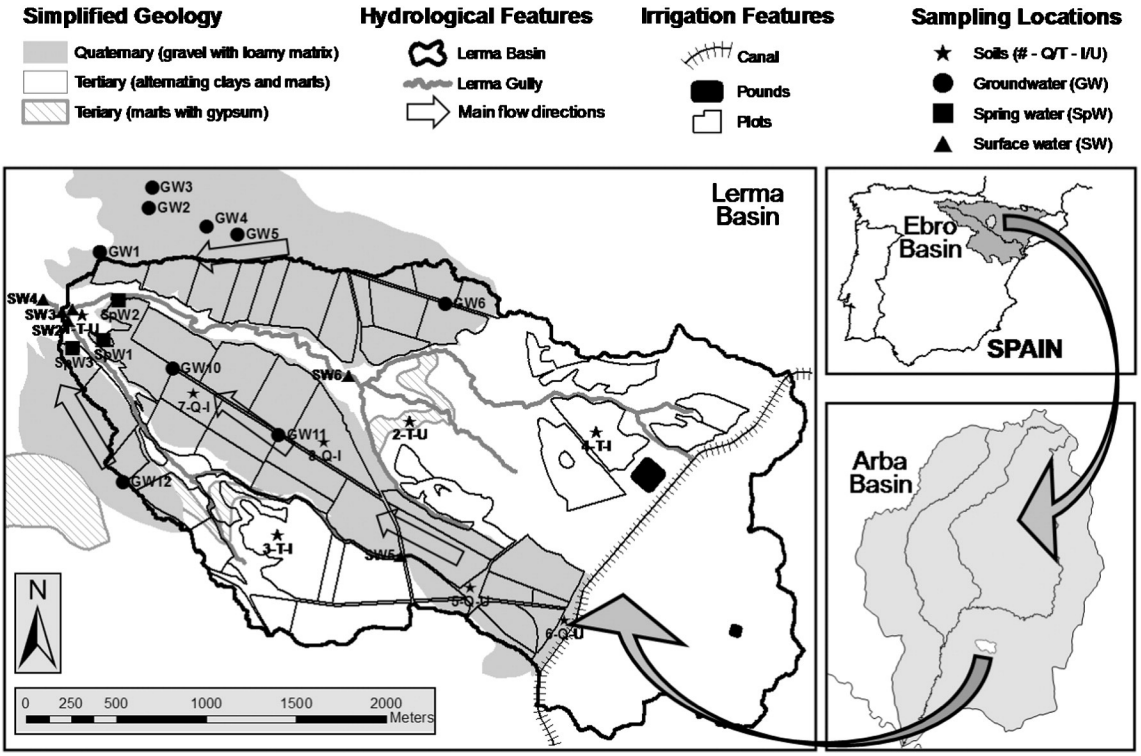

Fig. 1. Location, simplified geology, main hydrological and irrigation features, and sampling locations of the Lerma Basin.

Soils developed on Quaternary glacis (Calcixerollic Xerochrepts, Soil Survey Staff, 2014) display stony 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, 2014) have 30–45 cm of effective depth, high salinity and significant risk of erosion (slope > 10%). These characteristics identified Quaternary soils as suitable for conversion to irrigated land (Beltrán, 1986) and, in consequence, the irrigated area covers mainly the Quaternary surface (Fig. 1).

Regarding the hydrological behavior, Quaternary materials have medium to high permeability (hydraulic conductivity between 1 and 10 m day^{-1}), constituting free intergranular perched aquifers, whereas Tertiary materials have low permeability. Precipitation and irrigation water infiltrate through Quaternary materials down to the contact with the Tertiary unit, where they flow horizontally over it. Groundwater seeps to the surface through the contact between Quaternary and Tertiary and it feeds a network of gullies. Before irrigation started, these streams flowed mainly during spring and autumn, i.e., the more rainy seasons (Abrahão et al., 2011a) while, after the implementation of irrigation, the Lerma Gully has become a perennial stream.

The Lerma Basin receives water from the Aragón River Basin, via the Bardenas Irrigation Canal, during spring and summer (Fig. 2). Crops cultivated are typical of the Middle Ebro Valley: maize, winter cereal and vegetables. Associated with irrigated agriculture is the application of synthetic fertilizers, mainly through liquid and compound (NPK) fertilizers. It is important to mention the increase in Mg^{2+} in fertilizer applications experienced in recent years in the area, as a consequence of the decrease in this nutrient observed in soils (local fertilization advisors, pers. com.).

3. Methods

3.1. Sampling and chemical analysis of the Lerma Basin waters

Samples of the Lerma Basin waters were collected for chemical analysis in 2011, February the 10th (I) and July the 27th (II), and in 2012, January the 10th (III) and July the 31st (IV) (Fig. 2, Table 2), representing two non-irrigated and two irrigated seasons, along with two low water and two high water seasons, respectively. High waters in the gullies and the Quaternary aquifer took place in the late summer, at the end of the irrigated season. The sampling dates were selected to avoid taking samples in the week after any rainfall event. Sixty-three water samples were collected from the Lerma Basin throughout the study period: groundwaters (GW, 31 samples), spring waters (SpW, 8) and surface waters (SW, 24). These monitoring points were selected after some 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 to reach the Tertiary materials and penetrate them around 50 cm further. The Tertiary materials were always dry 20 cm below the contact with the Quaternary materials, which is a proof of their low permeability, since the Quaternary materials just above were saturated. The screened interval covered the whole piezometer.

Groundwater samples were collected using a high density polyethylene bailer, whereas spring or surface water samples were collected manually. In some of the piezometers and sampling campaigns, it was not possible to obtain enough water for analysis since the saturated thickness was lower than the bailer length.

Additionally, all available data of precipitation (P, 11 samples) and irrigation (I, 6 samples) waters, corresponding to samples collected between 2007 and 2012 (Table 2), were included in this study.

Field parameters (electrical conductivity corrected to 25 °C [EC], temperature [T], pH and alkalinity) were measured in situ just after sample collection, with previously calibrated instruments. EC-meter CRISON CM35, and pH-meter CRISON T25 were used for EC, T and pH. Alkalinity was measured using a HACH alkalinity test kit and was similar to that obtained in the laboratory analyses. The filtered samples (0.45 μm) were analyzed within a month of collection. The dissolved ionic concentrations (Na^+, K^+, Ca^{2+}, Mg^{2+}, CO_3^{2-}, HCO_3^-, SO_4^{2-}, Cl^-, NO_3^-) were analyzed by standard analytical methods at the Geological Survey of Spain (IGME) laboratories. Cations were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES), and anions were analyzed by high performance liquid chromatography (HPLC) technique. The charge balance was cross-checked as follows:

$$Charge\ \ balance\ \ (\%) = 200\frac{\sum meq\ \ cation - \sum meq\ \ anion}{\sum meq\ \ cation + \sum meq\ \ anion}.$$

(Weight, 2008)

Absolute charge balances averaged 2.5% (maximum 6.6%) in precipitation and irrigation waters and 4.4% (maximum 5.8%) in ground, spring and surface waters.

The interpretation of the water quality data was based on the use of indicators of water quality for irrigation purposes (sodium adsorption ratio and Kelly's ratio, related to irrigation water salinity) along with the hydrochemical interpretations (e.g., Piper diagram, ionic ratios).

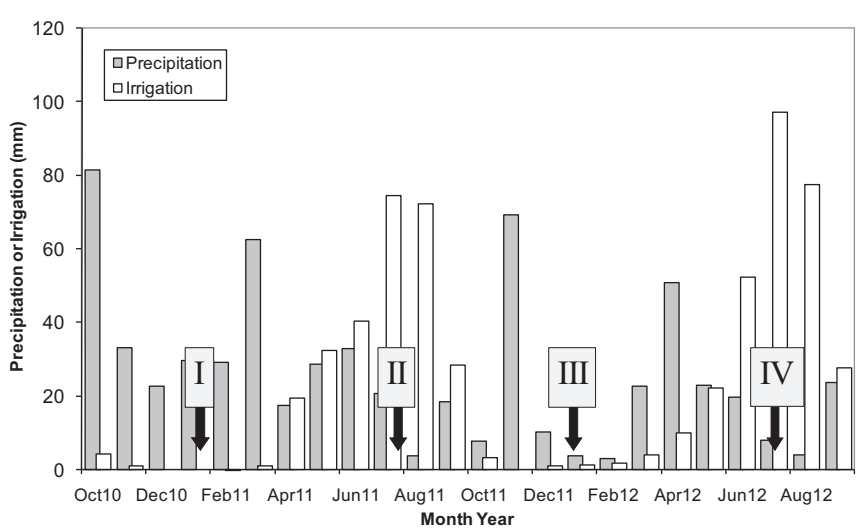

Fig. 2. Precipitation and irrigation in the Lerma Basin during the hydrological years 2010–2012. Sampling campaigns are indicated by black arrows.

The Kruskal–Wallis Test, a non-parametric method for testing whether the samples originate from the same distribution, was used to detect significant differences between groundwater, spring and surface water samples. The statistical package used was Statgraphics Centurion XVI (StatPoint Technologies, 2009).

3.2. Soil leaching experiments

In order to investigate the chemical components that the soils can supply to the waters, a soil sampling campaign was performed in 2013 January 28th. Eight soil samples (stars in Fig. 1) were collected from Tertiary and Quaternary materials in unirrigated and irrigated soils (with two samples in each combination, i.e., Tertiary unirrigated [1 and 2], Tertiary irrigated [3 and 4], Quaternary unirrigated [5 and 6] and Quaternary irrigated soils [7 and 8]), covering all the representative soils and characteristics in the study zone. The samples were collected from the topsoil (up to 25 cm depth). They were treated in the following way: after removing the fraction >2 mm, 100 g of dry sample was mixed with 250 ml of distilled water during 24 h. After this time, the water fraction was extracted, filtered (0.45 μm) and analyzed following the procedure described in the section above. In the preliminary stage, different mixing proportions (250 ml or 500 ml) and mixing times (24, 48 and 96 h) were tested to ensure a complete dilution of the soluble fraction. Results of these preliminary tests were compared through Sign and Signed-Rank Matched Tests (Helsel and Hirsch, 2002) and no significant differences were found what suggests that any of the used amounts of water and experimented contact times were enough to dissolve all the soluble fraction of the materials.

Additionally, mineralogical determinations were performed in the eight soil samples by X-ray diffraction. After removing the fraction >2 mm, around 5 g of dry sample was ground in an agate mortar and pestle and then sieved through 63 μm. X-ray diffraction was performed with XPERT PRO MPD equipment (PANanalytical), and the data were processed using the software HighScore 3.0.4 (PAN analytical). Samples were prepared in the Geochemistry Laboratory of the Earth Sciences Department at the University of Zaragoza, and the X-ray diffraction determinations were performed in the Geological Survey of Spain Laboratories.

3.3. Multivariate statistical analyses

Two multivariate statistical procedures were used to obtain a better understanding of the variety in the data set and the processes involved. The statistical package used was Statgraphics Centurion XVI (StatPoint Technologies, 2009) and the analyses included Principal Components and Hierarchical Cluster. Both were performed on the standardized (Z-scores) hydrochemical data of the 80 water samples from the Lerma Basin (precipitation, irrigation, groundwater, spring and surface waters). The variables included in these analyses were Na^+, K^+, Ca^{2+}, Mg^{2+}; HCO_3^-, SO_4^{2-}, Cl^-, NO_3^- and pH. EC was not included for being a proxy of salinity, represented by the specific cations and anions. The dissolved concentration of CO_3^{2-} was excluded from multivariate analysis since it was below detection limit in most of the samples. For those components occasionally below detection limit, 1/2 of the detection limit value was used.

Principal component analysis (PCA) was performed to infer the controlling variables (components) of the water chemistry. PCA has been widely applied to understand hydrological data (e.g., Morán-Tejeda et al., 2011) and, particularly, hydrogeochemical data: in surface waters (e.g., Cameron, 1996; Evans et al., 1996), groundwater (e.g., Adams et al., 2001; Koh et al., 2007) or both (Lorite-Herrera et al., 2008). PCA summarizes the data set in the minimum components that explain most of the variance. The Varimax method (Davis, 1986) was applied to maximize the variance explained by each component. Each of the new components is a lineal combination of pre-existing standardized variables with different loadings depending on the influence of the variable in that component. For component loadings, an approach similar to that of Evans et al. (1996) or Koh et al. (2007) was selected. A high loading was defined as higher than 0.75, and a moderate loading was defined as between 0.40 and 0.75. Loading of less than 0.40 was considered negligible.

The hierarchical cluster analysis (HCA), commonly applied in hydrological data (e.g., Abrahão et al., 2011b; Causapé et al., 2004a; Menció et al., 2012), was performed here to generate groups of similar samples. Several similarity measurement and linkage methods were tested and the groups obtained were fairly similar. The square Euclidean distance and the Ward method were used to obtain hierarchical associations, since they maximize the homogeneity inside the clusters and maximize heterogeneity between clusters (Hair et al., 1999).

3.4. Geochemical modeling

The USGS software PHREEQC (Parkhurst and Appelo, 1999) with its database *phreeqc.dat* was used for the geochemical modeling as it has been widely applied in all kind of hydrogeochemical problems (e.g., Carol et al., 2009; Edmunds, 2009; Han et al., 2011; van Asten et al., 2003; Zhu and Anderson, 2002). First, speciation-solubility calculations were performed to obtain the saturation indexes (SI) of the different water samples with respect to the mineral phases of interest, particularly, calcite, dolomite, gypsum and halite. Additionally, $CO_2(g)$ partial pressures were also computed based on the alkalinity and pH of the samples (e.g., Kehew, 2001; Appelo and Postma, 2005). Second, an inverse modeling approach, mass balance, was applied between selected water samples considered representative of the variety observed in the data set. Based on the variations in the water chemistry and the observed mineralogy, this approach allowed estimating the net geochemical reactions between samples assumed to be connected by a flow line. Finally, a forward modeling approach was applied using feasible chemical reactions to reproduce the evolution of the system. All the information provided by these geochemical modeling exercises was used to discard or confirm the hypotheses of the different processes inferred throughout the study.

4. Results and discussion

4.1. Soil leaching experiments

Tertiary marly soils (sample 1-T-U) provided the greatest dissolved Na^+ and Cl^- concentrations, 100 and 112 mmol L^{-1}, respectively (Table 1, Fig. 3). Soils over marls with nodular and tabular gypsum (sample 2-T-U) showed the highest dissolved SO_4^{2-}, Ca^{2+} and Mg^{2+} concentrations, 9.6, 4.9 and 8.9 mmol L^{-1}, respectively. The presence of soluble minerals such as halite (NaCl) and gypsum or epsomite ($CaSO_4 \cdot 2H_2O$, $MgSO_4 \cdot 7H_2O$) may explain these results. The samples of Tertiary age that were irrigated (3-T-I and 4-T-I) had values comparable with those of the Quaternary soil samples, probably as a consequence of the different amendments performed by farmers in these irrigated soils (addition of loamy textured soil, plowing, successive wash out of soluble fraction by irrigation water, etc.). Finally, samples from the soils over the Quaternary glacis (5-Q-U, 6-Q-U, 7-Q-I and 8-Q-I) showed the lowest concentrations for the different analyzed ions, with averages of 1.4 mmol L^{-1} for Cl^-, 0.5 mmol L^{-1} for SO_4^{2-}, 0.4 mmol L^{-1} for Na^+, 2.0 mmol L^{-1} for Ca^{2+} and 0.6 mmol L^{-1} for Mg^{2+} (Fig. 3). Thus, the salinity of the waters appears to be mainly controlled by the interaction between the recharge waters (precipitation and irrigation) and the Tertiary substrate.

The X-ray results (Table 1) indicated the predominance of calcite, quartz and clay minerals (mainly illite and chlorite) in all the samples. In fact, these minerals were the only ones detected in the samples from the Quaternary glacis (with the exception of traces of feldspar in some of them). Dolomite, ankerite and gypsum were also identified in the samples taken in the soils over the Tertiary marls and clays

Table 1
Selected soil samples results. Sample: A-B-C where A is the sample ID (1-8), B is a letter presenting the age (T for Tertiary and Q for Quaternary) and C is a letter presenting the land use (I for irrigated and U for unirrigated).

Sample	Description	Stones (wt.% >2 mm)	Water attacks (mmol L^{-1})					X-ray diffractions[a]
			Cl^-	SO_4^{2-}	Na^+	Ca^{2+}	Mg^{2+}	
1-T-U	Marls	0	100.4	3.2	112.3	0.5	1.0	Cal, Qtz, C.M., Dol, Fsp (t)
2-T-U	Marls gyps.	1	50.4	9.6	47.0	4.9	8.9	Cal, Qtz, C.M., Dol/Ank, Gp, Fsp (t)
3-T-I	Marls	2	0.6	1.0	2.1	1.4	0.5	Cal, Qtz, C.M., Dol/Ank, Fsp (t)
4-T-I	Marls	5	0.7	0.4	1.4	1.3	0.6	Cal, Qtz, C.M., Dol/Ank, Fsp (t)
5-Q-U	Glacis	32	0.1	0.1	0.2	1.3	0.5	Cal, Qtz, C.M., Fsp (t)
6-Q-U	Glacis	33	5.0	0.8	0.6	3.3	0.7	Cal, Qtz, C.M.
7-Q-I	Glacis	34	0.3	0.6	0.4	1.5	0.5	Cal, Qtz, C.M., Fsp (t)
8-Q-I	Glacis	45	0.3	0.6	0.5	1.7	0.4	Cal, Qtz, C.M., Fsp (t)

wt.%: percentage in weight.
[a] Cal: calcite; Qtz: quartz; C.M.: clay minerals (illite + chlorite); Dol: dolomite; Fsp: feldspar (t: trace, low intensities); Ank: ankerite; Gp: gypsum.

(Table 1). Despite the useful qualitative information obtained from the X-ray diffraction technique, it was unable to detect soluble mineral phases that could explain Cl^- and Na^+, contents in the waters. However, after a detailed revision of the difractograms, the presence of halite could not be discarded since its signal in diffractograms would overlap with that of other minerals detected. However, epsomite was not detected even after the detailed revision of the diffractograms. Taking the concentrations obtained in sample 1-T-U, the maximum obtained in the soil samples, a fraction of halite of maximum 6% can be estimated from total Na^+ and Cl^- leached and mass of soil used. Consequently, depending on the specific combination of minerals in the sample, it might remain undetected by X-ray diffraction. Similar assumptions can be done with other soluble minerals. In addition, the presence of halite and other soluble minerals is supported by the fact that the Tertiary materials were deposited in a saline lake environment (ITGE, 1988), where the presence of evaporitic minerals is common.

4.2. Hydrogeochemical characterization

Precipitation and irrigation water are the main input waters in the Lerma Basin (Table 2). They have a very low salinity, with typical EC values under 0.05 mS cm^{-1} for precipitation water and under 0.4 mS cm^{-1} for irrigation water. According to their positions in a Piper diagram (Fig. 4), precipitation and irrigation waters are mainly of Ca^{2+}-HCO_3^- type. Both, their low salinity and their water type, indicate a high quality for irrigation purposes, as indicated by several water quality indicators commonly used for irrigation waters. For instance, Sodium Adsorption Rate (SAR) values ranged from 0.04 to 0.55, with an average of 0.23, which indicates a very low sodium hazard in these waters (e.g., Fetter, 2001). Kelly's Ratio (KR) values ranged from 0.07 to 0.58, with an average of 0.19, indicating the good quality of the water for irrigation (Kelly, 1963).

A clear evolution from low salinity Ca^{2+}-HCO_3^- type in the input water to Na^+-mixed-to-Cl^- water type (Fig. 4) with increasing salinity can be observed using the 63 water samples collected in the Lerma Basin (Table 3). Samples with low salinity (an upper stream gully and some piezometers during the irrigation season) belong to the water types closer to precipitation and irrigation waters. There were significant differences (Kruskal–Wallis Test, $p < 0.05$) between the salinity of the groundwaters (average 1.75 mS cm^{-1}) and the salinity of the surface waters (average 2.63 mS cm^{-1}) while spring waters had intermediate salinity values. Thus, the quality of water for irrigation purposes decreases between recharge waters and water in the outlet of the basin, presenting slight restriction for irrigation purposes (EC > 0.7 mS cm^{-1}, Ayers and Westcost, 1992). In fact, some surface waters and the groundwater point GW12 in 2012 presented severe restriction for irrigation purposes (EC > 3 mS cm^{-1}). This decrease in quality is also indicated by the SAR values from 0.45 to 10.77, with a medium value of 5.76 (low to medium sodium hazards, e.g., Fetter, 2001) and KR values from 0.15 to 2.47, with an average value of 1.34 (waters with values higher than one are considered unsuitable for irrigation purposes, Kelly, 1963).

Additionally, significant differences (Kruskal–Wallis Test, $p < 0.05$) were observed in the physicochemical parameters and the major ions median content between ground and surface waters (Table 3). Significantly higher values in pH, Cl^-, SO_4^{2-}, Na^+, Ca^{2+}, and Mg^{2+}, and lower values in NO_3^- were observed in surface waters compared with groundwater. Spring waters showed values generally closer to those of groundwater except in the case of pH that they are

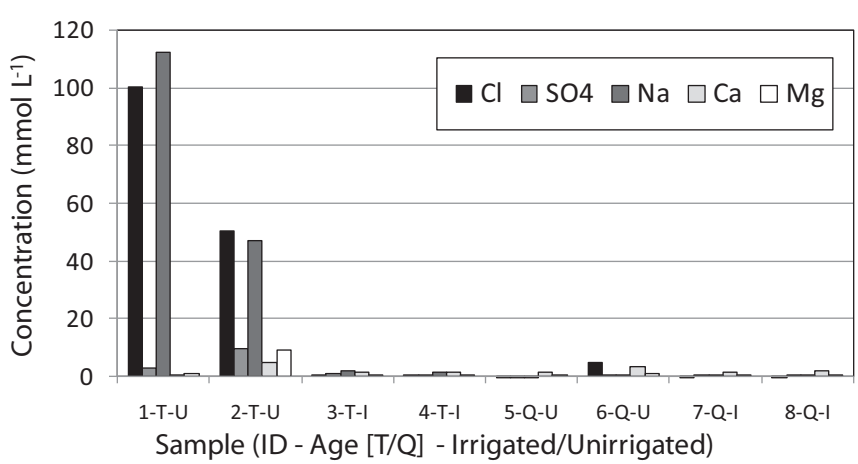

Fig. 3. Concentration of major ions after 24 h of contact and mixing between soil samples (100 g) and distilled water (250 g). Sample codification: A-B-C where A is the sample ID (1–8), B is a letter presenting the age of the materials (T for Tertiary and Q for Quaternary) and C is a letter presenting the land use (I for irrigated and U for unirrigated).

Table 2
Precipitation and irrigation hydrochemical data available from the Lerma Basin.

Sample	Date	EC mS cm^{-1}	pH	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	CO_3^{2-}	HCO_3^{-}	SO_4^{2-}	Cl^{-}	NO_3^{-}	C.B. %
				mmol L^{-1}									
P	16/11/2009	0.053	7.08	0.10	0.25	0.20	0.05	b.d.l.	0.38	0.06	0.14	0.00	4.0
P	15/12/2009	0.041	6.32	0.10	0.25	0.07	0.03	b.d.l.	0.29	0.05	0.06	0.03	2.3
P	19/01/2010	0.015	5.38	0.05	0.08	0.04	0.01	b.d.l.	0.11	0.03	0.03	0.01	−2.8
P	15/03/2010	0.048	5.58	0.45	0.08	0.04	0.00	b.d.l.	0.41	0.04	0.03	0.08	3.2
P	13/05/2010	0.045	5.43	0.40	0.08	0.06	0.01	b.d.l.	0.29	0.10	0.04	0.10	3.3
P	21/11/2011	0.008	5.03	0.10	b.d.l.	0.01	b.d.l.	b.d.l.	0.07	0.03	0.01	0.01	−6.6
P	17/11/2011	0.007	4.86	0.10	b.d.l.	0.02	b.d.l.	b.d.l.	0.07	0.03	0.02	0.01	−1.5
P	03/05/2012	0.029	6.56	0.10	0.16	0.03	b.d.l.	b.d.l.	0.21	0.03	0.02	0.03	−0.3
P	23/05/2012	0.032	5.15	0.05	0.25	0.10	0.01	b.d.l.	0.20	0.05	0.13	0.02	1.9
P	22/10/2012	0.027	7.50	0.10	0.16	0.02	b.d.l.	b.d.l.	0.25	0.01	0.01	0.00	5.3
P	08/11/2012	0.015	6.39	0.05	0.08	0.01	b.d.l.	b.d.l.	0.11	0.01	0.01	0.01	3.1
Average		0.039	5.71	0.15	0.13	0.05	0.01	–	0.22	0.04	0.05	0.03	
SD		0.017	0.76	0.14	0.09	0.06	0.02	–	0.12	0.02	0.05	0.03	
I	22/10/2007	0.360	n.a.	2.40	0.72	0.63	0.03	b.d.l.	2.56	0.55	0.66	n.a.	0.1
I	12/11/2007	0.380	n.a.	2.48	0.72	0.64	0.03	b.d.l.	2.64	0.48	0.78	n.a.	−0.9
I	24/07/2008	0.330	n.a.	2.87	0.48	0.27	0.02	b.d.l.	3.05	0.29	0.30	n.a.	0.0
I	17/09/2008	0.280	n.a.	2.40	0.64	0.30	0.03	b.d.l.	2.62	0.34	0.40	n.a.	0.1
I	27/07/2011	0.318	8.10	1.95	0.74	0.64	0.03	0.08	2.38	0.35	0.44	0.02	3.0
I	31/07/2012	0.318	8.10	2.30	0.16	0.43	0.01	b.d.l.	2.38	0.29	0.32	0.02	−3.5
Average		0.334		2.40	0.58	0.49	0.02	–	2.60	0.38	0.48	–	
SD		0.039		0.30	0.22	0.18	0.01	–	0.25	0.11	0.19	–	

SD: standard deviation. n.a.: not available. b.d.l.: below detection limit. C.B.: charge balance.

closer to those of surface waters. No significant differences were detected for HCO_3^- and K^+ values.

4.3. Ionic ratios

Ionic ratios in hydrochemical data have been useful in providing an insight into the hydrogeochemical processes controlling the changes in water quality. The molar ratio Na^+/Cl^- ranged from 0.75 to 4.91 (Fig. 5A), with low values for precipitation and irrigation waters (0.75–1.62) and also for surface waters (1.07–1.76), slightly higher values for springs (1.36–2.31) and the highest values in some groundwaters (0.90–4.91). A trend towards values close to 1.00 was observed with increasing salinity, which can be attributed to halite dissolution although in the samples with the lowest salinity an additional source of sodium is required. Ionic exchange could provide sodium to these low salinity samples (e.g., Lorite-Herrera et al., 2008), especially considering that irrigation water with low salinity and significant Ca^{2+} concentrations is added to soils, which favors the ionic exchange in this direction (Na^+ enters the solution, Ca^{2+} leaves the water solution, Appelo and Postma, 2005).

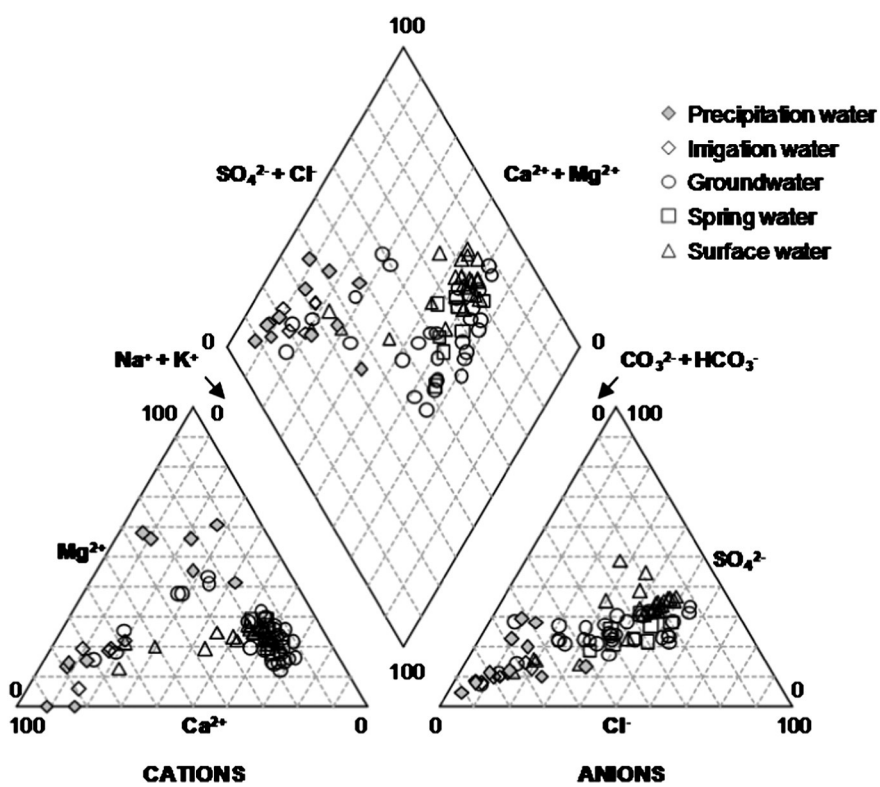

Fig. 4. Piper diagram showing the situation of the Lerma Basin waters.

Table 3
Surface (gullies, G), spring (S) and groundwater (wells, W) hydrochemical data available from the Lerma Basin.

Date		EC mS cm^{-1}	pH	T °C	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	CO_3^{2-}	HCO_3^{-}	SO_4^{2-}	Cl^{-}	NO_3^{-}	C.B. %
					mmol L^{-1}									
GW1-I	10-02-2011	1.43	7.9	10.1	2.59	2.88	10.20	0.21	b.d.l.	5.74	3.21	3.62	2.45	5.6
GW3-I	10-02-2011	1.48	7.8	10.8	3.04	3.37	14.42	0.08	b.d.l.	5.90	3.90	8.06	2.13	4.5
GW4-I	10-02-2011	1.39	8.0	13.0	1.95	2.30	10.48	0.09	b.d.l.	4.36	3.09	3.79	2.82	5.3
GW5-I	10-02-2011	1.67	7.8	13.4	3.39	3.87	11.49	0.15	b.d.l.	5.90	2.43	5.53	4.08	5.0
GW10-I	10-02-2011	1.63	7.8	11.6	2.79	5.76	10.48	0.21	b.d.l.	6.29	3.77	5.85	2.32	5.4
GW11-I	10-02-2011	1.52	7.6	13.4	4.04	7.49	5.53	0.17	b.d.l.	6.23	3.63	5.94	1.85	−2.4
GW12-I	10-02-2011	2.53	7.7	11.9	3.49	6.34	17.99	0.09	b.d.l.	6.39	7.62	10.92	1.54	5.3
SW1-I	10-02-2011	2.49	8.4	6.5	5.14	5.92	17.25	0.19	b.d.l.	6.88	8.41	10.70	1.20	4.7
SW2-I	10-02-2011	4.25	8.4	6.1	9.58	12.51	23.74	0.15	b.d.l.	6.72	15.29	21.52	1.18	2.8
SW3-I	10-02-2011	3.14	8.4	6.1	5.84	9.13	19.45	0.14	b.d.l.	7.05	10.30	14.10	1.23	5.6
SW4-I	10-02-2011	3.17	8.5	6.2	5.64	9.13	19.78	0.15	b.d.l.	7.18	10.31	14.19	1.22	5.3
SW5-I	10-02-2011	0.46	8.5	5.7	2.50	0.99	1.39	0.04	b.d.l.	3.02	0.72	0.93	0.03	4.8
SW6-I	10-02-2011	2.66	8.5	5.2	6.39	7.74	15.92	0.14	b.d.l.	6.72	10.88	10.85	0.13	5.4
GW1-II	27-07-2011	1.32	7.6	19.0	3.19	2.63	11.90	0.18	0.12	7.93	2.99	3.81	2.19	5.0
GW4-II	27-07-2011	1.31	7.6	16.8	2.45	2.63	10.14	0.11	0.16	5.70	2.59	3.56	2.66	4.3
GW5-II	27-07-2011	0.49	7.4	16.9	3.44	0.74	0.65	0.10	0.16	3.18	0.43	0.50	0.56	−0.4
GW6-II	27-07-2011	1.40	7.9	21.6	3.44	4.85	9.16	0.06	0.04	8.06	4.06	3.30	1.15	5.3
GW10-II	27-07-2011	1.64	7.5	17.6	2.99	6.09	10.44	0.22	0.20	7.31	3.38	5.73	2.27	4.4
GW11-II	27-07-2011	1.15	7.4	16.4	3.24	5.27	4.33	0.14	0.16	7.08	3.09	0.88	1.28	3.9
GW12-II	27-07-2011	2.79	7.5	17.7	4.24	6.91	18.26	0.10	0.08	5.11	7.38	14.17	1.61	4.0
SpW1-II	27-07-2011	1.81	7.5	21.1	2.94	4.11	13.36	0.13	0.12	8.29	3.26	5.77	2.10	5.0
SpW2-II	27-07-2011	1.78	8.2	18.9	3.19	5.60	12.12	0.20	0.08	6.56	4.29	6.33	2.73	5.5
SpW3-II	27-07-2011	2.63	8.2	21.4	5.14	5.18	18.53	0.07	b.d.l.	7.08	4.97	11.34	3.90	5.8
SW1-II	27-07-2011	2.60	8.2	18.8	4.64	6.50	17.30	0.17	b.d.l.	6.88	7.94	11.15	1.25	5.0
SW2-II	27-07-2011	4.28	8.2	16.5	7.69	10.86	32.78	0.14	b.d.l.	9.67	16.54	21.56	0.92	5.5
SW3-II	27-07-2011	3.30	8.3	17.4	6.14	8.89	20.74	0.16	b.d.l.	6.69	11.44	15.62	1.12	3.0
SW4-II	27-07-2011	3.32	8.2	16.5	5.99	9.13	20.16	0.16	b.d.l.	6.88	11.37	15.72	1.12	1.0
SW5-II	27-07-2011	0.36	8.3	22.6	2.30	0.82	0.78	0.03	0.08	2.72	0.42	0.57	0.01	3.2
SW6-II	27-07-2011	1.83	8.2	20.7	5.74	5.02	10.70	0.17	b.d.l.	7.08	7.15	6.10	0.09	5.7
GW1-III	10-01-2012	1.60	7.9	10.5	2.74	1.81	10.15	0.21	b.d.l.	3.82	3.30	4.04	2.95	5.6
GW3-III	10-01-2012	2.11	7.7	10.8	3.29	2.96	13.96	0.12	b.d.l.	4.51	3.90	9.08	1.77	5.4
GW4-III	10-01-2012	1.45	7.8	14.0	2.50	1.81	8.57	0.08	b.d.l.	3.05	2.64	3.79	2.76	5.7
GW5-III	10-01-2012	1.49	7.7	13.8	3.44	2.80	8.28	0.11	b.d.l.	3.82	2.43	3.84	3.74	5.6
GW6-III	10-01-2012	2.86	7.9	9.0	3.94	8.72	16.39	0.10	b.d.l.	6.29	8.06	11.41	1.90	5.2
GW10-III	10-01-2012	2.22	7.8	12.4	2.64	5.84	14.87	0.16	b.d.l.	4.74	4.68	10.72	2.18	5.2
GW11-III	10-01-2012	2.27	7.6	13.7	3.69	5.76	12.64	0.13	b.d.l.	5.08	5.69	8.29	1.97	5.5
GW12-III	10-01-2012	3.03	8.0	13.4	3.94	7.24	18.82	0.09	b.d.l.	3.46	8.32	14.73	2.00	5.4
SpW2-III	10-01-2012	2.04	8.4	9.5	3.19	5.02	11.48	0.17	b.d.l.	4.62	5.20	7.21	2.06	5.8
SpW3-III	10-01-2012	2.84	8.4	6.8	4.94	4.61	17.54	0.07	b.d.l.	4.31	6.19	11.51	3.74	5.3
SW1-III	10-01-2012	2.96	8.2	3.8	4.04	5.60	15.45	0.11	b.d.l.	4.75	7.82	9.92	1.36	5.5
SW2-III	10-01-2012	3.33	8.3	2.9	5.54	7.90	17.40	0.09	b.d.l.	4.03	10.46	13.99	0.87	5.2
SW3-III	10-01-2012	2.95	8.3	2.8	4.79	6.25	16.56	0.10	b.d.l.	4.54	8.87	11.63	1.17	5.6
SW4-III	10-01-2012	2.97	8.3	2.2	4.74	6.50	16.72	0.10	b.d.l.	4.39	9.06	11.93	1.15	5.6
SW5-III	10-01-2012	0.40	8.4	3.7	2.10	0.41	0.72	0.03	b.d.l.	2.03	0.50	0.58	0.02	4.0
SW6-III	10-01-2012	2.08	8.3	2.5	4.99	4.20	9.81	0.10	b.d.l.	3.39	8.01	6.65	0.05	5.3
GW1-IV	31-07-2012	1.70	7.5	18.6	3.49	2.47	10.89	0.21	b.d.l.	6.42	3.07	4.40	2.98	0.3
GW2-IV	31-07-2012	1.17	7.8	19.6	2.45	2.22	7.43	0.13	b.d.l.	5.57	2.24	2.40	1.63	3.2
GW3-IV	31-07-2012	1.35	7.5	18.9	4.39	1.97	1.38	0.03	b.d.l.	6.36	0.55	0.65	0.28	−0.8
GW4-IV	31-07-2012	0.90	7.6	18.7	3.04	3.21	2.32	0.08	b.d.l.	4.10	1.64	1.67	1.36	−1.2
GW5-IV	31-07-2012	0.49	7.9	18.5	2.55	0.74	0.74	0.07	b.d.l.	2.67	0.52	0.58	0.45	−3.8
GW6-IV	31-07-2012	1.64	7.5	20.0	5.84	6.42	4.92	0.09	b.d.l.	5.77	3.10	5.44	2.65	1.6
GW10-IV	31-07-2012	2.42	7.6	18.1	2.94	5.60	18.05	0.18	b.d.l.	5.47	5.00	12.87	2.01	5.4
GW11-IV	31-07-2012	2.42	7.5	17.3	3.29	6.67	15.08	0.12	b.d.l.	5.01	5.20	12.07	1.54	5.5
GW12-IV	31-07-2012	3.25	7.8	23.5	4.59	8.56	20.67	0.11	b.d.l.	4.02	10.99	17.80	1.44	0.9
SpW1-IV	31-07-2012	1.80	7.9	27.3	3.64	5.43	9.81	0.21	b.d.l.	5.44	3.69	7.10	1.84	5.5
SpW2-IV	31-07-2012	2.20	8.2	23.1	3.44	6.75	13.35	0.18	b.d.l.	5.38	5.50	9.80	1.91	4.9
SpW3-IV	31-07-2012	2.58	8.0	23.3	5.14	5.35	17.22	0.07	b.d.l.	9.18	4.78	9.15	3.18	5.5
SW1-IV	31-07-2012	2.25	8.2	18.6	4.44	5.27	13.99	0.17	b.d.l.	6.82	4.35	8.31	3.07	5.7
SW2-IV	31-07-2012	4.23	8.2	16.7	9.28	12.01	23.51	0.13	b.d.l.	7.57	16.47	22.00	0.86	-4.3
SW3-IV	31-07-2012	3.31	8.1	17.2	7.09	8.64	19.14	0.16	b.d.l.	7.01	10.30	15.08	1.94	2.0
SW4-IV	31-07-2012	3.36	8.2	17.5	7.29	8.64	19.34	0.15	b.d.l.	7.11	10.40	15.02	1.89	2.8
SW5-IV	31-07-2012	1.03	8.1	22.6	3.84	1.97	4.58	0.06	0.12	5.38	1.44	3.37	0.16	−0.2
SW6-IV	31-07-2012	2.48	7.9	20.0	8.98	7.24	13.01	0.12	b.d.l.	6.52	13.28	7.38	0.54	5.7

b.d.l.: below detection limit. C.B.: charge balance.

The Cl^- vs. SO_4^{2-} plot (Fig. 5B) shows the strong correlation between both solutes, suggesting an origin from the same source, i.e., high salinity Tertiary materials, as inferred in the soil leaching experiments. The molar ratio Ca^{2+}/SO_4^{2-} (Fig. 5C) ranged from 8.0 to 0.4, showing a clear decrease with salinity. Since average values in precipitation and irrigation water were around 4.9 either supplementary sulfate sources apart from gypsum or Ca^{2+} sinks (or both) are required to explain such a decrease. A similar pattern was observed for the ratio $(Ca^{2+} + Mg^{2+})/SO_4^{2-}$ (not shown), which also decreases with increasing salinity towards a value of 1.0. In fact, the plot SO_4^{2-} vs. $(Ca^{2+} + Mg^{2+})$ (Fig. 5D) presented a strong correlation coefficient ($R^2 = 0.89$) with a better fit equation of $(Ca^{2+} + Mg^{2+}) = 1.14 \cdot SO_4^{2-} + 2.51$. This indicates that similar amounts (in molar ratios) of $Ca^{2+} + Mg^{2+}$ and SO_4^{2-} (slope of

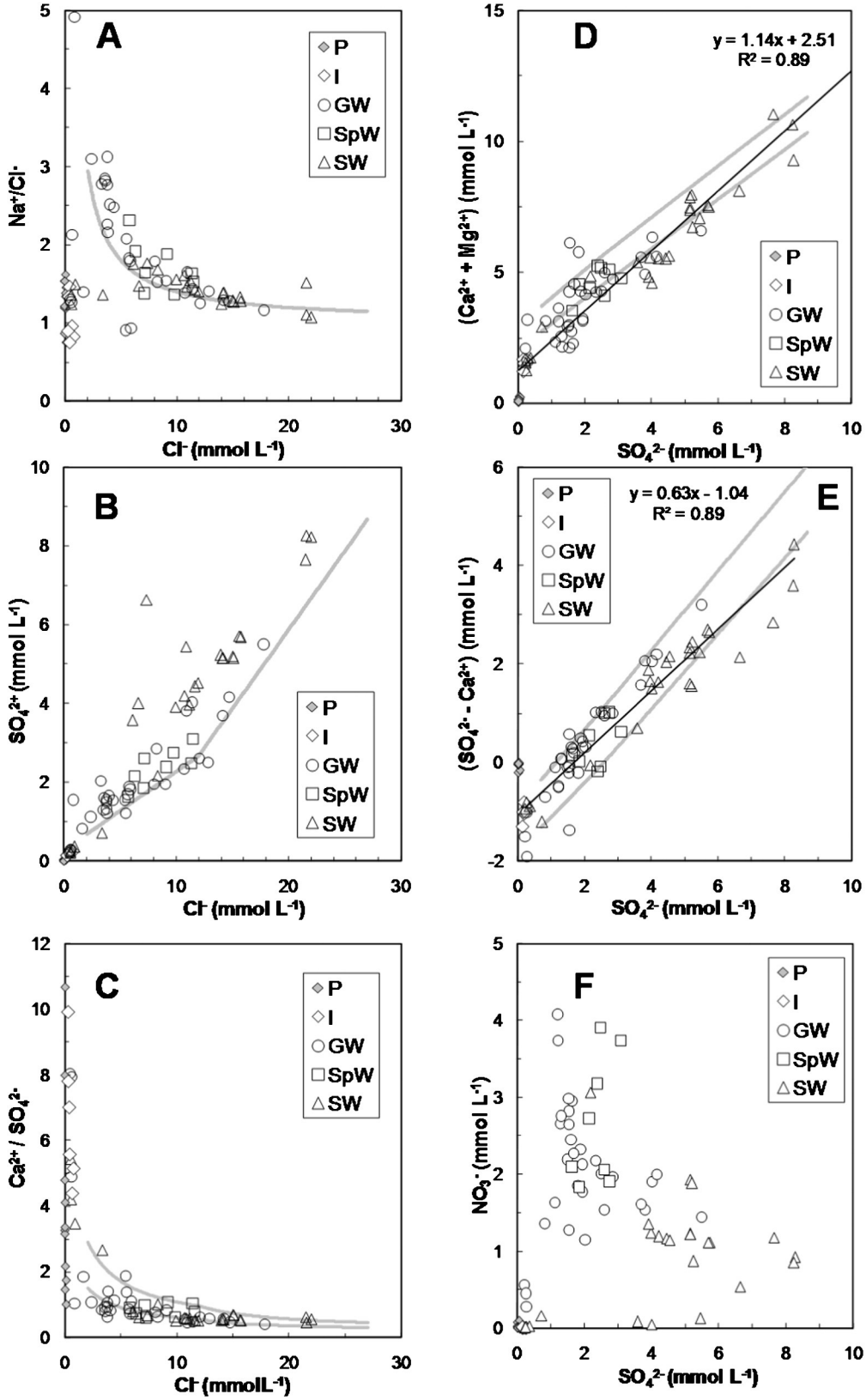

Fig. 5. Ionic ratio evolution with the increase in salinity, indicated by both chloride and sulfate. The gray line represents the geochemical evolution simulated with PHREEQC. Legend: P: precipitation; I: Irrigation; GW: groundwater; SpW: spring water; SW: surface water. When two lines are presented, they cover a range of partial pressures of CO_2 (from $10^{-2.5}$ to 10^{-3}) used in the simulations.

1.14) are being added to the water. The value for zero sulfate (intercept of 2.51) responds to the high Ca^{2+} low SO_4^{2-} irrigation or precipitation water.

The molar ratio $(Ca^{2+} + Mg^{2+})/HCO_3^-$ (not shown) ranged from 0.7 to 3.3, and it increased with salinity, which indicates a supplementary source of $Ca^{2+} + Mg^{2+}$ with respect to HCO_3^-, probably the dissolution

of non-carbonate minerals rich in Ca^{2+} and Mg^{2+} (e.g., gypsum, epsomite). The enrichment in these components may also be related to the addition of mineral fertilizers, as Ca^{2+} and Mg^{2+} are reported to suffer significant increases in areas under extensive application of synthetic fertilizers (Moussa et al., 2011; Stigter et al., 2006).

The plot ($Ca^{2+} + Mg^{2+} - SO_4^{2-} - HCO_3^-$) vs. ($Na^+ + K^+ - Cl^-$) (not shown) examines the excess of Ca^{2+} and Mg^{2+} gained or lost from gypsum, calcite and dolomite dissolution/precipitation, and the excess of Na^+ and K^+ gained or lost from sodium and potassium chlorides dissolution/precipitation, respectively. When dissolution of these minerals is enough to explain the hydrochemical composition, the samples plot around the origin. In the Lerma Basin waters, the samples presented a distribution so that a decrease in ($Ca^{2+} + Mg^{2+} - SO_4^{2-} - HCO_3^-$) was observed with increases in ($Na^+ + K^+ - Cl^-$), what suggests the existence of important cationic exchange or silicate weathering processes (Jalali, 2005, 2007).

The plot SO_4^{2-} vs. ($SO_4^{2-} - Ca^{2+}$) (Fig. 5E) displays the amount of SO_4^{2-} exceeding Ca^{2+} contents. Assuming that all the SO_4^{2-} has its origin in gypsum dissolution, this plot represents the amount of Ca^{2+} removed by either ionic exchange or calcite precipitation. In waters with very low salinity, the negative values belong to the high Ca^{2+} low SO_4^{2-} Ca^{2+}-HCO_3^- irrigation water type. A slope of ca. 0.6 with increasing salinity suggests that around half of the Ca^{2+} incorporated in gypsum dissolution may be lost through exchange reactions, calcite precipitation or both.

The evolution of previous ratios could be explained by the dissolution of gypsum in waters previously saturated with respect to calcite, with the consequent incongruent dissolution of dolomite (Kehew, 2001). The addition of Ca^{2+} will produce the precipitation of calcite (removing part of the Ca^{2+} added) and the concomitant dissolution of dolomite (adding Mg^{2+} to the water). Another explanation can be related to the hypothetical presence of Mg^{2+}-bearing mineral (e.g., epsomite) or the addition of Mg^{2+} through fertilization.

Finally, the plot SO_4^{2-} vs. NO_3^- (Fig. 5F) showed a lack of relationship between these two solutes, which may suggest different sources for them (Li et al., 2006). Many earlier studies have related high SO_4^{2-} levels to agricultural activities (e.g., Moussa et al., 2011; Kim et al., 2005; Sánchez et al., 2007) by means of its relationship to nitrate pollution, although there are cases in which this pattern is not present. However, the amount of sulfate originated in agricultural activities in the Lerma Basin waters seems to be negligible in comparison with that provided by the geological materials in the study area.

Thus, through the use of the ionic ratios the main processes controlling the evolution of the Lerma Basin water have been inferred. Cation exchange processes are probable, especially in the first phases of the geochemical evolution, i.e., the percolation through soils and the early stages of circulation in the Quaternary aquifers. After this, a pattern controlled by the dissolution of both halite and gypsum may explain the later phases in the geochemical evolution. Dissolution of gypsum probably triggers calcite precipitation and the concomitant dolomite dissolution, although dolomite dissolution kinetics is slow in comparison with the remaining processes and other magnesium sources can participate. The information generated in this section will be used later (saturation indexes and geochemical modeling) to test if these processes are thermodynamically feasible.

4.4. Speciation-solubility calculations

Speciation-solubility calculations provided the saturation indexes (SI) of several mineral phases (calcite, dolomite, gypsum and halite) and the CO_2(g) partial pressure in the different water samples of the Lerma Basin (Fig. 6).

Precipitation waters were highly undersaturated (SI < 0) with respect to all the considered mineral phases. However, irrigation waters were oversaturated (SI > 0) with respect to calcite and dolomite (Fig. 6A and 6B) whereas they were undersaturated (SI < 0) with respect to gypsum and halite (Fig. 6C and 6D). Irrigation waters came from a surface water reservoir in the Pyrenean Range with many carbonate aquifers in its recharge area. The conveyance of these waters in surface canals favors its degasification, which explains the oversaturation of these waters with respect to the carbonate minerals.

Significant differences were observed between ground- and surface waters. Most of them were in equilibrium or oversaturated with respect to calcite and dolomite (Fig. 6A and 6B), although SI values were slightly higher for surface waters (e.g., calcite $SI_{average}$ is 0.27 for groundwater and 0.93 for surface water). The same happens with respect to gypsum and halite, although both, ground- and surface waters, are undersaturated (SI < 0) the SI values were higher for surface waters (e.g., gypsum $SI_{average}$ is −1.6 for groundwater and −1.2 for surface waters; Fig. 6C and 6D). Calcite and dolomite SI were independent of EC, whereas gypsum and halite SI tend to increase with EC, pointing to the dissolution of these minerals as one of the reasons for the increase of salinity. In both cases, spring waters had an intermediate value between ground- and surface waters.

The partial pressure of CO_2(g) (pCO_2) shows significant differences between ground- ($pCO_{2\text{-average}} = 10^{-2.3}$), spring ($pCO_{2\text{-average}} = 10^{-2.6}$) and surface waters ($pCO_{2\text{-average}} = 10^{-2.9}$) (Fig. 6E). As expected, the values were higher in the groundwaters due to the presence of organic matter in soils, roots respiration and microbial decomposition (Kehew, 2001). A pattern of lower CO_2 with higher SI for calcite was inferred (Fig. 6F) suggesting degasification of the water in the flow from ground- to surface waters. Surface waters show values closer to equilibrium with atmospheric CO_2 but still higher than those of the atmospheric partial pressure, indicating that these waters will still lose CO_2 and, probably, precipitate calcite.

In summary, the results obtained for the saturation indexes and the pCO_2 supported the geochemical processes inferred previously, especially regarding gypsum and halite dissolution and calcite precipitation, which are thermodynamically favored.

4.5. Multivariate statistical analysis

4.5.1. Principal component analysis (PCA)

PCA results indicated that two components explained most of the variance (82%, Fig. 7). Component 1 had high loadings for SO_4^{2-}, Cl^-, Mg^{2+}, Ca^{2+} and Na^+, while it had moderate loadings for HCO_3^- and pH. It had insignificant loadings for NO_3^- and K^+. Component 1 can be interpreted as indicating the salinization occurring in the Lerma Basin waters, mainly through the dissolution of minerals bearing the above mentioned components. This component explained 68.8% of the dataset variance.

Component 2 appeared to be related to nitrate contamination as the NO_3^- loading was clearly higher than any other (Fig. 7). Also high loadings were detected for K^+, which can be related to the join application of nitrogen and potassium fertilizers (NPK, Otero et al., 2005). In addition, Component 2 presented moderate loadings of HCO_3^-, pH and Na^+. This factor explained 13.2% of the dataset variance. Those variables that presented high loadings for Component 2 presented low values for Component 1, and vice versa. This suggested independence in the processes controlling the geochemical evolution.

Thus, the main conclusion obtained after the PCA application was the isolation of the processes regarding the main problems in the study area, i.e., the salinization and nitrate pollution processes. Whereas the salinization process explained most of the variability in the dataset, it was not related to nitrate pollution and, as a consequence, to fertilizers applied in agriculture. Thus, nitrate pollution does not seem to affect the contents of dissolved solids in this study zone. These results contrast with those of Nakano et al. (2008) or Moussa et al. (2011), among others, who reported a relationship between salinization and nitrate pollution processes in agricultural areas in Japan and Tunisia, respectively. However, Lorite-Herrera et al. (2008) reported a case for the hydrogeochemistry of a regional alluvial aquifer in the Guadalquivir

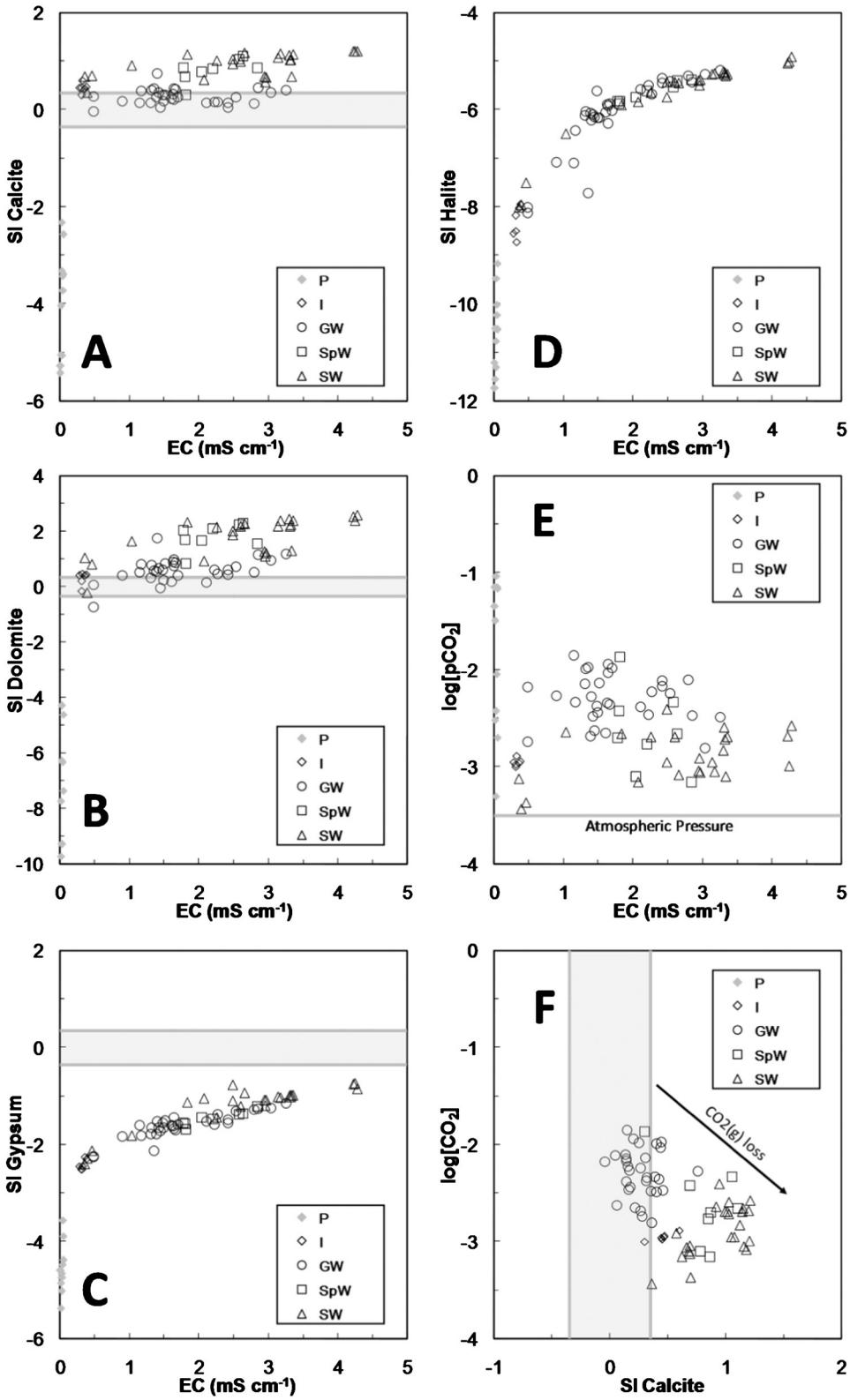

Fig. 6. Evolution with salinity (indicated as electrical conductivity) of saturation indexes of calcite (A), dolomite (B), gypsum (C), halite (D) and partial pressure of CO_2 (E). Partial pressure of CO_2 against calcite saturation index (F). Legend: P: precipitation; I: irrigation; GW: groundwater; SpW: spring water; SW: surface water. The shaded areas indicate the ranges of uncertainty for the calculated saturation indexes; ±0.22 for gypsum (Langmuir and Melchior, 1985), ±0.35 for calcite and ±0.5 for dolomite (Plummer et al., 1990).

River Basin (Spain) where salinization processes were not related to nitrate pollution. Thus, the relationship between salinization and nitrate pollution seems to depend on the specific characteristics of the study zone, with the expected influence of the natural salinity of the area. Apparently, the higher the natural salinity, the lower the influence of agriculture in the salinization of water bodies. However, the

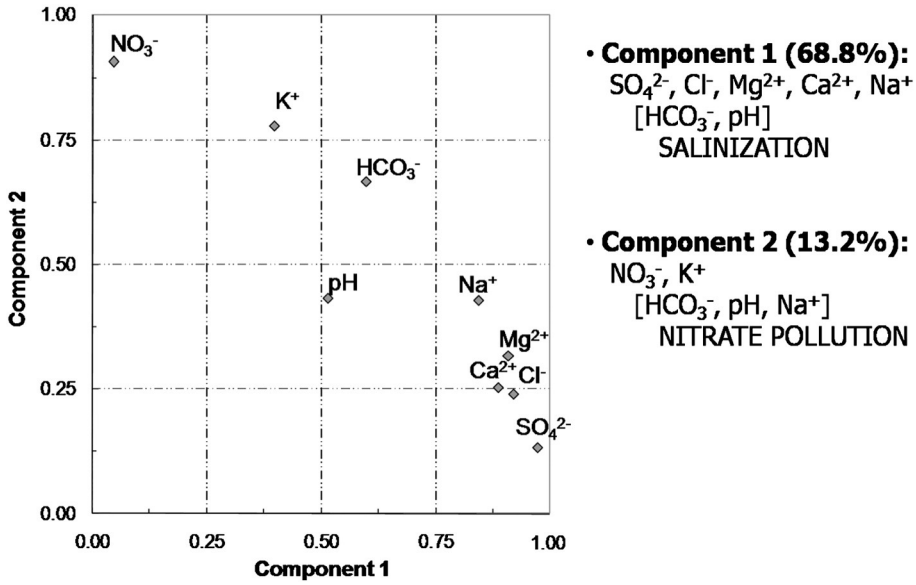

Fig. 7. Component loading diagrams for variables obtained after principal component analysis for Component 1 and Component 2. Variance of dataset explained, variables with high loading and moderate loading (in brackets) and main related process.

influence of salts provided by agriculture should be considered in low-salinity water bodies.

4.5.2. Hierarchical cluster analysis (HCA)

HCA results allowed the association of the Lerma Basin samples in two different branches (Fig. 8). Branch 1 grouped the recharge waters, and was divided into two sub-branches. Branch 1.1 included all the samples of the precipitation water (P) whereas Branch 1.2 included all the samples of irrigation water (I) along with several samples of groundwater and a sampling point of surface water. These ground- and surface water samples were highly influenced by the recharge water. The SW5 sampling point is located in an area dominated by low salinity Quaternary materials and it is close to the irrigation canal, probably receiving some seepage from it (Fig. 1). Samples in branch 1.2 of wells GW3, GW4 and GW5 correspond to the irrigated season, when the aquifer is highly influenced by the recharge of irrigation water (Fig. 8).

Branch 2 grouped most of the collected samples (69%) and it had two different subgroups. Branch 2.1 included most of the groundwater samples collected and all the spring samples, which was coherent since non-significant differences were detected between these two groups and non-significant changes in the water chemistry were found in the groundwater flow lines. Branch 2.2 included most of the surface water samples, which had a higher salinity in general, along with several groundwater samples (locations GW12 and GW6). These wells were located in the vicinity of the more gypsum-rich layer in the basin, which can explain its enrichment in salts and its similarity to the surface water (Fig. 1).

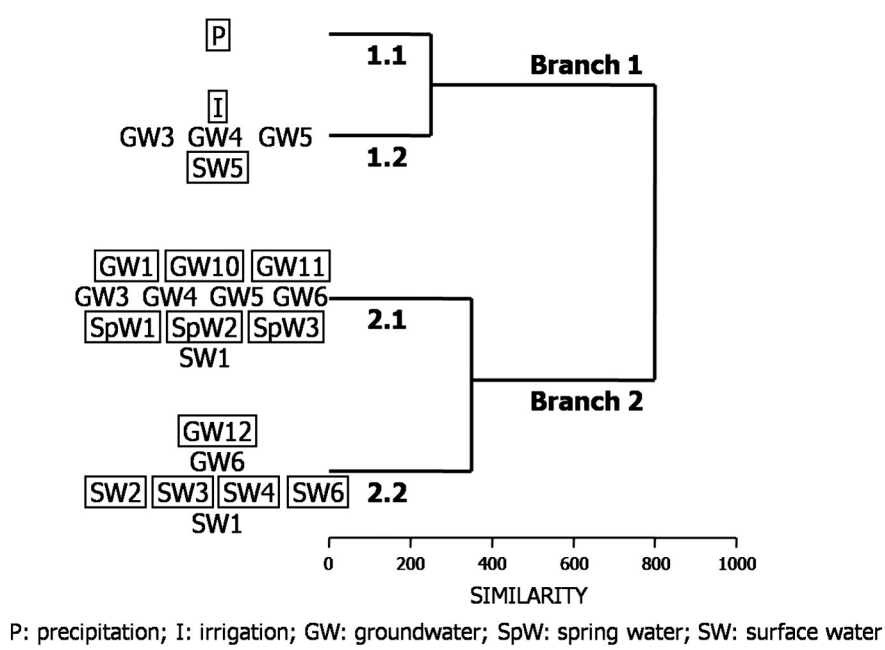

Fig. 8. Simplified results from hierarchical cluster analysis (HCA). For a better visualization, only clustering of similarities above 200 and sampling points (instead of individual samples) are shown. Sampling point names surrounded by a rectangle are the ones for which every single sample falls into the displayed grouping.

The cluster analysis provided several important results regarding the hydrological behavior of the Lerma Basin waters. The existence of irrigation canal seepage was detected by the identification of a surface water location in a group highly influenced by irrigation water. Moreover, high hydrochemical similarity was detected between ground- and spring water, which was in agreement with other observations in the ion–ion ratios or in the statistical comparisons. Groundwaters in some areas of the study zone, mainly southern glacis water body, where the nodular gypsum strata severely affects water quality, presented higher salt contents, providing a higher salinity to the waters in these areas of the basin. This fact is in line with the main hypothesis, which suggests that the geological set up controls the salinization processes in this area.

4.6. Geochemical modeling

4.6.1. Inverse modeling

Taking into account all the feasible mineral phases inferred in the previous sections, mass balance calculations were performed using PHREEQC software. The global uncertainty of analytical results was limited to 5%. The more simplistic models coherent with the observations made in previous sections of the study were selected. The possible processes considered in the mass balance include:

- Evapotranspiration of water with no dissolved content (only in those balances in which the initial water was precipitation or irrigation water).
- Dissolution of halite, gypsum and epsomite.
- Calcite precipitation.
- Dolomite dissolution.
- $CO_2(g)$ exchange.
- Cation exchange.
- NO_3^- sources/sinks.

Mass balance calculations were performed between water samples located in feasible flow lines, i.e., from precipitation and irrigation waters to groundwaters, from ground- to spring waters and from spring to surface waters. This approach assumes that surface water origin is mainly from springs and seepages coming from groundwater, which can be justified since intermittent streams became perennial streams after the implementation of irrigation in the Lerma Basin (Merchán et al., 2013). In most of the flow lines, the results gave the dissolution of either gypsum or epsomite to fit the sulfate concentration in the mass balance (Table 4). When gypsum was used, the addition of Ca^{2+} made necessary that higher amounts of calcite precipitate and dolomite dissolve to fit the concentrations of Ca^{2+} and Mg^{2+}. When epsomite was used, lower calcite precipitation and dolomite dissolution were required. A situation between these two extremes is probably happening in the Lerma Basin waters.

As an example, a flow line in the hydrological system is represented by samples I → GW11 → GW10 → SpW2 → SW3, i.e., irrigation water applied to the crops infiltrates and flows through the glacis until it reaches the Tertiary materials, where it seeps out to the surface. There, it follows a diffuse flow until it reaches the gullies (Fig. 9). Geochemical mass balance results for this flow line are shown in Table 4. The calculations correspond to the data from the sampling campaign on July 27th 2011, during the irrigation season, but they are also representative of those observed in other sampling dates.

According to these results, the groundwater chemical composition (I → GW11 in the example in Table 4) could be explained by the combination of the following processes: evapotranspiration of precipitation or irrigation water, cation exchange, halite and gypsum/epsomite dissolution, $CO_2(g)$ input and dissolution of NO_3^- from fertilizers.

Along the groundwater flow (GW11 → GW10 → SpW2 in the example in Table 4), the net geochemical reactions include the dissolution of small amounts of halite and gypsum/epsomite, and the addition of nitrate leached from agricultural soils. The degasification of $CO_2(g)$-enriched groundwater takes place at the inter-phase between groundwaters and surface waters, which produces the precipitation of calcite.

Finally, when the seeped groundwater reaches the surface drainage network (SpW2 → SW3 in the example in Table 4), the net geochemical reactions include the dissolution of important amounts of halite and gypsum/epsomite, with the consequent precipitation of calcite and dissolution of dolomite. The losses of nitrate are also significant processes in this step.

The mass balance approach supported the processes exposed in the previous sections. Thus, the main geochemical reactions required included: the evapotranspiration of 64%–81% of irrigation water (values in the range of those reported for irrigation efficiency in the study area by Abrahão et al., 2011a, 72%), the addition of $CO_2(g)$ (probably from soil respiration processes, Kehew, 2001), the cation exchange (mainly during the first part of the flow line) and the dissolution of halite and gypsum/epsomite. The dissolution of gypsum triggers the concomitant precipitation of calcite/dissolution of dolomite (e.g., Appelo and Postma, 2005). The enrichment in $CO_2(g)$ produced in soils is partially lost when the groundwater reaches the springs and gets into contact with the atmosphere. Finally, nitrate increases during the whole groundwater flow line and suffers a significant decrease in the surface waters. Merchán et al. (2014), proposed a combination of dilution with upstream waters and denitrification in diffuse surface flow paths as a probable explanation for the lower NO_3^- concentrations observed in surface waters in the Lerma Basin.

4.6.2. Direct modeling

The geochemical evolution of irrigation water was simulated by direct modeling with PHREEQC in order to confirm the main processes detected. The steps followed in this simulation are reported in Fig. 9. The simulations were performed with a fixed saturation index for calcite ($SI_{calcite} = 1.2$) which is around the maximum observed in the Lerma Basin waters. Additional tests were simulated using different

Table 4
Inverse modeling results (PHREEQC) after a mass balance between sampled points in a representative flow line during the irrigation season (July 27th 2011). In mass balances with two columns, results considering either gypsum (a), or both epsomite and gypsum (b), are presented. Positive values means mass entering water, negative values means mass leaving water and no value means no mass transfer.

Phases	I → GW11		GW11 → GW10	GW10 → SpW2	SpW2 → SW3	
(mmol L^{-1})	(a)	(b)			(a)	(b)
Halite			4.85	0.92	9.00	9.01
Gypsum	0.65			0.48	3.87	2.21
Epsomite		0.64				1.66
NaX	1.76	1.74	1.01			
CaX_2	−0.88	−0.87	−0.51			
$CO_2(g)$	0.64	0.65		−1.30	0.78	0.78
Calcite	−1.18	0.00		−0.31	−4.05	−0.73
Dolomite	1.08	0.49	0.43		1.66	0.00
NO_3^-	0.68	0.67	0.84	0.45	−1.61	−1.61
H_2O (mol L^{-1})	−25.20[a]	−25.54[a]				

[a] Implies c.a. 46% evapotranspiration.

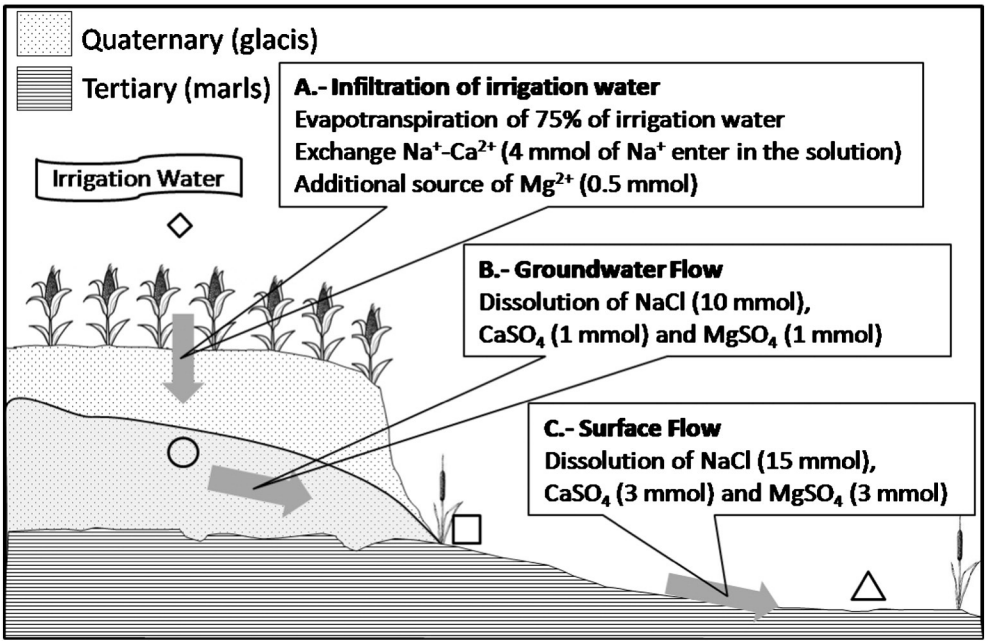

Fig. 9. Conceptual model with performed simulations in the Lerma Basin through PHREEQC. Diamond, circle, square and triangle indicate irrigation, ground, spring and surface waters respectively.

pCO_2 conditions covering the range observed in the Lerma Basin waters ($10^{-2.0}$ and $10^{-2.5}$). The modeling steps start with the infiltration of irrigation water in the aquifer (A, Fig. 9), then the enrichment in salts in groundwater (B, Fig. 9), and finally a higher enrichment in salts during the surface flow (C, Fig. 9). The proportions of solutes have been selected to match the observations from the mass balance results.

The theoretical results of these simulations are included in the previously discussed ionic ratio plots with the real measured data (gray lines in Fig. 5). They indicate that the combination of the processes inferred in previous sections reproduces fairly well the geochemical evolution of the dataset, underpinning confidence in the proposed processes.

Nitrification of non-nitrate fertilizers or denitrification have not been considered in this simulation, although in some studies significant changes in water geochemistry have been reported as a consequence of these processes (e.g., Kim et al., 2005; Koh et al., 2007). However, the fact that a rather good reproduction of the geochemical evolution can be achieved without considering NO_3^- pollution in the geochemical model supports our hypothesis on the independence of the salinization and nitrate pollution processes in this specific study case.

Consequently, our study suggests that the main factor controlling water salinization processes is the geological setup, while the anthropogenic influence seems to play a negligible influence compared to the natural processes. Therefore, the main possible remediation strategies should be linked to an adequate management of irrigation water to decrease the salt loads to downstream waters (Abrahão et al., 2011b; Duncan et al., 2008; García-Garizábal et al., 2009). However, the enrichment in inorganic ions (Na^+, Cl^-, Ca^{2+}, Mg^{2+} and SO_4^{2-}) is not the major component of agricultural pollution. Those components provided exclusively by agricultural pollution, such as NH_4^+, organic carbon or phosphate were not included in this study. Nevertheless, the influence of these other components in water salinity is expected to be negligible.

5. Conclusions

In this work, the geochemical processes affecting water salinization in an irrigated basin were studied through a multidisciplinary approach including laboratory and field data, statistics and modeling. All the information collected pointed to the natural control of salinization processes with non-significant influence of anthropogenic factors.

Among all the soils in the study zone, those developed over the Tertiary materials are the main providers of salts to the waters. The dissolution of halite and gypsum, along with cation exchange, are the main processes that increase water salinity. They generate a significant increase in salinity from recharge (precipitation and irrigation) to discharge water (surface water at the outlet of the basin), with consequent decrease in water quality.

Groundwater is in equilibrium with calcite and dolomite, but highly undersaturated with respect to gypsum and halite. Under these conditions, the dissolution of gypsum probably forces the precipitation of calcite and the concomitant dolomite dissolution. Surface water is oversaturated with respect to both calcite and dolomite, as a consequence of surface water degasification, but still undersaturated with respect to gypsum and halite.

Multivariate analysis suggests independence of the processes controlling water salinization and nitrate pollution, from natural and anthropogenic controls, respectively. Apart from recharge waters, two groups of waters are differentiated: ground- and spring water; and surface waters, with lower and higher salinity, respectively.

Finally, the hypotheses about geochemical reactions and the independence of nitrate pollution and salinization were confirmed through the use of modeling tools, supporting the predominance of natural processes controlling salinization in the Lerma Basin waters.

Acknowledgments

This work was performed within the framework of projects CGL-2009-13410-C02-01 (Spanish Ministry of Economy and Competitiveness) and CGL-2012-32395 (Spanish Ministry of Economy and Competitiveness–FEDER funds [EU]). Daniel Merchán acknowledges the support of grant BES2010-034124, from the same institution. Additionally, this study forms part of the activities of the Geochemical Modelling Group (Aragón Government and University of Zaragoza). Thanks are also due to Geological Survey of Spain and University of Zaragoza for providing equipment and infrastructure. Finally, we acknowledge the valuable help of Eduardo Garrido, Raphael Abrahão and Mónica Blasco (sampling campaigns), Enrique Oliver (lab support) and Begoña del Moral (X-ray diffractions). We also appreciate the thoughtful comments

of three anonymous reviewers, which greatly increased the quality of the manuscript.

References

Abrahão R, Causapé J, García-Garizábal I, Merchán D. Implementing irrigation: water balances and irrigation quality in the Lerma basin (Spain). Agric Water Manag 2011a;102:97–104.
Abrahão R, Causapé J, García-Garizábal I, Merchán D. Implementing irrigation: salt and nitrate exported from the Lerma basin (Spain). Agric Water Manag 2011b;102:105–12.
Acero P, Gutiérrez F, Galve JP, Auqué LF, Carbonel D, Gimeno MJ, et al. Hydrochemical characterization of an evaporite karst area affected by sinkholes (Ebro Valley, NE Spain). Geol Acta 2013;11(4):389–407.
Adams S, Titus R, Pietersen K, Tredoux G, Harris C. Hydrochemical characteristics of aquifers near Sutherland in the Western Karoo, South Africa. J Hydrol 2001;241:91–103.
AEMET (Agencia Estatal de Meteorología). Datos climatológicos (in Spanish). Spain: Gobierno de España, Ministerio de Alimentación, Agricultura y Medio Ambiente. www.aemet.es, 2014. [accessed 2nd July 2014].
Appelo CAJ, Postma D. Geochemistry, groundwater and pollution (2nd edition). The Netherlands: Leiden; 2005. 649 pp.
Ayers RS, Westcot DW. Water quality for agriculture. FAO Irrigation and Drainage Paper No. 29. Rome, Italy: Food and Agriculture Organization of the United Nations; 1992. p. 174.
Beltrán A. Estudio de suelos de la zona regable de Bardenas II. Sectores: VIII, XI, X, XII y XIII. Instituto Nacional de Reforma y Desarrollo Agrario. Spain: Ministerio de Agricultura, Pesca y Alimentación; 1986.
Cameron EM. Hydrogeochemistry of the Fraser River, British Columbia: seasonal variation in major and minor components. J Hydrol 1996;182:209–25.
Carol E, Kruse E, Mas-Pla J. Hydrochemical and isotopical evidence of ground water salinization processes on the coastal plain of Samborombón Bay, Argentina. J Hydrol 2009;365(3–4):335–45.
Carreira PM, Marques JM, Nunes D. Source of groundwater salinity in coastline aquifers based on environmental isotopes (Portugal): natural vs. human interference. A review and reinterpretation. Appl Geochem 2014;41:163–75.
Causapé J, Auqué L, Gimeno MJ, Mandado J, Quílez D, Aragüés R. Irrigation effects on the salinity of the Arba and Riguel Rivers (Spain): present diagnosis and expected evolution using geochemical models. Environ Geol 2004a;45:703–15.
Causapé J, Quílez D, Aragüés R. Assessment of irrigation and environmental quality at the hydrological basin level — I. Irrigation quality. Agric Water Manag 2004b;70:195–209.
Chaudhuri S, Ale S. Long term (1960–2010) trends in groundwater contamination and salinization in the Ogallala aquifer in Texas. J Hydrol 2014;513:376–90.
Davis JC. Statistics and data analysis in geology. New York: Wiley; 1986. 646 p.
Duncan RA, Bethune MG, Thayalakumaran T, Christen EW, McMahon TA. Management of salt mobilisation in the irrigated landscape — a review of selected irrigation regions. J Hydrol 2008;351:238–52.
Edmunds WM. Geochemistry's vital contribution to solving water resource problems. Appl Geochem 2009;24(6):1058–73.
Evans CD, Davies TD, Wigington Jr PJ, Tranter M, Krester WA. Use of factor analysis to investigate processes controlling the chemical composition of four streams in the Adirondack Mountains, New York. J Hydrol 1996;185:297–316.
Fetter Jr CW. Applied hydrogeology. 3rd ed. New York: Prentice-Hall Publishing Co.; 2001. p. 691.
García-Garizábal I, Causapé J, Abrahão R. Evolution of the efficiency and agro-environmental impact of a traditional irrigation land in the middle Ebro Valley (2001–2007). Span J Agric Res 2009;7(2):465–73.
García-Garizábal I, Gimeno MJ, Auqué LF, Causapé J. Salinity contamination response to changes in irrigation management — application of geochemical codes. Span J Agric Res 2014;12(2):376–87.
Hair J, Anderson R, Tatham R, Black W. Análisis Multivariante. Madrid: Prentice Hall Iberia; 1999. 832 pp.
Han D, Song X, Currell MJ, Cao G, Zhang Y, Kang Y. A survey of groundwater levels and hydrogeochemistry in irrigated fields in the Karamay Agricultural Development Area, northwest China: implications for soil and groundwater salinity resulting from surface water transfer for irrigation. J Hydrol 2011;405(3–4):217–34.
Helsel DR, Hirsch RM. Statistical methods in water resources. Techniques of water resources investigations, Book 4, Chapter A3. Reston, VA: US Geological Survey; 2002. p. 510.
Isidoro D, Quílez D, Aragüés R. Environmental impact of irrigation in La Violada District (Spain): I. Salt export patterns. J Environ Qual 2006;35:766–75.
ITGE. Mapa geológico de España. Ejea de los caballeros (map and memory). No. 284 27-12. Madrid: Instituto Tecnológico Geominero de España; 1988.
Jalali M. Assessment of the chemical components of Fameningroundwater, western Iran. Environ Geochem Health 2005;29:357–74.
Jalali M. Major ion chemistry of groundwaters in the Bahar area, Hamadan, western Iran. Environ Geol 2007;47:763–72.
Johansson O, Aimbetov I, Jarsjö J. Variation of groundwater salinity in the partially irrigated Amudarya River delta, Uzbekistan. J Mar Syst 2009;76(3):287–95.
Kehew AE. Applied chemical hydrogeology. Prentice Hall Inc.; 2001 [368 pp.].
Kelly WP. Use of saline irrigation water. Soil Sci 1963;95:385–91.
Kim K, Rajmohan N, Kim H-J, Kim S-H, Hwang G-S, Yun S-T, et al. Evaluation of geochemical processes affecting groundwater chemistry based on mass balance approach: a case study in Namwon, Korea. Geochem J 2005;39:357–69.
Koh D-C, Ko K-S, Kim Y, Lee S-G, Chang H-W. Effect of agricultural land use on the chemistry of groundwater from basaltic aquifers, Jeju Island, South Korea. Hydrogeol J 2007;15:727–43.
Kume T, Akca E, Nakano T, Nagano T, Kapur S, Watanabe T. Seasonal changes of fertilizer impacts on agricultural drainage in a salinized area in Adana, Turkey. Sci Total Environ 2007;408:3319–26.
Langmuir D, Melchior D. The geochemistry of Ca, Sr, Ba and Ra sulfates in some deep brines from the Paulo Duro Basin, Texas. Geochim Cosmochim Acta 1985;49:2423–32.
Li X-D, Masuda H, Kusakabe M, Yanagisawa F, Zeng H-A. Degradation of groundwater quality due to anthropogenic sulfur and nitrogen contamination in the Sichuan Basin, China. Geochem J 2006;40:309–32.
Lorite-Herrera M, Jiménez-Espinosa R, Jiménez-Millán J, Hiscock KM. Integrated hydrochemical assessment of the Quaternary alluvial aquifer of the Guadalquivir River, southern Spain. Appl Geochem 2008;23:2040–50.
Menció A, Folch A, Mas-Pla J. Identifying key parameters to differentiate groundwater flow systems using multifactorial analysis. J Hydrol 2012;472–473:301–13.
Merchán D, Causapé J, Abrahão R. Impact of irrigation implementation on hydrology and water quality in a small agricultural basin in Spain. Hydrol Sci J 2013;58(7):1400–13.
Merchán D, Otero N, Soler A, Causapé J. Main sources and processes affecting dissolved sulphates and nitrates in a small irrigated basin (Lerma Basin, Zaragoza, Spain): isotopic characterization. Agric Ecosyst Environ 2014;195:127–38.
Morán-Tejeda E, López-Moreno JI, Ceballos-Barbancho A, Vicente-Serrano SM. River regimes and recent hydrological changes in the Duero basin (Spain). J Hydrol 2011;404:241–58.
Moussa AB, Zouari K, Marc V. Hydrochemical and isotope evidence of groundwater salinization processes on the coastal plain of Hammamet-Nabeul, north-eastern Tunisia. Phys Chem Earth 2011;36:167–78.
Nakano T, Tayasu I, Yamada Y, Hosono T, Igeta A, Hyodo F, et al. Effect of agriculture on water quality of Lake Biwa tributaries, Japan. Sci Total Environ 2008;389:132–48.
Nielsen DL, Brock MA, Rees GN, Baldwin DS. Effects of increasing salinity on freshwater ecosystems in Australia. Aust J Bot 2003;51:655–65.
Otero N, Vitòria L, Soler A, Canals A. Fertiliser characterization: major, trace and rare earth elements. Appl Geochem 2005;20:1473–88.
Parkhurst DL, Appelo CAJ. User's guide to PHREEQC (version 2.0) — a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. Water-resources investigations report 99-4259. Denver, Colorado, USA: US Geological Survey; 1999. p. 326.
Peck AJ, Hatton T. Salinity and the discharge of salts from catchments in Australia. J Hydrol 2003;272:191–202.
Plummer N, Busby J, Lee R, Hanshaw B. Geochemical modelling of the Madison aquifer in parts of Montana, Wyoming, and South Dakota. Water Resour Res 1990;26:1981–2014.
Richter BC, Kreitler CW. Identification of sources of ground-water salinization using geochemical techniques. Oklahoma: U.S. Environmental Protection Agency. Ada; 1991. 273 pp.
Sánchez D, Vadillo I, Carrasco F, Mancera E. Contamination by agricultural-origin nitrogen compounds within a porous multilayer aquifer in southern Spain. In: Candela L, Vadillo I, Aagaard P, Bedbur E, Trevisan M, Vanclooster M, Viotti P, López-Geta JA, editors. Water pollution in natural porous media at different scales. Assessment of fate, impact and indicators. Instituto Geológico y Minero de España; 2007.
Soil Survey Staff. Keys to soil taxonomy. 12th ed. United States Department of Agriculture — Natural Resources Conservation Service; 2014.
Statpoint Technologies. Statgraphics Centurion XVI. User manual. StatPoint Technologies Inc.; 2009. p. 297.
Stigter TY, Carvalho-Dill AMM, Ribeiro L, Reis E. Impact of the shift from groundwater to surface water irrigation on aquifer dynamics and hydrochemistry in a semi-arid region in the south of Portugal. Agric Water Manag 2006;85:121–32.
Tanji K. Agricultural salinity assessment and management. Am Soc Civ Eng 1990;71:619.
Tedeschi A, Beltrán A, Aragüés R. Irrigation management and hydrosalinity balance in a semi-arid area of the middle Ebro river basin (Spain). Agric Water Manag 2001;49:31–50.
van Asten PJA, Barbiéro L, Wopereis MCS, Maeght JL, van der Zee SEATM. Actual and potential salt-related soil degradation in an irrigated rice scheme in the Sahelian zone of Mauritania. Agric Water Manag 2003;60(1):13–32.
Weight WD. Hydrogeology field manual. 2nd ed. USA: McGraw-Hill Companies Inc.; 2008. p. 751.
Yuce G, Pinarbasi A, Ozcelik S, Ugurluoglu D. Soil and water pollution derived from anthropogenic activities in the Porsuk River Basin, Turkey. Environ Geol 2006;49:359–75.
Zhu C, Anderson G. Environmental applications of geochemical modeling. Cambridge University Press; 2002. p. 284.

CHAPTER VII

WATER BALANCES AND IRRIGATION PERFORMANCE

PAPER IV

Merchán, D., Causapé, J., Abrahão, R., García-Garizábal, I. Assessment of a newly implemented irrigated area (Lerma Basin, Spain) over a 10-year period. I: Water Balances and Irrigation Performance. Accepted in *Agricultural Water Management* (April 24th 2015).

Impact factor: 2.333 (JCR 2013).
Quartile and category: Q1 (16/78), Agronomy; Q1 (18/79) Water Resources.

D. Merchán took part in the design of the study, contributed in the data collection, and performed the statistical analysis, data interpretation and writing, with assistance from all co-authors.

ASSESSMENT OF A NEWLY-IMPLEMENTED IRRIGATED AREA (LERMA BASIN, SPAIN) OVER A 10-YEAR PERIOD. I: WATER BALANCES AND IRRIGATION PERFORMANCE

Accepted in Agricultural Water Managemet (April 24th 2015).

D. Merchán[1], J. Causapé[1], R. Abrahão[2], I. García-Garizábal[3]

[1] Geological Survey of Spain – IGME, C/ Manuel Lasala 44 9ºB, Zaragoza, 50006, Spain.
[2] Federal University of Paraíba – UFPB, Cidade Universitária, João Pessoa, Paraíba, 58051-970, Brazil.
[3] Escuela Superior Politécnica del Litoral – ESPOL, Facultad de Ingeniería en Ciencias de la Tierra - FICT. Km. 30.5 Vía Perimetral, Campus Gustavo Galindo, Guayaquil, Ecuador.
Corresponding author: D. Merchán (0034 976 55 52 82; d.merchan@igme.es; eremad@hotmail.com)

Abstract

Implementation of irrigated agriculture is common in semi-arid areas around the world. An assessment of irrigation performance is presented herein for a hydrological basin with an area of 7.38 km^2, representative of pressurized irrigated areas within the Ebro Basin (Spain). The study covers ten hydrological years, comprehending periods before (2004-2005), during (2006-2008) and after (2009-2013) transformation to irrigated land. Water balances were carried out for each of the 55 agricultural plots and for the totality of irrigable area. Once the water balance for the basin is validated, indicators of irrigation performance were obtained from the soil water balances for the vegetative cycle of the crops in each plot. Water balances presented good results, with balance errors below 10.0% for most of the studied years and an error of 1.2% across the entire study period. After implementation of irrigation, irrigation became the main water input to the basin (approximately 60%) whereas actual evapotranspiration accounted for the major output (approximately 70%). Irrigation efficiency reached 76.1%, while the losses of efficiency were due to evaporation and wind drift of sprinkler irrigation (13.5%) and drainage fraction (10.4%). A water deficit of 17.8% was estimated. The irrigation efficiency increased (1.05% $year^{-1}$), while the irrigation drainage fraction decreased (0.95% $year^{-1}$). However, improvements in irrigation performance were not guaranteed as water deficits also increased (0.95% $year^{-1}$). Optimal water use could be achieved through adequate design of irrigation schedules, i.e., irrigation rates adjusted to the requirements of crops and minimization of evaporation and wind drift losses.

Keywords: irrigation efficiency; irrigation drainage fraction; evaporation and wind drift losses; water deficit.

1. Introduction

During the last decades, transformation of rainfed areas into irrigated agriculture areas is a common process reported in several locations around the world (FAO, 2003a). Transformed areas experience an increase in productivity, crop stability and diversity. Hydrological basins with a significant proportion of surface affected by this land use experience changes in hydrological behaviour from quantitative and water quality perspectives (e.g., Abrahão et al., 2011a, 2011b). For example, irrigation return flows play an important role in water balances of hydrological basins, especially in arid and semi-arid climates, where perennial lakes or streams rely on inputs from irrigation return flows (Scott et al., 2011; Merchán et al., 2013).

The progressive water scarcity reported in many areas of the globe implies in a great effort to evaluate all different water uses. Irrigated agriculture is recognised as the main consumer of water resources worldwide (FAO, 2003b). Consequently, studies have addressed the efficiency of water use in irrigated agriculture through several irrigation quality indexes (e.g., Skhiri and Dechmi, 2012; Soto-García et al., 2013).

Quantitative comparison between studies on irrigation efficiency –and other indexes– is difficult, since different definitions are adopted across studies (Lankford, 2012). Definitions range from irrigation efficiency at a plot level (Setegn et al., 2011; Ahadi et al., 2013) to irrigation district level (Jia et al., 2013), or even economic definitions dealing with mass of harvest or income generated by water volume applied (Soto-García et al., 2013). However, in a study area with a long record of data and consistent study methodology, quantitative comparison and assessment of the evolution of irrigation performance is feasible. Even though there are differences in the results produced by different irrigation performance definitions, qualitative comparison between studies may be of use (Lankford, 2012), as an idea of the better irrigation scenarios can be provided.

On-plot irrigation efficiency depends on various on-farm design and management factors such as soil type, field length, crop type, crop cultural practices and irrigation scheduling (Ahadi et al., 2013). Thus, irrigation efficiency is both spatially and temporally variable. Consequently, a standard set of mandatory best management practices (BMP) has no utility, as these BMP should be adapted to the particular study case (Hernández and Uddameri, 2010).

Moreover, it is expected that in its first years of operation, a newly-developed irrigation area would not achieve optimal performance levels that are typical of the utilized irrigation system. Farmers that have been accustomed to different systems (i.e., different agricultural practices such as those developed in rainfed areas) need time to adapt to the new technology and possibilities of irrigated systems. In fact, a similar statement could be made regarding modernization of irrigation structures, such as the shift from flood to pressurized irrigation. In both cases, such evolutions are especially interesting as the

improvement of irrigation performance influences individual farmers (water savings) and the water management authority of the basin (modification of irrigation return flows downstream; Jia et al., 2013). Besides, irrigation performance severely affects the leaching of pollutants from irrigated agriculture (e.g., salts, Duncan et al., 2008; nitrate, Quemada et al., 2013)."

The irrigation performance in Spain has been deeply studied (e.g., Lorite et al., 2004; Farré and Faci, 2009; Salvador et al., 2011; Soto-García et al., 2013), as the climatic conditions and high population density in some areas make water scarcity a great problem. Particularly, irrigated agriculture in the Ebro Basin has received wide attention (Isidoro et al., 2004; Playán et al., 2005; García-Garizabal and Causapé, 2010; Barros et al., 2011; Andrés and Cuchí, 2014).

In this context, the objective of this study was: (i) to assess the changes in the water balance after transformation from rainfed to pressurized irrigated agriculture; and (ii) to study the evolution of irrigation performance during the years after the transformation. This paper presents the first part of a study that also assessed the agro-environmental impact caused by salts and nitrate from this newly-implemented irrigated area.

2. Description of the study area

The study area is the hydrological basin of the Lerma Gully (7.38 km^2, Fig. 1), located on the left side of the Middle Ebro River Valley, in Northeast Spain, in the Arba River Basin. In the early 2010's, the original project was to transform half of its surface in irrigated land, with water originating from the Yesa Reservoir (located in a neighbour hydrological basin, Aragón River Basin). The irrigated surface increased gradually between 2006 and 2013 (Table 1). The main increase was observed between 2006 and 2008, although complete transformation was not reached until 2013 (352 ha), the last year included in this study.

Before implementation of irrigation, the main crops were wheat and barley, which were seeded in winter and harvested in June or July. Production relied on meteorological conditions, with good harvest in wet years. An interruption in cultivation occurred between 2003 and 2005, when construction for the implementation of irrigation took place (new distribution of plots, building of access ways, main pipe network and ponds installation). After the installation of on-farm equipments, maize (44%), barley (12%), sunflower (9%), pea (9%), wheat (7%) and tomato (6%) were the main crops in the area (Table 1). Sprinkler irrigation accounted for 93% of the irrigated surface, with drip irrigation used for the remaining area. Irrigation water rates (average of 5,680 m^3 ha^{-1}) were influenced by the annual crop pattern and its water requirements, as well as by the presence of double cropping (16% of the cultivated surface, on average).

Table 1. Dynamics of the transition into irrigated land for the Lerma Basin.

		2006	2007	2008	2009	2010	2011	2012	2013	Average[a]
Irrigated area	ha	127	269	316	319	322	331	331	352	-
	%[b]	36.1	76.3	89.6	90.5	91.2	93.8	93.8	100	-
Irrigation system	Sprinkler (%)	91.2	97.9	94.5	90.8	90.6	97.5	88.2	90.8	92.6
	Drip (%)	7.8	2.1	5.5	9.2	9.4	2.5	11.8	9.2	7.4
	m^3/ha irrigated	4860	5750	5750	6200	5660	5320	6630	4900	5680
Crops	Summer extensive (%)	71.1	64.2	48.2	65.0	34.9	60.9	57.0	43.2	53.2
	Vegetables (%)	28.9	8.0	21.6	19.7	34.5	17.2	20.7	26.9	22.4
	Winter extensive (%)	0.0	27.8	25.6	9.7	23.2	15.5	18.9	18.2	18.8
	Grass (%)	0.0	0.0	3.7	4.5	5.1	3.9	0.8	9.6	4.0
	Fruit trees (%)	0.0	0.0	0.9	1.1	2.3	2.5	2.6	2.1	1.6
	Maize (%)	64.8	64.3	41.8	49.5	28.2	46.5	44.9	35.9	44.3
	Barley (%)	0.0	17.1	19.0	7.6	10.1	4.6	11.5	15.2	11.6
	Sunflower (%)	6.3	0.0	6.4	15.6	6.7	14.5	12.1	7.2	8.9
	Pea (%)	0.0	0.0	11.8	6.0	21.6	7.9	6.3	6.6	8.7
	Wheat (%)	0.0	10.7	6.6	2.1	13.1	10.9	7.4	3.0	7.2
	Tomatoes (%)	7.8	2.1	5.5	8.1	7.1	0.0	9.2	7.1	5.8
	Broccoli (%)	21.1	2.5	1.7	2.1	1.7	0.0	0.0	6.6	3.1
	Onion (%)	0.0	3.4	2.6	3.5	0.0	0.8	5.2	4.1	2.6
	Leek (%)	0.0	0.0	0.0	0.0	4.1	8.5	0.0	2.4	2.2
	Almond tree (%)	0.0	0.0	0.9	1.1	2.3	2.5	2.6	2.1	1.6
	Vetch (%)	0.0	0.0	0.0	0.0	0.0	3.9	0.8	4.1	1.3
	Ray grass (%)	0.0	0.0	0.0	4.5	5.1	0.0	0.0	0.0	1.3
	Alfalfa (%)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.5	0.9
	Sorghum (%)	0.0	0.0	3.7	0.0	0.0	0.0	0.0	0.0	0.5
	Double cropping (%)	0.0	2.5	27.1	8.7	26.3	14.2	10.9	23.9	15.7

[a] Weighted average considering the transformed area.
[b] Percentage of total irrigable area.

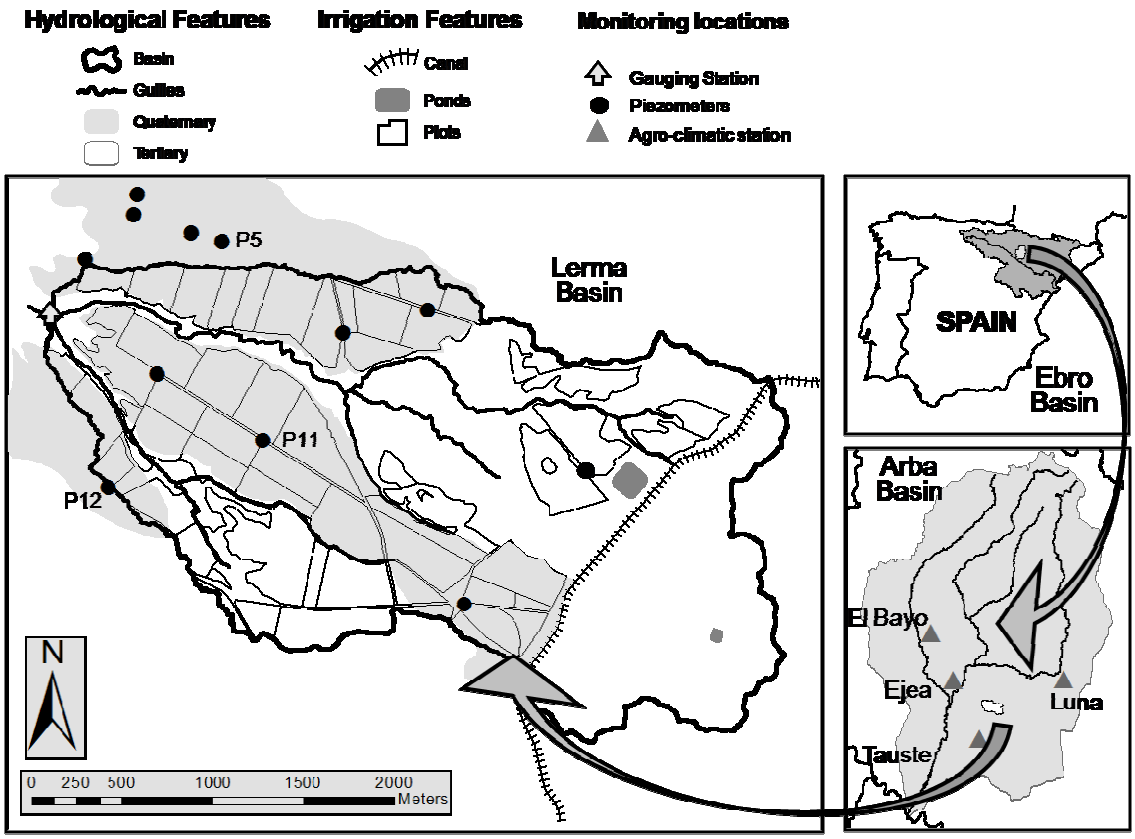

Fig. 1. Location of the Lerma Basin, Arba and Ebro River Basins. Hydrological and irrigation features, monitoring locations. Agro-climatic stations in the proximity of the Lerma Basin.

The geology of the study area is composed by Tertiary materials consisting of relatively thin layers of marls, clays, limestone and gypsum (66% of the surface, Fig. 1), covered locally (34%) by Quaternary glacis consisting of gravels with loamy matrix (ITGE, 1988). A network of twelve piezometers and a geophysical study provided data on the thickness of the Quaternary materials, with a maximum of 12 m, and more frequent thickness values between 1 m and 6 m (Plata, 2011). Soils developed on the glacis (Calcixerollic Xerochrepts, Soil Survey Staff, 2014) display loamy textures, with an effective depth of 60–90 cm. The low salinity (electrical conductivity of the saturation extract: $EC_e < 4$ dS m^{-1}) and small risk of erosion (slope < 3%) characterized these zones as suitable for conversion into irrigated land (Beltrán, 1986), and therefore most of the irrigated area covers the Quaternary surface (Fig. 1). In contrast, soils developed in the valleys of the Lerma Basin (Typic Xerofluvent, Soil Survey Staff, 2014) have a lower effective depth (between 30 and 45 cm), limited by limestone or tabular gypsum levels, which provide slow drainage. These Tertiary valleys were classified as not appropriate for irrigation due to of higher salinity values (EC_e between 4 and 8 dS m^{-1}) and steep slopes (>10%) (Beltrán, 1986).

According to the agro-climatic stations of the Integrated Irrigation Advisory Service (SIAR Network: http://oficinaregante.aragon.es), temperatures ranged from monthly averages of approximately 4 ºC (February) to 22 ºC (August), with a yearly average of

14 ºC. Average rainfall for the ten study years (hydrological years 2004–2013) was 382 mm year^{-1} with a high annual variability (coefficient of variation: CV = 31%). A typical year consists of two dry seasons (summer and winter) and two wet seasons (spring and autumn) (Fig. 2). The average reference evapotranspiration (ET_0) calculated by the Penman–Monteith method (Allen et al., 1998) was three times higher (1307 mm year^{-1}) than rainfall, less variable (CV = 6%) with no even distribution throughout the year, presenting 75% of ET_0 occurring between April and September (Fig. 2).

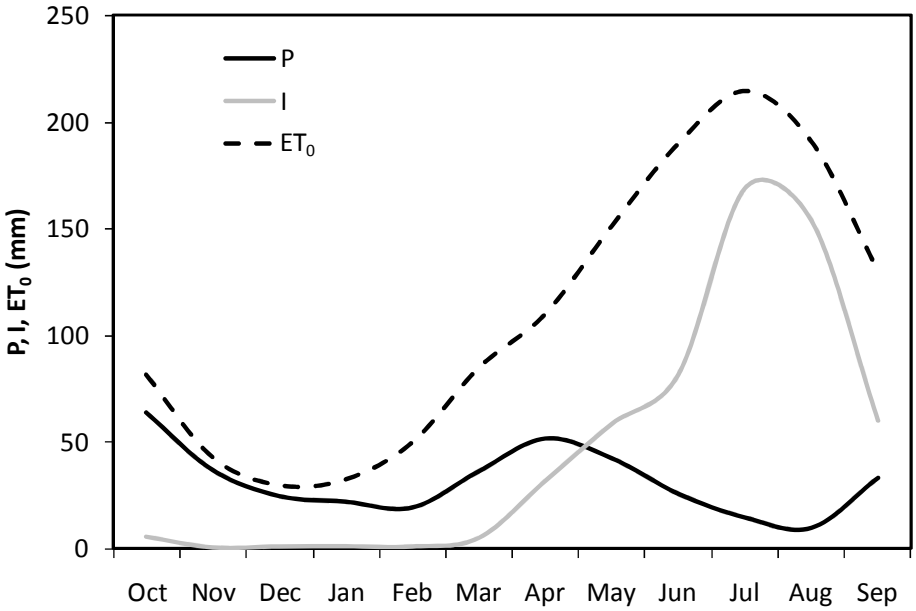

Fig. 2. Average monthly precipitation (P), irrigation (I) and reference evapotranspiration (ET_0) of the Lerma Basin during 2004-2013. For irrigation, only the years 2009-2013 were used.

3. Methodology

Daily water balances for the irrigable area of Lerma Basin were carried out for each of the 55 plots throughout the period 2004-2013. An assessment of irrigation performance through the computation of indices was also accomplished. Calculations were automated through the utilization of EMR 2.0 (Irrigation Land Environmental Tool – EMR–, from its Spanish abbreviation, Causapé, 2009a). This methodology has been applied to several irrigated areas in the Middle Ebro River Basin (Causapé, 2009b; García-Garizábal et al., 2009, 2011; Abrahão et al., 2011a; Skhiri and Dechmi, 2012; Andrés and Cuchí, 2014).

3.1. Water balances

3.1.1. Soil water balances

The meteorological data required for calculation for the water balances was obtained from four agro-climatic stations of the SIAR Network, located between 4 to 18 km away from the study zone in all directions (El Bayo, Ejea, Luna and Tauste, Fig. 1). The EMR software utilizes the inverse square distance technique to interpolate the climatic variables from the different stations to obtain a daily value for every plot in Lerma. Daily irrigation volumes were provided by the Irrigation Authority XI of the Bardenas Irrigation District, obtained from flow meters at the plot level.

Data on precipitation (P), irrigation (I), combined losses due to evaporation and wind drift of sprinkler irrigation (EWDL), and potential evapotranspiration (ET_0) were utilized to develop daily soil water balances (SWB) to estimate actual evapotranspiration (ET_a), soil drainage (D_{SWB}) and soil water storage (ΔS) in each of the 55 irrigated plots:

$$(P + I) - (ET_a + D_{SWB} + EWDL) = \Delta S \qquad (1)$$

A percentage of losses was applied to the irrigation volume to quantify the combined losses by evaporation and wind drift of sprinkler irrigation, based on wind speed 2 m above the surface (WS, m s^{-1}) and relative humidity 1.5 m above ground level (RH, %) (Playán et al., 2005):

$$EWDL\ (\%) = 20.34 + 0.214\ WS^2 - 2.29 \times 10^{-3}\ RH^2 \qquad (2)$$

The daily crop potential evapotranspiration (ET_C) was calculated (Allen et al., 1998), from reference evapotranspiration (ET_0) and the monthly crop coefficients (k_c) obtained from Martínez-Cob (2004) for the study zone:

$$ET_C = ET_0 \times k_c \qquad (3)$$

It is not the objective of this work to present a detailed explanation of the crop cycle and irrigation management for every crop or plot, nor its influence on the estimation of ET_C. However, maize deserves a more detailed explanation since it is predominating crop with high water demands (Table 1). In the study area, maize is sowed in early April (as a single crop) or mid-June (as a secondary crop), and harvested in October (Fig. 3). It is irrigated approximately every week between April and June, when three or four irrigation events per week are conducted until late August-early September, when the crop coefficients peak (Fig. 3).

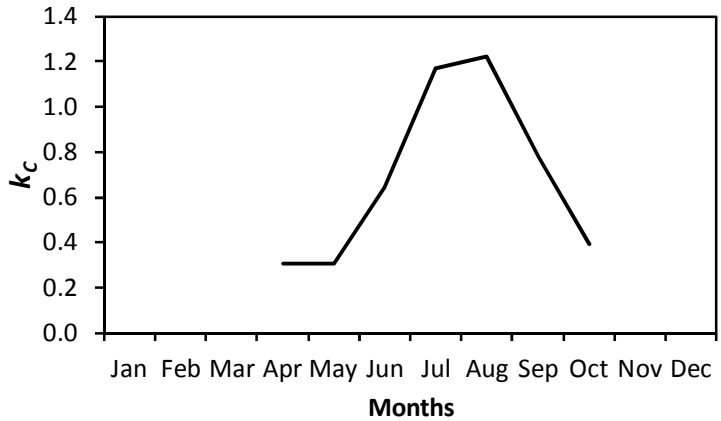

Fig. 3. Crop coefficient (k_C) used for maize, covering the period between early April and early October (Martínez-Cob, 2004).

The water holding capacity of the soil (WHC, mm) for plants was estimated from the average apparent electrical conductivity of the soil (EC_a, dS m^{-1}) (Causapé et al., 2009; Grisso et al., 2009) for each field, which depended on the water content of the soil. EC_a was derived from 43,433 measurements made throughout two weeks after significant rainfalls (soils at field capacity). A mobile geo-referenced electromagnetic sensing system (Urdanoz et al., 2008) was utilized for these measurements and the WHC of 10 soil samples (representative of the EC_a range of Lerma) was analyzed in the laboratory according to the methodology of the Soil Survey Laboratory (1995) –WHC: field capacity (0.33 bar of soil water tension) minus wilting point (15 bar)–. The statistically significant relationship established between EC_a and WHC was:

$$WHC = 415.7\ EC_a + 2.42; \quad R^2 = 0.91; \quad p < 0.001 \qquad (4)$$

Due to the uncertainty in this estimation, in a preliminary stage a range of WHC values were used for each plot, consisting of the 20% higher and 20% lower values of WHC. The impact of utilizing this range of values was assessed, as in turn, WHC influences the estimated components from the soil water balance.

Therefore, starting from an initial volume of available water for plants in the soil (AW), EMR adds the daily inputs by net irrigation (I − EWDL) and precipitation (P). EMR considers that ET_a = ETC if $AW_{initial}$ + P + I − EWDL > ETC, but otherwise ET_a = $AW_{initial}$ + P + I – EWDL; hence, the soil has a wilting point level of moisture at the end of that day (AW = 0). However, if $AW_{initial}$ + P + I − EWDL − ET_a > WHC, the program interprets that the field soil capacity has been surpassed, and drainage from soils (D_{SWB}) occurs in amounts equal to D_{SWB} = $AW_{initial}$ + P + I − EWDL − ET_a − WHC, which means that the soil presents field capacity (maximum AW = WHC) at the end of that day. The calculation of water balances started one year before the beginning of the study (October 1st, 2002), assuming the water content was equal to ½ WHC in the first day.

The effective precipitation (P_{ef}, share of precipitation that contributes to the water requirements of crops) was estimated for each day and each field, considering that if $P < WHC + ET_a - AW$ then $P_{ef} = P$, and otherwise $P_{ef} = WHC + ET_a - AW$. This estimate does not consider the existence of preferential flows or the runoff that could be generated. Nevertheless, it is a valid estimate as the fields in the study area are terraced and intense rain is needed to generate runoff or fast percolation.

The drainage volume proceeding from irrigation (D_I) was estimated by considering, for the days and fields with drainage, that if $AW + P - ET_a \geq WHC$ then $D_I = I - EWDL$ and otherwise $D_I = [I - EWDL] - [WHC - (AW + P - ET_a)]$. This means that, on any given day, rainfall will always occur before irrigation and, thereby, irrigation drainage has priority over rainfall drainage. It is assumed that a farmer should take rainfall into consideration when deciding whether to irrigate, and thus drainage is assigned preferentially to irrigation rather than to precipitation.

3.1.2. Water balances in the irrigable area

Water balances were obtained for the irrigable area considering also the incoming water flows (IWF), water drained through the Lerma Gully (LG) and the storage of water in the aquifer (ΔA) to complete a basin water balance:

$$(P + I + IWF) - (ET_a + LG + EWDL) - (\Delta S + \Delta A) = \text{Balance error} \quad (5)$$

The water evacuated via drainage was quantified by a gauging station (Fig. 1) equipped with continuous monitoring instruments, which allowed for the registry of water height (h, m) measurements every 10 minutes. These measurements were converted into flow units (Q, $m^3\ s^{-1}$) according to the equations provided by the software Winflume (Wahl, 2000):

$$Q = 1.73 \times (h + 0.00347)^{1.624} \text{ for } h \leq 0.5 \text{ m} \quad (6)$$

$$Q = 10.28 \times (h + 0.01125)^{1.725} \text{ for } h > 0.5 \text{ m} \quad (7)$$

From the beginning of the study (October 1st, 2003) until the gauging station was operational (August, 2005), the flow of Lerma Gully was estimated from precipitation data and based on a runoff coefficient of 10.1% and on the shape of the recession curves obtained for the period when the gauging station was available and the first irrigation season had not started (October, 2005 to March, 2006).

IWF was constituted of the runoff generated in the unirrigated area, channel filtrations, and several leakages (from broken pipes) that produced increases in the discharge. For the unirrigated area, the aforementioned runoff coefficient was applied to estimate the incoming water flows. Irrigation channel filtrations were estimated through chemical

gauging in several locations and seasons. A high-resolution hydrograph was utilized to estimate the amount of water generated by pipe breakages.

Finally, the annual water storage in the aquifer was estimated based on the aquifer area (251 ha) and on the saturated thickness provided by three representative piezometers located in each independent groundwater body (Fig. 1). An effective porosity of 5% was considered, which was obtained from pumping tests performed in the piezometers. The effective porosity obtained was within the range provided for the lithology of the aquifer (Custodio and Llamas, 1983). In March, 2008, eight piezometers were installed, and in April, 2010, four additional piezometers were installed, completing the piezometers network. Therefore, storage in the aquifer could only be estimated for the hydrological years 2009-2013. Given the uncertainty embedded in the effective porosity estimation, initially the balance calculations were performed with different values of porosity to assess the sensitivity of the global results to this parameter. A "double and half" approach was used, testing porosities of 2.5, 5.0 and 10.0%.

The difference between inputs (IN), outputs (OUT) and storage (ST) constituted the balance error (BE), which was evaluated in percentage terms (Causapé, 2009a):

$$BE\ [\%] = 200 \times [(IN - OUT - ST)/(IN + OUT + ST)] \quad (8)$$

As several components of the water balance were roughly estimated, BE of approximately 10% are generally accepted in this type of studies.

3.2. Water use and irrigation performance indices

Analysis of irrigation performance involved the computation of net hydric needs (HNn), irrigation efficiency (IE), irrigation drainage fraction (IDF), and water deficit (WD). These indices were calculated for each field and during crop cycles, from data provided by water balances in the soil (Causapé, 2009a):

$$HNn = (ET_C + AW_{final}) - (AW_{initial} + P_{ef}) \quad (9)$$

$$IE = [1 - (D_I + EWDL)/I] \times 100 \quad (10)$$

$$IDF = (D_I/I) \times 100 \quad (11)$$

$$WD = [(ET_C - ET_a)/ET_C] \times 100 \quad (12)$$

HNn estimates the volume of irrigation water necessary to avoid crop yield losses due to water stress. IE quantifies the percentage of irrigation that has been used to either meet the water requirements of the crops or be stored as soil water. IDF quantifies the percentage of irrigation lost in drainage and is influenced by the irrigation volume

applied and the soil water content when irrigation occurs. Finally, WD evaluates the extent to which the water requirements of crops have not been met.

High quality irrigation is experienced when WD and IDF are close to zero and IE approaches 100%. It must be noted that some irrigation events are not intended to meet water requirements, but to optimize humidity in the soil for specific agronomic activities (e.g., seed irrigation, tillage, testing irrigation equipment). Conversely, it may be necessary to apply excessive irrigation under certain circumstances to promote the leaching of salts with the subsequent generation of drainage and, therefore, loss of irrigation efficiency (Corwin et al., 2007). Furthermore, controlled deficit irrigation techniques might be applied to cause an intended water deficit (Farré and Faci, 2009).

During the years 2007, 2008 and 2012, surveys were conducted (by phone and face-to-face enquiries) with all farmers included in the Lerma Basin. Information regarding crops, times of sowing and harvest, and yields were registered to better understand the results of the irrigation performance indicators.

4. Results and discussion

4.1. Water balances

The total amount of the input components in the water balance for the irrigated area of the Lerma Basin was significantly modified with the implementation of irrigation (Table 2, Fig. 4). Overall inputs values ranged from 262 mm (dry year) to 711 mm (wet year) during the rainfed period. During the irrigated period, inputs exceeded 800 mm even in dry years (Table 2), which demonstrates the relevance of irrigation. The temporal distribution was also affected, shifting from precipitation- to irrigation-controlled, i.e., the main inputs were centred in the rainy months for the rainfed period whereas inputs were centred in the irrigated season for the irrigated period (Fig. 2).

Precipitation ranged between 227 and 632 mm year^{-1}, with an average of 382 mm year^{-1} (CV = 31%). Opposing extreme situations occurred before implementation of irrigation (Table 2). During the irrigated years, precipitation was, in general, closer to average values. Effective precipitation averaged 85%, ranging from 58 to 96% throughout the different years (Fig. 4); this value was higher than what is generally obtained from theoretical estimation (75%), typically used in other studies (Cuenca, 1989).

Table 2. Annual and cumulative water balance components for the irrigable area of the Lerma Basin. In: inputs [precipitation (P), irrigation (I), incoming water flows (IWF) from unirrigated area]; Out: outputs [actual evapotranspiration (ET_a), potential evapotranspiration (ET_C); water drained through the Lerma Gully (LG), combined losses by both evaporation and wind drift of sprinkler irrigation (EWDL)]; St: storage [soil (ΔS), aquifer (ΔA)]; and balance errors (BE) for years 2004–2013.

		Annual balance										Cumulative balance									
	Year	04	05	06	07	08	09	10	11	12	13	04	05	06	07	08	09	10	11	12	13
In	P	632	227	444	406	367	380	307	336	240	480	632	430	434	427	415	409	395	387	371	382
	I	0	0	177	452	539	559	562	569	618	528	0	0	59	157	234	288	327	357	386	401
	IWF	79	35	59	53	49	54	57	47	34	65	79	57	58	57	55	55	55	54	52	53
	ΣIn	711	262	681	910	955	992	927	951	892	1073	711	487	551	641	704	752	777	799	809	835
Out	ET_a	335	260	466	687	697	747	664	760	688	763	335	397	354	437	489	532	551	577	589	607
	(ET_C)	(354)	(416)	(584)	(765)	(902)	(880)	(852)	(950)	(985)	(856)	(354)	(385)	(451)	(530)	(604)	(650)	(679)	(713)	(743)	(754)
	LG	133	51	141	122	135	337	289	227	133	286	133	92	109	112	117	153	173	179	174	185
	EWDL	0	0	25	68	68	78	84	86	86	60	0	0	8	23	32	40	46	51	55	56
	ΣO	469	311	632	878	900	1161	1038	1074	907	1109	469	390	470	572	638	725	770	808	819	848
St	ΔS	30	-52	56	-41	7	-16	16	-14	8	7	30	-11	11	-2	0	-3	0	-2	-1	0
	ΔA	-	-	-	-	-	-3	-14	-38	-6	36	-	-	-	-	-	-1	-2	-7	-7	-3
	ΣSt	30	-52	56	-41	7	-20	2	-51	2	43	30	-11	11	-2	0	-3	-2	-9	-7	-2
	BE	213	3	-8	73	47	-149	-112	-71	-17	-80	213	108	69	70	66	30	10	0	-2	-10
	%[a]	35.2	1.2	-1.2	8.4	5.1	-14.0	-11.4	-7.2	-1.9	-7.2	35.2	25.0	13.4	11.6	9.8	4.1	1.2	-0.1	-0.3	-1.2

[a] Balance error [%]= 200 · [(In-O-S)/(In+O+S)].

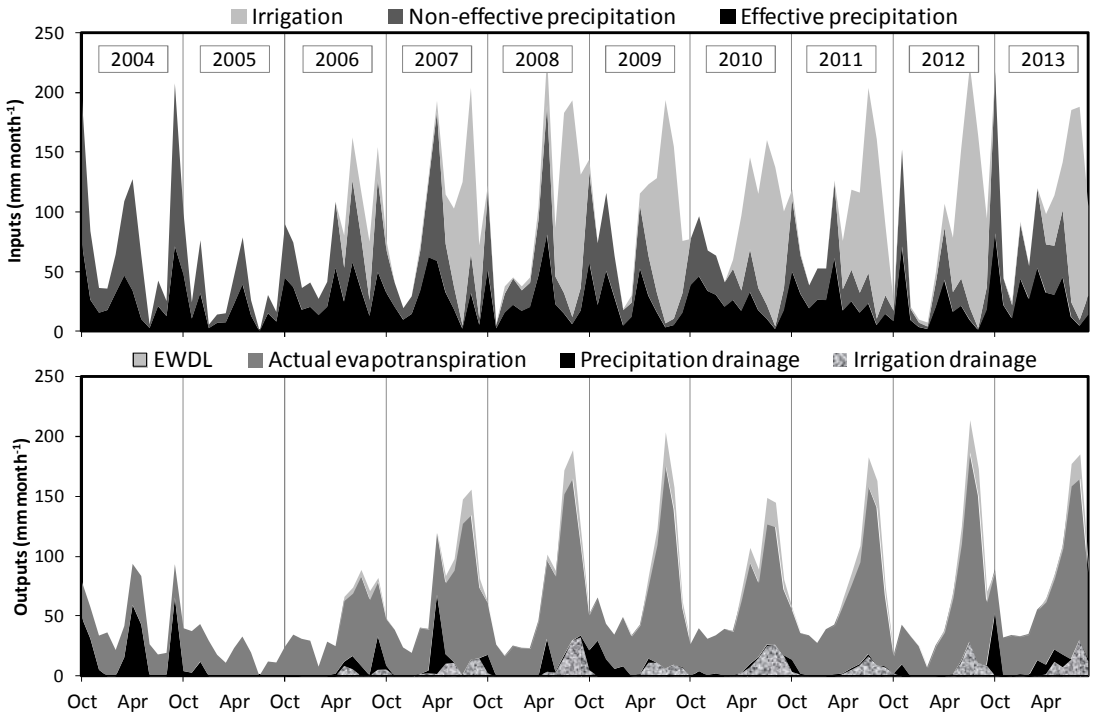

Fig. 4. Monthly inputs (irrigation, non effective precipitation and effective precipitation) and outputs (combined losses by both evaporation and wind drift-EWDL, actual evapotranspiration, precipitation drainage and irrigation drainage) during hydrological years 2004-2013.

Although precipitation was the greatest input during 2004–2006 (which covers the unirrigated period and the first irrigated year), it was surpassed by irrigation in the year 2007 (Table 2, Fig. 4). Annual irrigation reached 618 mm (in 2012) with an average of 401 mm for the entire study period. Average annual irrigation was 567 mm for the period when irrigation was consolidated (2009-2013, Table 2). The irrigation season comprehends the period April-September, but July and August presented more intense irrigation (Fig. 2). Irrigation was also the most important input in other semi-arid irrigated areas in the Ebro Basin (García-Garizábal et al., 2011; Andrés and Cuchí, 2014) as well as around the world (e.g., Scott et al., 2011).

Incoming water flows (IWF) from the unirrigated area had to be considered in the estimation of the balance in the irrigable area,. IWF included runoff generated over the unirrigated area (80% of IWF), filtration along the channel (17%) and some localized leaks in the pipe system (3%). Throughout the study period, leaks supposed 7% of inputs, ranging from 4 to 13% in the different years (Table 2).

The main output was actual evapotranspiration, accounting for 73% (CV = 9%) of the outputs, ranging from 64 to 84% (Table 2). The highest ET_0 were recorded in the driest years (2005 and 2012). ET_C greatly increased its values with the expansion of irrigation (Table 2). Consequently, ET_a increased progressively throughout the study period. However, ET_a never reached the potential ET_C values due to scarcity of available water in the soil during specific periods. ET_a was the most affected variable when different

water holding capacities were tested; nevertheless, 20% variations in WHC resulted in very small differences in ET_a (between 1.8 and 2.3%).

The flow in Lerma Gully accounted for 22% of outputs (Table 2), ranging from 15% in dry years (2005 and 2012) to 29% (2009), possibly as a consequence of the installation of artificial drainage to avoid plot flooding. A shift was observed in the monthly distribution of gully discharge, changing from a precipitation-driven pattern to one controlled by precipitation and irrigation.

The combined losses by evaporation and wind drift of sprinkler irrigation, absent in the unirrigated period, ranged from 4 to 10% of outputs during the irrigated period, averaging 7% (Table 2).

Water storage in the soil ranged from -52 to 56 mm year^{-1} across the study period (Table 2). This parameter is very dependent on the specific hydrologic conditions of a particular year, as the amount of water stored in soils can vary significantly with irrigation or precipitation in the last days of the hydrological year.

The water table in the aquifers varied considerably during the irrigation season (Fig. 5), rising sharply at the end of the irrigation season and decreasing during the remainder of the year. Although aquifer storage could not be estimated for the first five years, it ranged from -38 to 36 mm year^{-1} during the period 2009-2013 (Table 2). The accumulated value of aquifer storage was -3 mm year^{-1}, which can be explained by the construction of drains, as reported by farmers (Irrigation Authority XI, personal communication). Given the proximity of a low permeability layer in large areas of the basin (Plata, 2011), several plots experienced problems related to the rise of water table and consequently, artificial drainage was installed in different plots. Aquifer storage was utilized to close the balance in the period 2004-2008, providing an average storage of 30 mm year^{-1} throughout the study period, which is in line with the change from intermittent to perennial gullies dependent on groundwater (Merchán et al., 2013). It is probable that the saturated thickness in the aquifer increased during the first years of the study.

Balance error (Table 2) was within the interval ±10% for most of the studied years and thus is considered an acceptable balance closure. Testing different WHC and porosities did not produce relevant changes in balances errors (between ±0.3%), as soils and aquifer storage were negligible in comparison with other components. In addition, the cumulative water balance improved with time, resulting in ±1.2% in the last years. Finally, the difference observed between the drainage estimated from the soil water balance and drainage from the difference between the discharge and incoming water flows of Lerma Gully for the entire study period was 10%. This demonstrated that the estimated drainage from soil water balances is of the same order of magnitude than the drainage measured in the gully. Therefore, the water balances were acceptable, allowing for the quantification of irrigation performance indices.

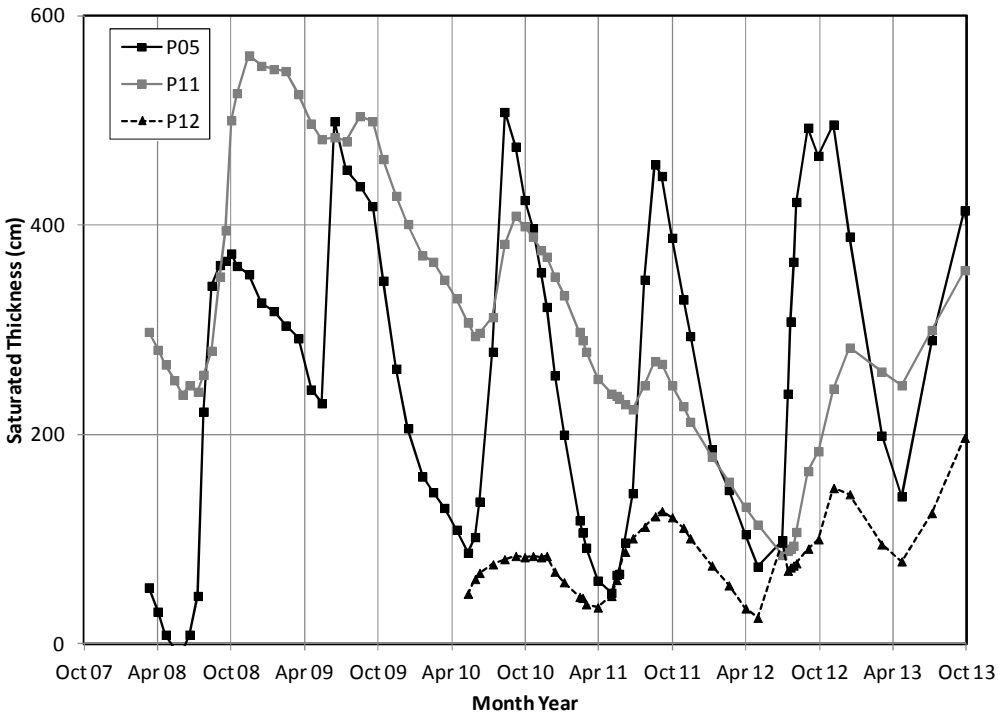

Fig. 5. Saturated thickness in selected piezometers for the years 2007–2013.

4.2. Irrigation Performance

The expansion of the irrigated area resulted in increases in the net hydric requirements, from 0.59 hm^3 in 2006 up to 2.28 hm^3 in the dry year of 2012 (Table 3). Nevertheless, in a wet year such as 2013, with irrigation completely implemented (100%) and similar crop distribution, HNn were 1.55 hm^3. Specific HNn for crops were higher than the average reported by Salvador el al. (2011) for large irrigation districts in the Ebro Basin. This is probably due to the specific climatic characteristics of the study zone (i.e., lower precipitation and higher ET_0) as well as differences in the distribution of crops.

Average irrigation efficiency reached 76.1% (ranging from 75.1 to 77.0% with ±20% WHC tested). No significant trends were observed in the annual dynamics due to inter annual variation (ranging from 64.4% in 2006 to 80.7% in 2012). However, cumulative annual irrigation efficiency presented a significant upward trend (1.05% $year^{-1}$, Table 3).

The IE reported in other sprinkler irrigation districts in the Ebro Basin presented similar figures (72%, Skhiri and Dechmi, 2012; 76%, Andrés and Cuchí, 2014). These values were higher than those obtained for flood irrigated areas (45 – 62%, Causapé et al., 2004; 67%, García-Garizábal and Causapé, 2010). However, simple alternatives in irrigation management (García-Garizábal et al., 2011) or improvements in irrigation infrastructure (Barros et al., 2011) can significantly increase flood irrigation efficiency,

Table 3. Annual and cumulative net hydric needs (HNn), irrigation efficiency (IE), combined losses by both evaporation and wind drift of sprinkler irrigation (EWDL), irrigation drainage fraction (IDF) and water deficit (WD) during the irrigated period for the Lerma Basin.

Year	HNn ($hm^3 year^{-1}$)	IE (%)	EWDL (%)	IDF (%)	WD (%)	Cumulative	HNn ($hm^3 year^{-1}$)	IE (%)	EWDL (%)	IDF (%)	WD (%)
2006	0.59	64.4	13.1	22.5	13.1	06	0.59	64.4	13.1	22.5	13.1
2007	1.31	73.6	14.7	11.7	11.5	06-07	0.95	70.6	14.3	15.1	12.0
2008	1.83	78.1	12.7	9.2	20.4	06-08	1.25	74.0	13.5	12.5	15.8
2009	1.83	78.5	13.6	7.9	15.8	06-09	1.39	75.3	13.6	11.1	15.8
2010	1.71	74.4	14.0	11.6	20.0	06-10	1.46	75.1	13.7	11.2	16.8
2011	1.94	80.7	14.5	4.8	22.0	06-11	1.54	76.3	13.7	10.0	17.8
2012	2.28	78.1	13.9	8.0	24.7	06-12	1.64	76.5	13.9	9.6	18.9
2013	1.55	73.6	11.5	14.9	11.5	06-13	1.63	76.1	13.5	10.4	17.8
Trend[a]	ns	ns	ns	ns	ns	Trend	***	**	ns	*	**
Slope[a]	-	-	-	-	-	Slope	+0.11	+1.05	-	-0.97	+0.95

[a] Significant trend and slope with Mann-Kendall test and Sen's slope (Helsel and Hirsch, 2002).
ns: non significant trend ($p > 0.1$); *: $p < 0.1$; **: $p < 0.05$; ***: $p < 0.01$.

up to values of the same order of those obtained for pressurized irrigation. In these cases, the goal is to control runoff and the irrigation drainage fraction.

One of the reasons why well-managed flood irrigated plots can reach high IE values, close to those obtained in sprinkler irrigated plots, is the absence of evaporation and wind drift losses. In the case of the Lerma Basin, EWDL averaged 13.5% of total irrigation (Table 3) and 14.7% of applied sprinkler irrigation. No significant trends were detected for either annual or cumulative data.

The second component responsible for the loss of irrigation efficiency was irrigation drainage fraction (IDF), with an average value of 10.4% (ranging from 9.6 to 11.5% with ±20% WHC tested). The cumulative values presented significant downward trend (0.97% year^{-1}, Table 3), which could be related to the decreasing trends detected in the flow when irrigation was consolidated (Merchán et al., 2013). IDF values were similar to those of other pressurized irrigation areas (11%, Skhiri and Dechmi, 2012; 12%, Andrés and Cuchí, 2014). Flood irrigation areas with low WHC soils can present higher IDF (44%, García-Garizábal et al., 2011), although the implementation of management improvements decreased IDF to 11 - 24%.

The water deficit obtained was 17.8% (ranging from 16.6 to 19.3% with ±20% WHC tested). The cumulative data presented an upward trend of 0.95% year^{-1}. WD values were higher than those reported in other irrigation systems (9%, Skhiri and Dechmi, 2012; 13%, Andrés and Cuchí, 2014; 14%, García-Garizábal et al., 2011) and this was probably related to, among other factors, the lower water holding capacity of the soils in the Lerma Basin.

The irrigation performance of Lerma Basin is within the observed values for other pressurized irrigation areas in the Ebro Basin. Regarding its temporal evolution, the trends for the different variables show a progressive increase in IE and decrease in IDF. Farmers that originally used rainfed or flood irrigation schemes may have adapted to new pressurized irrigation equipment and possibilities, and obtained a better knowledge of the system. However, an increase in WD was observed, requiring further knowledge to elucidate the causes.

Of the main crops (87% of irrigated surface), barley, sunflower and wheat presented net hydric needs higher than irrigation rates, generating expected water deficits (over 20%, Table 4). In the case of winter cereals, the deficit occurred mainly at the end of the vegetative cycle. This water deficit may have affected yields (approximately 4,500 kg ha^{-1}, according to surveys with the farmers). However, the decrease in yield produced by the water deficit depends absolutely on the phase within the cycle, as increased productivity has been observed when small water deficits occurred in specific moments. Sunflower was traditionally under-irrigated, and cultivated with strong subsidies from the Common Agricultural Policy; in 2003 the subsidies were “decoupled” for particular crops (http://ec.europa.eu/agriculture). Although these

associated subsidies are no longer available since 2003, farmers still experience "inertia" regarding shifts in the traditional management of sunflower.

Table 4. Number of plots available for each crop (N), area percentage, net hydric needs (HNn), irrigation (I), irrigation efficiency (IE), combined losses by both evaporation and wind drift of sprinkler irrigation (EWDL), irrigation drainage fraction (IDF) and water deficit (WD) during the period 2006–2013 for the main crops of the Lerma Basin.

Crop	N	Area (%)[a]	HNn (mm year^{-1})	I (mmyear^{-1})	IE (%)	EWDL (%)	IDF (%)	WD (%)
Maize	155	44.3	647	740	77.0	15.2	7.8	11.0
Barley	31	11.6	271	177	81.2	13.6	5.2	25.9
Sunflower	26	8.9	609	527	80.7	15.3	4.0	25.8
Wheat	22	7.2	349	295	78.4	14.3	7.3	21.0
Tomatoes	24	5.8	637	645	83.7	0.0	16.3	16.1

[a] Proportion of the irrigated area.

Maize and tomato, for which HNn were lower than irrigation rates, presented relevant water deficits (11.0 and 16.1%, respectively). This indicates an inappropriate irrigation schedule. Tomatoes presented maximum IE (83.7%), mainly due to the absence of EWDL, which supports the higher efficiency of drip irrigation systems (Table 4). However, tomatoes also presented the highest IDF due to excessive application of irrigation in punctual moments.

Maize, the predominant crop, deserves a detailed assessment. Maize presented the lowest IE (77.0%) and irrigation surpassed HNn for all years, with values between 6 and 29% higher (Table 5). Such over-irrigation of maize is reported in several other location of the irrigated area of the Ebro Basin (Skhiri and Dechmi, 2012; Andrés and Cuchí, 2014) and is a general pattern for the entire Ebro Basin (average of 20%, Salvador et al., 2011). This is related to the sensitivity of maize to water stress, a fact that is well-known by the farmers (Barros et al., 2011), who try to avoid water stress through excessive irrigation.

Irrigation efficiency ranged from 74.1 to 80.2% and losses by EWDL ranged from 15 to 16%, presenting low variability (CV = 3%). However, IDF ranged between 4 and 12% (CV = 35%) and was related to the net hydric needs ($R^2 = 0.78$, $p < 0.01$): the higher the HNn (dry and hot years), the lower the IDF. This is due to a dryer state of soils in those years, along with a major effort from the farmers to achieve good water use in years of scarcity as also reported in other studies (Soto-García et al., 2013).

The water deficit for maize averaged 11.0% (ranged from 6.4 to 14.4%, CV = 25%), and was negatively correlated with the over-irrigation ratio (I/HNn, $R^2 = 0.87$, $p < 0.01$), i.e., the more irrigation applied exceeding the crop requirements, the lower the water deficit. The obtained WD for maize was slightly lower than what was reported in other

irrigated areas of the Ebro Basin (13%, Andrés and Cuchí, 2014; 14%, Barros et al., 2011).

A detailed analysis of the irrigation schedule followed by different farmers is beyond the scope of this paper. Instead, as a conclusive summary, the most common examples of inadequate irrigation management are presented in Fig. 6: components of the soil water balance in a maize plot with sprinkler irrigation. IE in this plot reached 69.0% with EWDL losses (15.3%) similar to those of IDF (15.7%). EWDL were related to high wind speeds in the study zone. As observed in Fig. 6A, there are irrigation events in days with high wind speed, with an extreme case of 8 m s^{-1} on June 2nd. Tarjuelo et al. (1992) consider 3 m s^{-1} as a threshold over for sprinkler irrigation: above this wind speed value, sprinkler irrigation should not be applied. However, this threshold is hard to implement in windy areas such as the Lerma Basin (average wind speed 3.2 m s^{-1}, Fig. 6A). Nevertheless, it would be advisable to irrigate during the night (lower average wind speed and higher relative humidity, Playán et al., 2005) and to avoid irrigation in extremely windy days to minimize EWDL. Additional measures, such as upgrading to drip irrigation in applicable crops could reduce EWDL.

IDF was related to irrigation events that exceeded the water requirements of the crop, when the available water in the soil was close to its water holding capacity (Fig. 6B and 6C). Also, some irrigation events were carried out just after important precipitation events (July 20th, after a rainfall event of 30 mm). However, this problem presents difficult solution as farmers must require water two days in advance. After irrigation is scheduled, there are difficulties to cancel the event due to operational system limitations (distance to Yesa reservoir, storage capacity of ponds). An ambitious objective would be to achieve null irrigation drainage although some drainage will always occur in connection with precipitation events, limiting the accumulation of salts in soil profiles, and consequently compromising yields.

Finally, ET_a did not reach ET_C in some periods of the crop cycle (Fig. 6B), and water deficit occurred (14.1%) as a consequence of irrigation rates slightly below crop requirements and lack of available water in those periods. The average yields obtained were approximately 11,500 kg ha^{-1} (farmer surveys), with maximum yields of 14,000 kg ha^{-1}, which could be partially due to this water deficit.

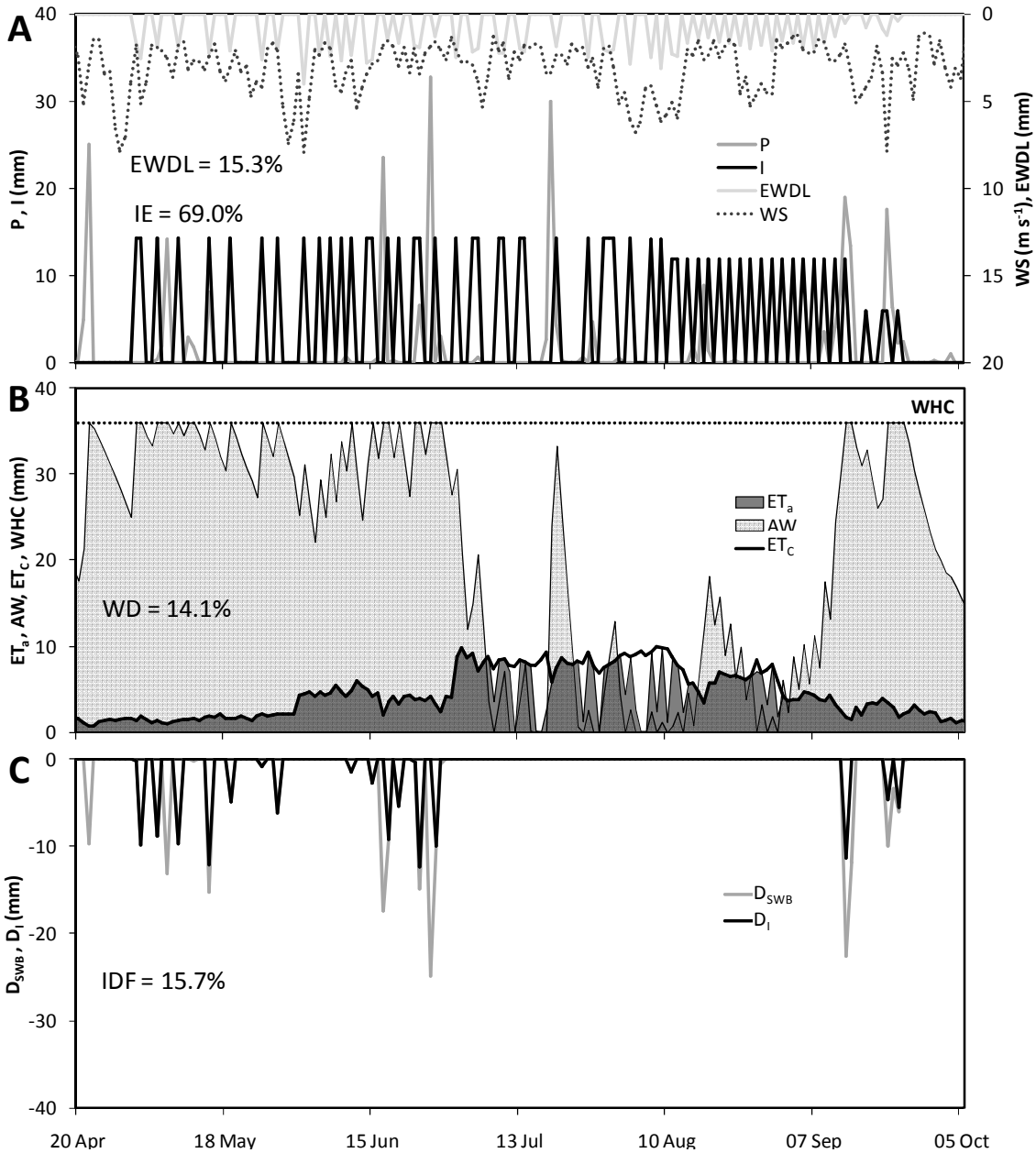

Fig. 6. Components of the soil water balance during the maize crop cycle in 2006 for a selected plot. A: precipitation (P), irrigation (I), wind speed (WS) and evaporation and wind drift losses (EWDL). B: actual evapotranspiration (ET_a), available water in the soil (AW), potential evapotranspiration (ET_C) and water holding capacity (WHC). C: total drainage from soil water balance (D_{SWB}) and irrigation drainage (D_I).

The exposed facts imply in the existence of margins of improvement through the implementation of measures to decrease both IDF and EWDL. Adjustment of irrigation rates to the water requirements of the crop, according to the stage of its vegetative cycle, will not only minimize water deficit but also reduce drainage and increase efficiency. For instance, the automation of irrigation in accordance with soil humidity and climatic sensors would enable the adjustment of irrigation to the water requirements of the crop, provided that the irrigation infrastructures allows for it.

Table 5. Number of plots available each year (N), net hydric needs (HNn), irrigation volume (I). Annual and cumulative irrigation efficiency (IE), combined losses by both evaporation and wind drift of sprinkler irrigation (EWDL), irrigation drainage fraction (IDF) and water deficit (WD) for maize in the irrigated period.

Year	N	HNn (mm year^{-1})	I (mm year^{-1})	IE (%)	EWDL (%)	IDF (%)	WD (%)	Cumulative	IE (%)	EWDL (%)	IDF (%)	WD (%)
2006	13	595	645	75.6	15.2	9.2	14.4	06	75.6	15.2	9.2	14.4
2007	24	619	760	74.1	15.8	10.1	9.2	06-07	74.6	15.6	9.8	10.9
2008	19	591	761	74.2	14.7	11.1	6.4	06-08	74.4	14.4	10.2	9.4
2009	21	681	757	80.0	15.1	4.9	10.3	06-09	76.0	15.3	8.7	9.7
2010	12	712	872	76.3	15.9	7.8	8.8	06-10	76.1	15.3	8.6	9.6
2011	25	681	725	79.4	15.5	5.1	14.0	06-11	76.8	15.4	7.8	10.5
2012	21	735	803	80.2	16.1	3.7	11.9	06-12	77.3	15.5	7.2	10.7
2013	20	560	618	75.0	13.4	11.6	12.8	06-13	77.0	15.2	7.8	11.0
Trend[a]	ns	ns	ns	ns	ns	ns	ns	Trend	*	ns	*	ns
Slope[a]	-	-	-	-	-	-	-	Slope	+0.40	-	-0.37	-

[a] Significant trend and slope with Mann-Kendall test and Sen's slope (Helsel and Hirsch, 2002).
ns: non significant trend ($p > 0.1$); *: $p < 0.1$; **: $p < 0.05$; ***: $p < 0.01$.

5. Conclusion

After the transition was completed (100% implementation), irrigation was the main water input in the basin (approximately 60%) whereas the main output was actual evapotranspiration (73%). Other outputs were the discharge through the Lerma Gully (22%) and the evaporation and wind drift losses of sprinkler irrigation (5%). Soil and aquifer storage were accounted for, but negligible in comparison with other components of the water balance. Differences between inputs and outputs were minimal, with an average of -1.2% across the study period, allowing for a trustworthy estimation of irrigation performance.

The irrigation performance of Lerma Basin was within the observed values for other pressurized irrigation areas of the Ebro Basin. Irrigation efficiency reached 76.1%, while the losses of efficiency were due to evaporation and wind drift losses (13.5%) and drainage fraction (10.4%). A water deficit of 17.8% was estimated. The irrigation efficiency increased (1.05% year^{-1}) while irrigation drainage fraction decreased (0.97% year^{-1}) throughout the period 2006-2013. No significant changes in evaporation and wind drift losses of sprinkler irrigation were detected. Despite these facts, an improvement in irrigation performance was not verified, as water deficit also increased (0.95% year^{-1}).

It is necessary to improve irrigation management in order to continue increasing irrigation efficiency, while decreasing evaporation and wind drift losses, drainage fraction, and water deficit. Optimal water use could be achieved if irrigation rates were adjusted to the requirements of crops, if the irrigation infrastructure allows for it.

Irrigation performance is important not only because it prevents water deficit or saves water. An adequate management of irrigation increases the good use of water resources and decreases the environmental impacts in irrigated areas, especially the leaching of salt and nitrates from irrigated soils, which is the objective of the second part of this study, presented in a companion manuscript.

Acknowledgements This work was carried out within project CGL2012-32395 (Spanish Ministry of Economy and Competitiveness – Feder-EU Funds) and benefited from grant BES2010-034124 (Spanish Ministry of Economy and Competitiveness). Dr. Iker García-Garizábal was supported by PROMETEO grant from SENESCYT-Ecuador. The authors are thankful to Juan Plata, Felix Rubio and Antonio Azcón, from the Geological Survey of Spain. Thanks are also extended to the Irrigation Authority XI of Bardenas Irrigation Scheme, for facilitating irrigation data and providing help in several field-related issues.

REFERENCES

Abrahão, R., Causapé, J., García-Garizábal, I., Merchán, D., 2011a. Implementing irrigation: Water balances and irrigation quality in the Lerma basin (Spain). Agricultural Water Management 102: 97-104. doi: 10.1016/j.agwat.2011.10.010

Abrahão, R., Causapé, J., García-Garizábal, I., Merchán, D., 2011b. Implementing irrigation: Salt and nitrate exported from the Lerma basin (Spain). Agricultural Water Management 102: 105-112. doi: 10.1016/j.agwat.2011.10.011

Ahadi, R., Samani, Z., Skaggs, R., 2013. Evaluating on-farm irrigation efficiency across the watershed: A case study of New Mexico's Lower Rio Grande Basin. Agricultural Water Management 124: 52-57. doi: 10.1016/j.agwat.2013.03.010

Allen, R.G., Pereira, L.S., Raes, D., Smith, M., 1998. Crop Evapo-Transpiration: Guidelines for Computing Crop Water Requirements. United Nations Food and Agriculture Organization, Irrigation and Drainage Paper No. 56. FAO, Rome, Italy.

Andrés, R., Cuchí, J.A., 2014. Analysis of sprinkler irrigation management in the LASESA district, Monegros (Spain). Agricultural Water Management 131: 95-107. doi: 10.1016/j.agwat.2013.09.016

Barros, R., Isidoro, D., Aragües, R., 2011. Long-term water balances in La Violada Irrigation District (Spain): II. Analysis of irrigation performance. Agricultural Water Management 98: 1569-1576. doi: 10.1016/j.agwat.2011.10.004

Beltrán, A., 1986. Estudio de suelos de la zona regable de Bardenas. II. Sectores: VIII, XI, X, XII y XIII. Instituto Nacional de Reforma y Desarrollo Agrario, Ministerio de Agricultura, Pesca y Alimentación, Spain.

Causapé, J., 2009a. A computer-based program for the assessment of water-induced contamination in irrigated lands. Environmental Monitoring Assessment 158: 307-314.

Causapé, J., 2009b. Agro-environmental evaluation of irrigation land– I. Water use in Bardenas irrigation district (Spain). Agricultural Water Management 96: 179-187. doi: 10.1016/j.agwat.2008.08.004

Causapé, J., Quílez, D., Aragües, R., 2004. Assessment of irrigation and environmental quality at the hydrological basin level– I. Irrigation quality. Agricultural Water Management 70: 195-209. doi: 10.1016/j.agwat.2004.06.005

Causapé, J., Clavería, I., Abrahão, R., García-Garizábal, I., 2009. Cartografía edáfica mediante un Sensor Electromagnético Móvil Georreferenciado (SEMG). XXVII Reunión Científica del Suelo. Sociedad Española de la Ciencia del Suelo. Huesca.

Corwin, D.L., Rhoades, J.D., Šimůnek, J., 2007. Leaching requirement for soil salinity control: Steady-state versus transient models. Agricultural Water Management 90: 165-180.

Cuenca, R.H., 1989. Irrigation System Design. An Engineering Approach. Prentice Hall, New Jersey, United States.

Custodio, E., Llamas, M., 1983. Hidrología Subterránea. Barcelona. Ediciones Omega.

Duncan, R.A., Bethune, M.G., Thayalakumaran, T., Christen, E.W., McMahon, T.A., 2008. Management of salt mobilisation in the irrigated landscape – A review of selected irrigation regions. Journal of Hydrology 351: 238-252. doi: 10.1016/j.jhydrol.2007.12.002

FAO, 2003a. Unlocking the Water Potential of Agriculture.United Nations Food and Agriculture Organization, FAO, Rome, Italy.

FAO, 2003b. World Agriculture Towards 2015/2030. A FAO Perspective. United Nations Food and Agriculture Organization, FAO, Rome, Italy.

Farré, I., Faci, J.M., 2009. Deficit irrigation in maize for reducing agricultural water use in a Mediterranean environment. Agricultural Water Management 96 (3): 383–394. doi: 10.1016/j.agwat.2008.07.002

García-Garizábal, I., Causapé, J., 2010. Influence of irrigation water management on the quantity and quality of irrigation return flows. Journal of Hydrology 385: 36-43. doi: 10.1016/j.jhydrol.2010.02.002

García-Garizábal, I., Causapé, J., Abrahão, R., 2009. Evolution of the efficiency and agro-environmental impact of a traditional irrigation land in the middle Ebro Valley (2001-2007). Spanish Journal of Agricultural Research 7(2): 465-473. doi: 10.5424/sjar/2009072-1499

García-Garizábal, I., Causapé, J., Abrahão, R., 2011. Application of the Irrigation Land Environmental Evaluation Tool for flood irrigation management and evaluation of water use. Catena 87: 260-267. doi: 10.1016/j.catena.2011.06.010

Grisso, R., Alley, M., Holshouser, D., Thomason, W., 2009. Precision Farming Tools: Soil Electrical Conductivity. Virginia Cooperative Extension Publication 442-508.

Helsel, D.R., Hirsch, R.M., 2002. Statistical methods in water resources. Techniques of water resources investigations, Book 4, Chapter A3. Reston, VA: US Geological Survey.

Hernández, E.A., Uddameri, V., 2010. Selecting agricultural best management practices for water conservation and quality improvements using Atanassov's Intuitionistic Fuzzy Sets. Water Resources Management 24: 4589-4612. doi: 10.1007/s11269-010-9681-1

Isidoro, D., Quílez, D., Aragües, R., 2004. Water balance and irrigation performance analysis: La Violada irrigation district (Spain) as a case study. Agricultural Water Management 64, 123-142. doi: 10.1016/S0378-3774(03)00196-3

ITGE, 1988. Mapa Geológico de España, Ejea de los Caballeros (map and memory). No. 284 27-12. Instituto Tecnológico Geominero de España, Madrid.

Jia, Z., Wu, Z., Luo, W., Xi, W., Tang, S., Liu, W.L., Fang, S., 2013. The impact of improving irrigation efficiency on wetland distribution in an agricultural landscape in the upper reaches of the Yellow River in China. Agricultural Water Management 121: 54-61. doi: 10.1016/j.agwat.2013.01.003

Lankford, B., 2012. Fictions, fractions, factorials and fractures; on the framing of irrigation efficiency. Agricultural Water Management 108: 27-38. doi: 10.1016/j.agwat.2011.08.010

Lorite, I.J., Mateos, L., Fereres, E., 2004. Evaluating irrigation performance in a Mediterranean environment. II. Variability among crops and farmers. Irrigation Science 23, 89-92. doi: 10.1007/s00271-004-0096-8

Martínez-Cob, A., 2004. Revisión de las necesidades hídricas netas de los cultivos de la cuenca del Ebro. Confederación Hidrográfica del Ebro (internal document, in Spanish).

Merchán, D., Causapé, J., Abrahão, R., 2013. Impact of irrigation implementation on hydrology and water quality in a small agricultural basin in Spain. Hydrological Sciences Journal 58(7): 1400-1413. doi: 10.1080/02626667.2013.829576

Plata, J.L., 2011. Informe sobre la determinación de la potencia de glacis en el barranco de Lerma (Zaragoza) mediante Sondeos Eléctricos Verticales. Informe IGME Centro de Documentación nº 64098 (in Spanish).

Playán, E., Salvador, R., Faci, J.M., Zapata, N., Martínez-Cob, A., Sánchez, I., 2005. Day and night wind drift and evaporation losses in sprinkler solid-sets and moving laterals. Agricultural Water Management 76: 139-159. doi: 10.1016/j.agwat.2005.01.015

Quemada, M., Baranski, M., Nobel-de Lange, M.N.J., Vallejo, A., Cooper, J.M., 2013. Meta-analysis of strategies to control nitrate leaching in irrigated agricultural systems and their effects on crop yield. Agriculture, Ecosystems and Environment 174: 1-10. doi: 10.1016/j.agee.2013.04.018

Salvador, R., Martínez-Cob, A., Cavero, J., Playán, E., 2011. Seasonal on-farm irrigation performance in the Ebro basin (Spain): Crops and irrigation systems. Agricultural Water Management 98: 577-587. doi: 10.1016/j.agwat.2010.10.003

Scott, J., Rosen, M.R., Saito, L., Decker, D.L., 2011. The influence of irrigation water on the hydrology and lake water budgets of two small arid-climate lakes in Khorezm, Uzbekistan. Journal of Hydrology 410: 114-125. doi: 10.1016/j.jhydrol.2011.09.028

Setegn, S.G., Chowdary, V.M., Mal, B.C., Yohannes, F., Kono, Y., 2011. Water balance study and irrigation strategies for sustainable management of a tropical ethiopian lake: a case study of Lake Alemaya. Water Resources Management 25: 2081-2107. doi: 10.1007/s11269-011-9797-y

Skhiri, A., Dechmi, F., 2012. Impact of sprinkler irrigation management on the Del Reguero river (Spain). I: Water balance and irrigation performance. Agricultural Water Management 103: 120-129. doi: 10.1016/j.agwat.2011.11.003

Soil Survey Staff, 2014. Keys to Soil Taxonomy. 12th Edition. United States Department of Agriculture – Natural Resources Conservation Service.

Soil Survey Laboratory, 1995. Information Manual. Soil Survey Investigations Report No. 45. Version 1.0. United States Department of Agriculture, Washington DC, United States.

Soto-García, M., Martínez-Álvarez, V., García-Bastida, P.A., Alcon, F., Martin-Gorriz, B., 2013. Effect of water scarcity and modernisation on the performance of irrigation districts in south-eastern Spain. Agricultural Water Management 124: 11-19. doi: 10.1016/j.agwat.2013.03.019

Tarjuelo, J.M., Valiente, M., Lozoya, J., 1992. Working conditions of sprinkler to optimize application of water. Journal of Irrigation and Drainage Engineering – American Society of Civil Engineers 118 (6): 895–913. doi: 10.1061/(ASCE)0733-9437(1992)118:6(895)

Urdanoz, V., Amezketa, E., Clavería, I., Ochoa, V., Aragües, R., 2008. Mobile and georeferenced electromagnetic sensors and application for salinity assessment. Spanish Journal of Agricultural Research 6(3): 469-478. doi: 10.5424/sjar/2008063-339

Wahl, T., 2000. Winflume User's Manual. United States Department of the Interior.

CHAPTER VIII

SALT AND NITRATE EXPORTED FROM THE IRRIGATED AREA

PAPER V

Merchán, D., Causapé, J., Abrahão, R., García-Garizábal, I. Assessment of a newly implemented irrigated area (Lerma Basin, Spain) over a 10-year period. II: Salts and Nitrate exported. Accepted in *Agricultural Water Management* (April 24th 2015).

Impact factor: 2.333 (JCR 2013).
Quartile and category: Q1 (16/78), Agronomy; Q1 (18/79) Water Resources.

D. Merchán took part in the design of the study, contributed in the data collection, and performed the statistical analysis, data interpretation and writing, with assistance from all co-authors.

ASSESSMENT OF A NEWLY IMPLEMENTED IRRIGATED AREA (LERMA BASIN, SPAIN) OVER A 10-YEAR PERIOD. II: SALTS AND NITRATE EXPORTED

Accepted in Agricultural Water Managemet (April 24th 2015).

D. Merchán[1], J. Causapé[1], R. Abrahão[2], I. García-Garizábal[3]

[1] Geological Survey of Spain – IGME, C/ Manuel Lasala 44 9ºB, Zaragoza, 50006, Spain.
[2] Federal University of Paraíba – UFPB, Cidade Universitária, João Pessoa, Paraíba, 58051-900, Brazil.
[3]Escuela Superior Politécnica del Litoral – ESPOL, Facultad de Ingeniería en Ciencias de la Tierra - FICT, Km. 30.5 Vía Perimetral, Campus Gustavo Galindo, Guayaquil, Ecuador.

Corresponding author: D. Merchán (0034 976 55 52 82; d.merchan@igme.es; eremad@hotmail.com)

Abstract

Irrigated agriculture impacts the quality of water bodies receiving irrigation return flows. The leaching of salts and nitrate from Lerma Basin (7.38 km^2), a newly-implemented pressurized irrigated area in the Ebro Basin (Spain), was assessed in this study for the hydrological years 2004-2013, covering years before (2004-2005), during (2006-2008) and after (2009-2013) the implementation of irrigation. The concentration of salts and nitrate were measured for all the components of the water balance and the amounts of these pollutants coming from the irrigated surface (352 ha) were estimated. Besides, salt and nitrate contamination indices were computed. Under unirrigated conditions, the studied area exported 1.89 Mg ha^{-1} $year^{-1}$ and 11.4 kg ha^{-1} $year^{-1}$ of salts and NO_3^--N, respectively. These amounts increased to 3.51 Mg ha^{-1} $year^{-1}$ for salts and 30.8 kg ha^{-1} $year^{-1}$ for NO_3^--N after the implementation of irrigation. Salt and nitrate contamination indices (SCI and NCI, respectively) increased by a factor of three from unirrigated to irrigated conditions, reaching values of 0.96 [Mg ha^{-1} $year^{-1}$]/[dS m^{-1}] and 0.12, respectively. Despite these values being well under the threshold considered for more sustainable irrigated areas (SCI < 2.0 [Mg ha^{-1} $year^{-1}$]/[dS m^{-1}] and NCI < 0.2), it would be advisable to improve irrigation management to increase water use and decrease leaching. Complementary measures such as adjusting fertilization rates to temporal crop necessities or the use of catch crops may prove to be useful.

Keywords: diffuse pollution; land use change; leaching; salinization; agro-environmental impact.

1. Introduction

Agriculture is recognized as the main source of diffuse pollution for both ground and surface water. Externalities of modern agriculture include downstream impacts on water quality through off-site migration of agrochemicals (e.g., Oliver and Kookana, 2012). In particular, irrigated agriculture causes enhanced impacts on water bodies receiving irrigation return flows, for surface water (Barros et al., 2012a, 2012b; Causapé et al., 2004a; García-Garizábal et al., 2012, 2014) and ground water (Arauzo et al., 2011; García-Garizábal, 2012; Stigter et al., 2006). The leaching of salts and nitrate are of special interest when considering the main environmental impacts.

The leaching of salts is a requirement of irrigated agriculture (Letey et al., 2011), as the accumulation of salts in soil profiles is deleterious for plants, producing productivity losses and even, in extreme situations, forcing the abandonment of cultivation. Thus, there are cases where an excess of irrigation water is necessary to leach salts. Irrigation return flows with high levels of salts can impact both water supply systems and ecosystems (Duncan et al., 2008; Nielsen et al., 2003). The actual amount of leached salts depends on several factors such as climate, hydrogeological conditions or irrigation management (Causapé et al., 2004a; García-Garizábal et al., 2012). However, in newly-developed irrigated saline soils, a significant decrease in soil salinity after several years of irrigation has been reported (Wang et al., 2012). Thus it can be expected that, with adequate irrigation management, salt leaching decreases over time in newly-irrigated saline soils.

Nitrate pollution is a major concern in irrigated areas as high nitrate concentrations have been regarded as a threat for human health and ecosystems (Höring and Chapman, 2004; Sutton et al., 2011). Nitrogen is usually applied to crops in excessive amounts and leached during main rain events, although even in adequate amounts, irrigation water can also produce nitrogen leaching (García-Garizábal et al., 2012; He et al., 2012). Additionally, water availability implies in changes in the strategies of farmers, who tend to grow more productive crops and, thus, increase fertilization rates (Gaydon et al., 2012). Leached nitrogen not only supposes a loss of efficiency for the farmer's investment, but also implies in an increase of nitrate concentration in irrigation return flows (Arauzo et al., 2011; Merchán et al., 2013). Considerable increases in nitrate concentration of ground and surface waters have been linked to irrigated agriculture around the world (e.g., Stigter et al., 2006; Thayalakumaran et al., 2008; Lassaletta et al., 2009). As a consequence, it is expected that the implementation of irrigation increases nitrogen leaching until a new equilibrium between inputs, processes and outputs is reached.

Leaching of salts and nitrate has been studied in several irrigated areas of the Ebro River Basin (Spain). In these studies, differences have been reported between traditional flood (Causapé et al., 2004a) and modern pressurized (Tedeschi et al., 2001) irrigation systems. Besides, offsite pollution levels in rainfed areas can be close to those of

irrigated systems in areas with high rainfall (Casalí et al., 2008). Even though the results of these studies are reported in unitary terms, differences in climate, hydrological conditions, and irrigation and fertilization management hinder comparisons. However, studies carried out in a same area eliminate differences, and allow for differences in offsite pollution to be related to agricultural management, given a certain grade of variety due to climatic factors.

In a basin where the main land use is irrigated agriculture, long term monitoring of irrigated agriculture is necessary to adequately assess the evolution of salts and nitrate leaching. In this context, the objective of this study was to assess the salt and nitrogen pollution induced by a newly-irrigated area during the implementation and consolidation phases of irrigated agriculture. This was carried out based on water balances performed in a companion paper for a basin meeting these requirements (Merchán et al. COMPANION)

2. Description of study area

The complete climatic, geographical, geological and agronomical description of the study area (Lerma Basin, Zaragoza, Spain) can be found in the companion paper that presents the first part of this study (Merchán et al. COMPANION). This section provides additional information on soil salinity and nitrogen fertilization, specific to the objective of this work.

2.1. Soil salinity

Maps of the apparent electrical conductivity (EC_a) were generated (Urdanoz et al., 2008; Causapé et al., 2009) to obtain better information on the spatial variability of the soil salinity in the basin. The maps showed that the average apparent electrical conductivity in horizontal configuration (EC_{ah}) of the Lerma Basin soils (Fig. 1) was low (0.20 dS m^{-1}), although depressed areas at the bottom of the Tertiary valleys presented EC_{ah} values above 5.5 dS m^{-1}. EC_{ah} and electrical conductivity of the soil saturation extract (EC_e) (until 1 m soil depth) were correlated and it was verified that 92% of soils of the study area up to this depth presented EC_e below 4 dS m^{-1}, which represents a soil salinity that does not affect the performance of crops in the area.

The average apparent electrical conductivity in vertical configuration (EC_{av}) for the Lerma Basin (0.34 dS m^{-1}) was nearly twice that of EC_{ah} (0.20 dS m^{-1}), indicating the predominance of normal profiles where soil salinity increases with depth, which is coherent with the proximity to Tertiary saline substrate (Plata, 2011). However, inverted profiles were observed in 19% of the basin surface, especially close to the gullies and in uncultivated areas. Therefore, despite the fact that most of the soils present low salinity, the presence of Tertiary materials substrata (alternating marls, clays and gypsum, ITGE, 1988) constitutes the main source of salts.

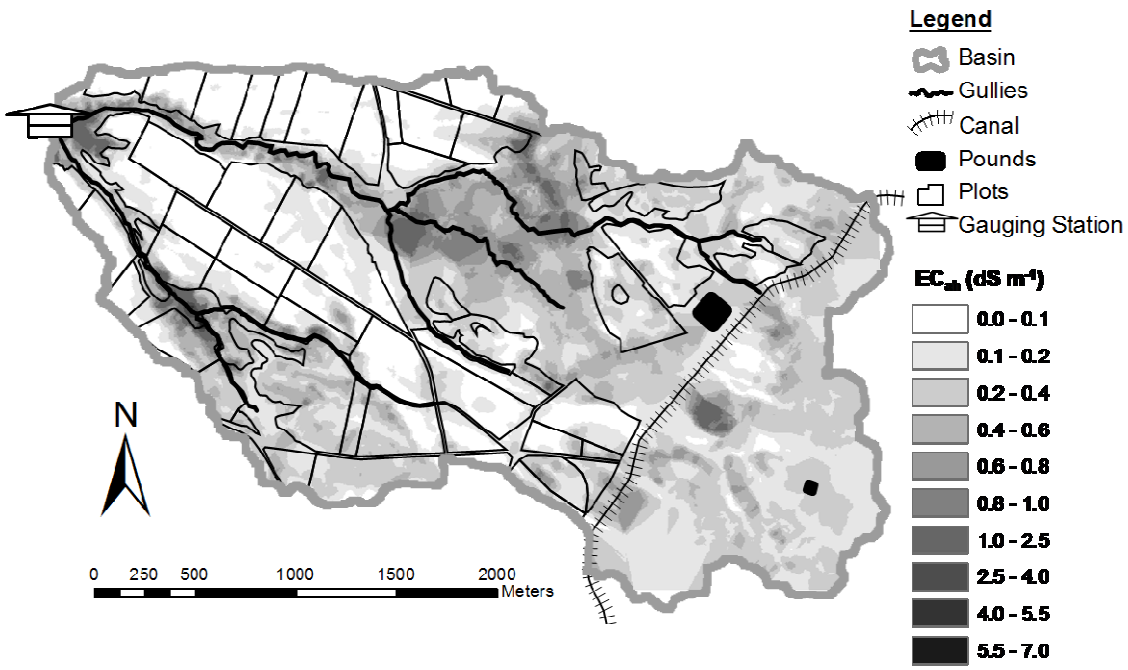

Fig.1. Apparent electrical conductivity in horizontal configuration (EC_{ah}) for the soils of the Lerma Basin. Selected hydrological, irrigation and monitoring features.

2.2. Nitrogen fertilization

Surveys were conducted during the years 2007, 2008 and 2012 (by phone and face-to-face enquiries) with all farmers included in Lerma Basin. The fertilization of the main crops of the study area (Merchán et al. COMPANION) is presented in this section. Fertilization of maize represented an average of 352 kg N ha^{-1} year^{-1}. The general agronomic management consisted of sowing fertilization with compound fertilizers (NPK, mainly 8-15-15 and 15-15-15), followed by multiple applications of liquid fertilizers (32% N: 16% urea and 16% ammonium nitrate) by “fertigation”. Winter cereals (wheat and barley) received 143 kg N ha^{-1} year^{-1}, distributed between the first applications as compound fertilizers a few days before sowing and the remainder as urea in early spring. Fertilization of tomato was characterized by frequent applications of small rates throughout the cycle, with the aim of overcoming the different nutritional requirements of each vegetative stage. Compound fertilizers and liquid fertilizers (fertigation through drip irrigation systems) were mainly used, with an average annual contribution of 124 kg N ha^{-1} year^{-1}. Finally, sunflower received an average of 104 kg N ha^{-1} year^{-1} through two applications, the first before sowing and a side-dressing in early June.

The remaining crops constituted a minority in the Lerma Basin, associated in part with double cropping of a plot in the same year (Merchán et al. COMPANION). The main associations were peas with maize or sunflower, and winter cereal with sunflower, maize or other summer crops. When winter cereal was followed by maize cultivation in the same year and plot, N fertilization reached 410 kg N ha^{-1} year^{-1}. Although existent,

the application of organic fertilizers such as manure or pig slurry was minimal and not used systematically (only in a few plots and punctually). In addition, there was no isotopic evidence of organic origins for nitrate dissolved in either ground or surface water (Merchán et al., 2014).

3. Methodology

3.1. Salt balance and exported nitrate

Salt balances were carried out and the nitrate exported was quantified during the period 2004–2013 for the irrigable area (352 ha). Salt and nitrate concentrations were assigned to the water balance components (Merchán et al. COMPANION). Null concentrations were assigned to evapotranspiration, wind drift and evaporation losses from sprinkler irrigation and storage in the soil, because these components have negligible concentrations or represent negligible contribution to salt balance and nitrate exported.

The salt and nitrate concentrations of precipitation (P) were determined from the average of eleven samples collected by a pluviometer with an applied sheet of liquid paraffin, in the study area. Average precipitation total dissolved solids (P_{TDS}) and nitrate-nitrogen (P_{NO3-N}) concentrations were 84 and 0.1 mg L^{-1}, respectively. The salt and nitrate concentrations of irrigation water were determined from the average of six samples taken from the irrigation canal (I_{TDS} = 275 mg L^{-1}; I_{NO3-N} = 0.5 mg L^{-1}), which presented low variability (coefficient of variation: CV_{TDS} = 9%, CV_{NO3-N} = 7%).

A great sampling effort was made to determine the concentration of salt and nitrate in the water exported from the Lerma Gully. This gully was initially sampled on a monthly basis until construction of the gauging station in 2005 (Fig. 1), when an automatic sampler (ISCO Model 3700) allowed for daily sampling. Water samples collected in the gully were transported to the laboratory, where the electrical conductivity of water corrected to 25 ◦C (EC) and nitrate-nitrogen concentration (NO_3^--N) were determined. An Orion-5 Star conductivimeter was utilized for the conductivity measurements, and an AutoAnalyzer 3 equipment was used to determine NO_3^--N by colorimetry. In July 2010 the daily sample procedure was replaced by an automatic water quality station which recorded, in 10-minute time steps, EC and NO_3^--N through a conductivimeter and a Hach-Lange Nitratax equipment connected to a *ad hoc* designed data-logger.

Seventeen water samples were selected within the range of variation of EC in the Lerma Gully, from which the concentration of bicarbonate (HCO_3^-) and dry residue (DR) were determined. From these concentrations, the total dissolved solids (TDS) were calculated from Eq. (1) (Custodio and Llamas, 1983):

$$TDS = DR + 1/2\ HCO_3^- \qquad (1)$$

For these water samples, the relationship between EC (dS m^{-1}) and TDS (mg L^{-1}) was used to convert EC into TDS through Eq. (2):

$$TDS = 712.22 \cdot EC - 104.83; \qquad R^2 = 0.99; \qquad p < 0.01 \qquad (2)$$

Eq. (2) was also used to estimate the total dissolved solids in the incoming water flows from the unirrigated area and water in the aquifer. The concentration of salt and nitrate of these waters was estimated from water samples manually collected at a gully before entrance into the irrigable area and in a net of piezometers. Incoming water flows from the unirrigated area were sampled monthly, and the salts and nitrate concentrations were assigned to the entire month. This component had relatively low influence on the water balance (6% of inputs) and therefore its influence on salts and nitrate balances is expected to be marginal. Variations of salt and nitrate stored in the aquifer were estimated through annual samples taken on October 1st, at the closure of water balances, and the variation in the saturated thickness in three representative piezometers (Merchán et al. COMPANION), located in each of the Quaternary materials units (lowest salinity surfaces in Fig. 1).

The product of concentrations and water volumes yields the mass of salt and nitrate for each component of the water balance. Note that herein the mass of nitrogen is estimated in the form of nitrate and not total nitrogen. However, it is considered a reasonable approach since nitrate accounted for 90% of total nitrogen in the Lerma Basin waters (Merchán et al., 2014). Nevertheless, this estimation should be considered as a minimum, and the actual amount of N leaving the basin may be slightly higher.

The difference between inputs (P: precipitation, I: irrigation, IWF: incoming water flows from the unirrigable area included in the basin), outputs (LG: Lerma Gully) and storage (A: aquifer) of the salinity balance corresponds mainly to the end result of the set of dissolution-precipitation processes. The influence of fertilizers was not considered in salt balances, since dissolution of soluble salts was the main salinization process and independency between nitrate pollution and salinization processes was reported in the study area (Merchán et al., 2015). Plant uptake of salts was considered negligible in this study.

$$\text{Inputs} - \text{Outputs} - \text{Storage} = (P + I + IWF) - (LG) - (A) \qquad (3)$$

In the case of nitrate, the objective was not necessarily to close a balance but to quantify the masses exported as well as the contribution from precipitation, irrigation and the unirrigated area in the basin. The difference between inputs, outputs and storage can be attributed to the combination of nitrogen cycle components not taken into account (e.g., fertilization inputs, crop exports, volatilization of ammonia in mineral fertilizers, nitrification and denitrification).

3.2. Contamination indices

The unit masses of exported salts and nitrate from the irrigable area (D_S and D_N, respectively) were obtained after discounting the contaminants introduced by the incoming water flows from the unirrigated area. Two indices proposed by Causapé (2009) were applied to further analyze the agro-environmental impact produced: salt contamination index (SCI) and nitrate contamination index (NCI):

$$SCI = D_S\ [Mg\ ha^{-1}\ year^{-1}] / EC_{NI}\ [dS\ m^{-1}] \quad (4)$$

$$NCI = D_N\ [kg\ ha^{-1}\ year^{-1}] / FN\ [kg\ ha^{-1}\ year^{-1}] \quad (5)$$

Where EC_{NI} is the average electrical conductivity of drainage during the unirrigated season of every year and represents the salinity of the geological materials of a specific irrigated land. FN represents the fertilization needs, which were annually estimated from the surfaces occupied by crops, harvest production, and the nitrogen extracted by the crops (Orús and Sin, 2006).

These two indices allow for the comparison of the impacts generated in different areas by irrigation. Comparison is possible as the indices adjust the exported unit masses by natural factors such as salinity from the local geology in the case of SCI, and climatic and socioeconomic factors (e.g., crops planted and respective nitrogenous fertilization requirements) in the case of NCI. Therefore, these indices are more permissive to unfavourable irrigated areas, presenting limits that well-managed irrigation areas with different characteristics should not exceed.

4. Results and discussion

4.1. Salts

4.1.1. Salts balance

The main entrance of salts into the system corresponded to the inputs through irrigation water, representing 45% of total inputs over the study period, despite the low salinity of irrigation water (EC < 0.4 dS m^{-1}) (Table 1). However, water flows from the unirrigable zone accounted for 43% of inputs. Precipitation presented the lowest salinity (EC < 0.1 dS m^{-1}) of all components considered, contributing with 12% of the salt inputs. Note that other salt entrances, such as those carried by fertilizers, have not been considered herein since the salinization of water has been mainly attributed to natural ongoing dissolution processes (Merchán et al., 2015).

The only output of salts considered was the water drained by the Lerma Gully (Table 1). Before the irrigation period, an average of 3.17 Mg ha^{-1} $year^{-1}$ was being exported whereas with the implementation of irrigation the output of salts increased up to

Table 1. Salt masses. Annual and cumulative inputs (IN) [precipitation (P), irrigation (I), incoming water flows (IWF) from the unirrigable area]; outputs (OUT) [water drained through the Lerma Gully (LG)]; and storage (ST) [in the aquifer (ΔA)] and differences between inputs, outputs and storage (IN-OUT-ST) for the years 2004-2013. Cumulative values are presented with annual values to facilitate comparison.

Year	IN								OUT		ST		IN-OUT-ST	
	P		I		IWF		Σ In		LG		ΔA			
	Annual	Cumulative	Annual	Cumulative	Annual	Cumulative	Annual	Cumulative	Annual	Cumulative	Annual	Cumulative	Annual	Cumulative
	---------- Mg ha^{-1} year^{-1} ----------													
2004	0.53	0.53	0.00	0.00	1.86	1.86	2.40	2.40	4.47	4.47	-	-	-2.04	-2.07
2005	0.19	0.36	0.00	0.00	0.71	1.28	0.90	1.65	1.88	3.17	-	-	-1.03	-1.53
2006	0.37	0.37	0.49	0.16	1.35	1.31	2.21	1.84	3.22	3.19	-	-	-0.95	-1.35
2007	0.34	0.36	1.24	0.43	1.18	1.27	2.76	2.07	2.68	3.06	-	-	0.04	-0.99
2008	0.31	0.35	1.48	0.64	1.08	1.24	2.87	2.23	3.68	3.19	-	-	-0.81	-0.96
2009	0.32	0.34	1.54	0.79	1.16	1.22	3.02	2.36	8.45	4.06	0.24	0.04	-5.54	-1.74
2010	0.26	0.33	1.55	0.90	1.00	1.19	2.81	2.42	5.41	4.25	-0.20	0.01	-2.57	-1.84
2011	0.28	0.33	1.56	0.98	1.01	1.17	2.86	2.48	4.13	4.24	-0.48	-0.06	-0.63	-1.71
2012	0.20	0.31	1.70	1.06	0.69	1.12	2.59	2.49	2.82	4.08	-0.13	-0.06	-0.16	-1.53
2013	0.40	0.32	1.45	1.10	1.49	1.15	3.35	2.58	6.72	4.35	0.50	-0.01	-3.96	-1.76

4.35 Mg ha^{-1} $year^{-1}$. Such an increase was mainly due to an increase in discharges (Merchán et al. COMPANION) as the water salinity in the Lerma Gully decreased with the implementation of irrigation (Merchán et al., 2013).

As occurred for the water balances previously performed in Lerma (Merchán et al. COMPANION) in the years when estimation of aquifer storage could be carried out, there were both negative and positive values, covering a range from -0.50 to +0.48 Mg ha^{-1} $year^{-1}$. A clear pattern was not apparent and the value of each year was dependent on the specific hydrological conditions of that year. The average storage for the entire study period was close to zero and therefore negligible in the long term balances.

The results of the annual balance show a predominance of dissolution processes over precipitation processes (IN-OUT-ST < 0, Table 1), with the only exception in 2007 when the aquifer storage was not estimated. Under unirrigated conditions, the dissolved mass of salts ranged between -1.03 Mg ha^{-1} $year^{-1}$ (212 mm of precipitation that year) and -2.04 Mg ha^{-1} $year^{-1}$ (627 mm), whereas in irrigated conditions the dissolved mass of salts reached up to -5.54 Mg ha^{-1} $year^{-1}$. Before irrigation, net dissolved masses reached -1.53 Mg ha^{-1} $year^{-1}$, whereas at the end of the balance net dissolved masses reached -1.76 Mg ha^{-1} $year^{-1}$, showing the increased dissolution caused by the addition of irrigation water.

Causapé et al. (2004b) had already identified dissolution processes as responsible for increases in salt contents in another irrigated area close to the study zone, with similar geological settings. In addition, Merchán et al. (2015) identified the main processes in the same study area through an extensive geochemical sampling. They concluded that dissolution of halite and gypsum were the main reason for the observed increase in salinity.

4.1.2. Salt Contamination Index

The unirrigated years presented the lowest value of masses of salts exported in the dry year 2005, 1.17 Mg ha^{-1} (Table 2) and 2.60 Mg ha^{-1} in the wet year 2004, covering a range of unirrigated conditions. These values were lower than others reported in unirrigated agricultural areas with similar precipitation but more saline groundwater in Western Australia (2.9 Mg ha^{-1} $year^{-1}$, Salama et al., 1993). With irrigation implementation, exports values up to 7.29 Mg ha^{-1} were reached in 2009. Before irrigation, 1.89 Mg ha^{-1} $year^{-1}$ was exported whereas during the irrigated period salts exported increased up to 3.51 Mg ha^{-1} $year^{-1}$.

Table 2. Annual and cumulative mass of exported salts from the irrigable area (D_S), average electrical conductivity of drainage during the unirrigated period (EC_{NI}) and salt contamination index (SCI) during the study years (2004-2013). Cumulative values are presented with annual values to facilitate comparison.

Year	D_S		EC_{NI}		SCI	
	Annual	Cumulative	Annual	Cumulative	Annual	Cumulative
	Mg ha^{-1} year^{-1}		dS m^{-1}		[Mg ha^{-1} year^{-1}]/[dS m^{-1}]	
2004	2.60	2.60	4.89	4.89	0.53	0.53
2005	1.17	1.89	5.45	5.17	0.21	0.36
2006	1.87	1.87	3.79	3.79	0.49	0.49
2007	1.50	1.68	3.78	3.79	0.40	0.44
2008	2.60	1.99	4.24	3.93	0.61	0.51
2009	7.29	3.32	4.59	4.10	1.59	0.81
2010	4.41	3.53	3.13	3.91	1.41	0.90
2011	3.12	3.46	2.81	3.72	1.11	0.93
2012	2.13	3.27	3.15	3.64	0.68	0.90
2013	5.23	3.51	3.86	3.67	1.36	0.96
Trend[a]	ns	**	ns	***	ns	*
Slope[a]	-	+0.23	-	-0.11	-	+0.06

[a] Significant trend and slope with Mann-Kendall test and Sen's slope (Helsel and Hirsch, 2002).
ns: non significant trend ($p > 0.1$); *: $p < 0.1$; **: $p < 0.05$; ***: $p < 0.01$.

Duncan et al. (2008) reviewed several studies of salt leaching from irrigated areas in Australia, Spain and United States, reporting ranges of salt loads between 0.04 and 40.9 Mg ha^{-1} year^{-1}. This range was narrowed in the irrigated area of the Ebro Basin from 0.67 Mg ha^{-1} year^{-1} in low salinity pressurized irrigated areas (Andrés and Cuchí, 2014) to 19.8 Mg ha^{-1} year^{-1} in high salinity flood irrigated soils (Barros et al., 2012a). As seen, irrigated agriculture presents a wide range of salt leaching depending on differences in hydrological settings, irrigation and drainage management, or climatic trends (Duncan et al., 2008).

Increasing salt loads in Lerma Basin contrast with the decrease of salts available in the study zone, indicated by the electrical conductivity of the water during the unirrigated period, with a significant decreasing trend of -0.11 dS m^{-1} year^{-1} (Table 2). The reported increases in irrigation drainage with the implementation of irrigation (Merchán et al. COMPANION) explain the rising values of the mass of salts exported in the study area (+0.23 Mg ha^{-1} year^{-2}) as well as the salt contamination index (annual +0.06 [Mg ha^{-1} year^{-1}]/[dS m^{-1}]). In fact, implementation of irrigation supposed an increase from 0.36 (unirrigated conditions) to average values of 1.23 [Mg ha^{-1} year^{-1}]/[dS m^{-1}] in the period in which irrigation was consolidated (2009-2013). These values were in the range of other pressurized irrigated areas of the Ebro Basin, where SCI values between 0.3 and 1.7 [Mg ha^{-1} year^{-1}]/[dS m^{-1}] were obtained for low saline and very high saline soils,

Table 3. Irrigation efficiency (IE), mass of salts exported by the irrigated area (D_S), electrical conductivity of the outlet water during the non irrigated period (EC_{NI}), salt contamination index (SCI), mass of nitrate-nitrogen exported by the irrigated area (D_N), fertilization needs (FN) and nitrate contamination index (NCI) for several irrigation districts in the Ebro Basin.

Study Area Irrig. District	Irrig. System	Study period	Area	IE	D_S	EC_{NI}	SCI	D_N	FN	NCI
			ha	%	[Mg ha^{-1} year^{-1}]	[dS m^{-1}]	[Mg ha^{-1} year^{-1}]/[dS m^{-1}]	kg NO_3^--N ha^{-1} year^{-1}	kg N ha^{-1} year^{-1}	-
DXIX[a] Bardenas I	flood (improved)	2001	100	56	4.5	1.1	4.3	101	115	0.88
		2005-2008		83	1.3	1.1	1.2	51	76	0.67
La Violada[b] Monegros II	flood (improved)	1996-1998	4k	47	19.8	1.8	10.7	106	242	0.44
		2006-2008		58	10.2	2.0	5.0	22	115	0.19
Lasesa[c] Alto Aragón	Pressurized mature	2010	1.4k	76	0.5	1.5	0.3	49	288	0.17
DIX & DXI[d] Monegros II	pressurized	1997-1999	494	80	-	-	-	18	225	0.08
		1997-1998	470		14.0	8.4	1.7	49	223	0.22
Lerma Basin Bardenas II	pressurized recent	2009-2013	352	76	4.4	3.5	1.2	41	267	0.16

[a] García-Garizábal et al., 2012, 2014.
[b] Barros et al., 2012a, 2012b.
[c] Andrés and Cuchí, 2014.
[d] Tedeschi et al., 2001 (salts data), Cavero et al., 2003 (nitrate data).

Table 4. Nitrate masses. Annual and cumulative inputs (IN) [precipitation (P), irrigation (I), incoming water flows (IWF) from the unirrigable area]; outputs (OUT) [water evacuated through the Lerma Gully (LG)]; and storage (ST) [in the aquifer (ΔA)] and differences between inputs, outputs and storage (IN-OUT-ST) for the years 2004-2013. Cumulative values are presented with annual values to facilitate comparison.

Year	IN								OUT		ST		IN-OUT-ST	
	P		I		IWF		Σ IN		LG		ΔA			
	Annual	Cumulative	Annual	Cumulative	Annual	Cumulative	Annual	Cumulative	Annual	Cumulative	Annual	Cumulative	Annual	Cumulative
	----------						kg NO_3^--N ha^{-1} $year^{-1}$		---------					
2004	0.53	0.53	0.00	0.00	0.50	0.50	1.03	1.03	14.26	14.26	-	-	-13.23	-13.23
2005	0.19	0.36	0.00	0.00	0.21	0.36	0.40	0.72	9.27	11.77	-	-	-8.87	-11.05
2006	0.37	0.36	0.80	0.27	0.38	0.36	1.55	0.99	6.93	10.15	-	-	-5.38	-9.16
2007	0.34	0.36	2.04	0.71	0.33	0.36	2.71	1.42	11.89	10.59	-	-	-9.18	-9.16
2008	0.31	0.35	2.44	1.06	0.31	0.35	3.05	1.75	22.34	12.94	-	-	-19.29	-11.19
2009	0.32	0.34	2.53	1.30	0.33	0.34	3.18	1.99	56.61	20.22	-6.0	-1.01	-47.38	-17.22
2010	0.26	0.33	2.54	1.48	0.33	0.34	3.13	2.15	40.50	23.11	-3.6	-1.38	-33.77	-19.59
2011	0.28	0.32	2.57	1.61	0.29	0.34	3.14	2.27	36.86	24.83	-0.8	-1.31	-32.89	-21.25
2012	0.20	0.31	2.79	1.74	0.21	0.32	3.20	2.38	24.21	24.76	-7.2	-1.96	-13.85	-20.43
2013	0.40	0.32	2.39	1.81	0.41	0.33	3.20	2.46	49.42	27.23	10.0	-0.77	-56.20	-24.00

respectively (Table 3, Andrés and Cuchí, 2014; Tedeschi et al., 2001). Flood irrigated areas with low and high natural salinity presented higher SCI, reaching values of 4.3 and 10.7 [Mg ha^{-1} $year^{-1}$]/[dS m^{-1}], respectively (García-Garizábal et al., 2014; Barros et al., 2012a).

Since the irrigated surface and irrigation rates have stabilized, it is expected that the system has reached a new steady state, and variations in the different years are due to variation in water availability (both by precipitation and irrigation rates). However, confirmation in the long term is strongly recommended (Thayalakumaran et al., 2007) as changes in drainage water salinity have been observed in other saline irrigation areas after more than 50 years of irrigation implementation (Barros et al., 2012a).

4.2. Nitrate

4.2.1. Exported nitrate

Among the components directly estimated in this study, the most significant nitrate input in the Lerma Basin during the study period was irrigation water (corresponding to 57%), followed by incoming flows from unirrigable areas (33%) and rain water (10%, Table 4). Annually, these percentages varied depending on the volume of rainfall and irrigation applied: the greatest components were rainwater and incoming flows from the unirrigated area at the beginning of the study (2004-2006) and then major component was irrigation (2007-2013). These water balance components presented low concentrations of nitrate (average values of 0.4 mg L^{-1} for precipitation water, 2 mg L^{-1} for irrigation water and 8 mg L^{-1} for incoming flows from unirrigable areas).

Before implementation of irrigation, Lerma Gully carried 14.26 kg NO_3^--N ha^{-1} $year^{-1}$ in the wet year of 2004 and 9.27 kg NO_3^--N ha^{-1} $year^{-1}$ in the dry year 2005. These values were higher than those observed for the first years of irrigation (2006-2007) due to remaining N from when the basin was rainfed-cultivated only (stored in soils and aquifer of the basin before irrigation implementation). The absence of fertilization coupled with the lack of rain caused a decrease in the nitrate exported in the years 2005 (9.1 kg NO_3^--N ha^{-1}) and 2006 (6.5 kg NO_3^--N ha^{-1} $year^{-1}$).

The gradual implementation of irrigation, which began in 2006, led to a progressive increase in the use of fertilizers in the area, increasing the nitrogen applied as well as the NO_3^--N loads in the gully. The greatest mass of nitrate flowing in Lerma Gully was recorded in 2009 (56.61 kg NO_3^--N ha^{-1} $year^{-1}$), right after high fertilization needs (294 kg N ha^{-1}) were recorded in 2008. These dynamics suggest a delay of 1-2 years in the response to N inputs. Until the remaining N was leached, Lerma Gully presented concentrations comparable to those recorded during the irrigated period, approximately 80 mg L^{-1} (Merchán et al., 2013). The delay in the hydrological behaviour of N depends on predominant hydrological flow paths and the scale of the study zone, and thus is very site specific. For instance, Howden et al. (2011) reported a delay of ≈ 37 years in the N

hydrological response in a highly groundwater-controlled, small scale, headwater basin in the Thames River Basin with an average of 40 m unsaturated zone. In the Lerma Basin, with shallow aquifers and a high degree of connection between the aquifers and the gullies, the delay is minimal as exposed previously.

In the years where storage could be estimated, storage ranged from values of -7.2 to 10.0 kg NO_3^--N ha^{-1} $year^{-1}$. Its accumulated value was -0.77 kg NO_3^--N ha^{-1} $year^{-1}$, which is a significant value when compared to other considered inputs.

The sum of considered inputs accounted for 12% of nitrate-nitrogen exported from the Lerma Gully (27.23 kg NO_3^--N ha^{-1} $year^{-1}$, Table 4), providing a value for IN-OUT-ST of -24.00 kg NO_3^--N ha^{-1} $year^{-1}$. This pattern was recorded every year, indicating that, of the components not taken into account, inputs (e.g., nitrogen fertilization) were higher than outputs (e.g., exported N in harvest, volatilization or denitrification).

4.2.2. Nitrate contamination index

Under unirrigated conditions (2004-2005), the mass of nitrate exported was, on average, 11.4 kg NO_3^--N ha^{-1} $year^{-1}$ (Table 5, cumulative value for 2005). In small basins with contrasting land uses, which were monitored for ≈ 10 years in other areas of the Ebro River Basin, N loads of 5 kg ha^{-1} $year^{-1}$ for forests, 12 kg ha^{-1} $year^{-1}$ for pastures and between 17 and 37 kg ha^{-1} $year^{-1}$ for rainfed agriculture areas have been reported (Casalí et al., 2008, 2010). Similar figures were found for rainfed agriculture in other countries, such as Sweden, where the N leaching in 21 agricultural catchments with similar precipitation ranged from 6 to 32 kg N ha^{-1} $year^{-1}$ (Kyllmar et al., 2014).

With irrigation, the mass of exported nitrate-nitrogen in Lerma Basin increased significantly (2.6 kg NO_3^--N ha^{-1} $year^{-2}$, Table 5) until reaching average values of 30.8 kg NO_3^--N ha^{-1} $year^{-1}$, with a maximum of 56.3 kg NO_3^--N ha^{-1} $year^{-1}$ for the year 2009. This average value was approximately three times the values recorded under unirrigated conditions. Other pressurized irrigated areas exported similar values (between 18 to 49 kg ha^{-1} $year^{-1}$; Cavero et al., 2003; Andrés and Cuchí, 2014; Table 3). However, flood irrigated areas of the Ebro River Basin presented higher values, over 100 kg NO_3^--N ha^{-1} $year^{-1}$ (García-Garizábal et al., 2012; Barros et al., 2012b).

The comparison with the net N load from cultivated areas does not take into account specific characteristics of the area, such as fertilization needs of different crops. Fertilization needs increased (8.8 kg N ha^{-1} $year^{-2}$, Table 5) mainly during the first three years (2006-2008), as a consequence of the progressive transformation into irrigated land. Fertilization needs reached an average of 251 kg N ha^{-1} $year^{-1}$ across the irrigated period, with a maximum of 302 kg N ha^{-1} $year^{-1}$ for the last year (2013). These values were one of the highest reported in the Ebro Basin irrigated areas (Table 3) due to the high proportion of crops with high fertilization needs (e.g., maize).

Table 5. Annual and cumulative mass of nitrate exported from the irrigable area (D_N), fertilization needs (FN) and nitrate contamination index (NCI) during the study years (2004-2013). Cumulative values are presented with annual values to facilitate comparison.

Year	D_N		FN		NCI	
	Annual	Cumulative	Annual	Cumulative	Annual	Cumulative
	kg NO_3^--N ha^{-1} $year^{-1}$		kg N ha^{-1} $year^{-1}$		-	
2004	13.8	13.8	-	-	-	-
2005	9.1	11.4	-	-	-	-
2006	6.5	6.5	123	123	0.05	0.05
2007	11.6	9.1	255	189	0.05	0.05
2008	22.0	13.4	294	224	0.07	0.06
2009	56.3	24.1	267	235	0.21	0.10
2010	40.2	27.3	219	232	0.18	0.12
2011	36.6	28.9	266	237	0.14	0.12
2012	24.0	28.2	281	244	0.09	0.12
2013	49.0	30.8	302	251	0.16	0.12
Trend[a]	ns	***	ns	***	ns	**
Slope[a]	-	+2.6	-	+8.8	-	0.01

[a] Significant trend and slope with Mann-Kendall test and Sen's slope (Helsel and Hirsch, 2002).
ns: non significant trend ($p > 0.1$); *: $p < 0.1$; **: $p < 0.05$; ***: $p < 0.01$.

Nitrate contamination index gradually increased with the transformation of the basin, from 0.05 in 2006 to a maximum of 0.21 in 2009 (Table 5). The average for the entire irrigated period was 0.12 and its accumulated values were practically constant since 2010. Therefore, the implementation of irrigation supposed an increase of 0.01 $year^{-1}$. However, this NCI trend is lower than that observed for the exported mass of nitrate (2.6 kg NO_3^--N ha^{-1} $year^{-1}$), as a consequence of the higher increasing trend in FN (8.8 kg N ha^{-1} $year^{-2}$). In other pressurized irrigated areas of the Ebro Basin, similar figures were recorded (Table 3): 0.17, Andrés and Cuchí, 2014; 0.08 to 0.22, Cavero et al., 2003. Flood irrigated areas with lower FN (115-242 kg NO_3^--N ha^{-1} $year^{-1}$) presented higher NCI (from 0.44 to 0.88, García-Garizábal et al., 2012; Barros et al., 2012b).

Despite the apparent stabilization in NCI, it is necessary to continue monitoring the area, especially considering the expected changes in fertilization management imposed by the designation of the study zone as a vulnerable zone to nitrate pollution (BOA, 2009).

4.3. Agro-environmental assessment

The values obtained for exported mass of salts and nitrate in the Lerma Basin are within those observed in other areas of the world. However, comparison of actual figures is difficult as a consequence of the different natural and agronomic conditions of each area. Causapé (2009) compared SCI and NCI values of different irrigated areas of the Ebro Basin and related them to irrigation management, concluding that SCI values < 2.0 [Mg ha^{-1} $year^{-1}$]/[dS m^{-1}] and NCI values < 0.2 are indicative of an acceptable water use (irrigation efficiency > 80%), with a relatively small mass of exported salts and nitrate for the natural and agronomic conditions of the irrigated system.

In this sense, pollution indices once the irrigated area was consolidated ($SCI_{09\text{-}13}$ = 1.2 [Mg ha^{-1} $year^{-1}$]/[dS m^{-1}] and $NCI_{09\text{-}13}$ = 0.16) were below the exposed thresholds, and may be probably reduced with higher irrigation efficiency, which did not reach 80% (Merchán et al. COMPANION). Although increases were verified in the masses of salts and nitrate exported during the first years of irrigation, the values obtained were still low considering the salinity and fertilization needs of the area.

Other irrigated areas with more favourable conditions (low salinity and fertilization needs) presented higher pollution indices, which could be related to the management of the irrigated system. Data reported for several irrigation areas (Table 3) show how higher efficiencies in irrigation provided lower pollution indices (Fig. 2), being these key factors to minimize agro-environmental impacts. However, this relationship was not as clearly observed in the case of the nitrate pollution index as in the salt pollution index. Nitrate pollution is affected by several other factors, both natural (e.g., soil texture) and anthropogenic (e.g., fertilization management), and therefore is more variable.

As an example of how improved management can reduce pollution indices, García-Garizábal et al. (2012, 2014) demonstrated how small improvements in irrigation management incremented irrigation efficiencies in flood irrigation areas (from 56 and 83%) and decreased SCI in 70% (reaching levels of 1.2 [Mg ha^{-1} $year^{-1}$]/[dS m^{-1}]) and NCI in 24% (reaching values of 0.67) (Table 3). In a similar way, decreases of approximately 50% in SCI and 56% in NCI were observed after structural and management improvements in another flood irrigation system, reaching levels of SCI and NCI of 5.0 [Mg ha^{-1} $year^{-1}$]/[dS m^{-1}] and 0.19, respectively (Barros et al., 2012a, 2012b).

These observations were in line with the general thinking that the adaptation of water application to crop needs is the most effective measure to reduce N leaching (Quemada et al., 2013). Thus, irrigation management appears as a key factor to improve agro-environmental quality. Improvements in irrigation management for the Lerma Basin were deeply discussed in the first part of this study (Merchán et al. COMPANION).

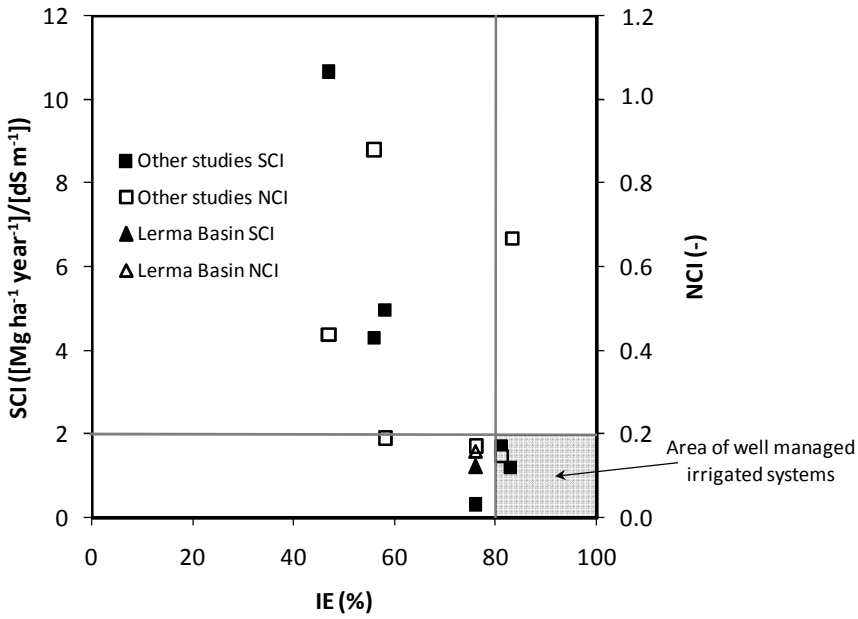

Fig. 2. Relation between irrigation efficiency (IE, %) and pollution indexes: salt contamination index (SCI, [Mg ha^{-1} $year^{-1}$]/[dS m^{-1}]) and nitrate contamination index (NCI, -). Data from the studies included are presented in Table 3. More sustainable irrigated areas are within the zone with IE >80%, ICS <2 [Mg ha^{-1} $year^{-1}$]/[dS m^{-1}] and NCI <0.2, thresholds indicated by grey lines and shaded area.

Apart from irrigation, there are other management factors affecting the leaching of salts and nitrate from irrigated agriculture. For instance, significant reductions in salts (from 7.5 to 4.7-5.3 Mg ha^{-1} $year^{-1}$) and nitrate (from 99 to 37-70 kg NO_3^--N ha^{-1} $year^{-1}$) leaching from maize plots were observed in a treatment with two different cover crops (Gabriel et al., 2012a, 2012b).

Moreover, the application of recommended fertilization rates decreased nitrate leaching. However, significant reductions in yield were observed in several trials, which could be avoided with optimal application times (Quemada et al., 2013). In fact, the application of nitrogen fertilizers over a threshold value does not increase yield significantly. Instead, nitrate leaching is increased (e.g., Arbat et al., 2013; He et al., 2012), with even decreasing yields being reported when extreme fertilization rates were applied to some crops (Castellanos et al., 2013).

Other factors, out of the control of farmers, are also relevant to nitrate pollution. In a long term study carried out in similarly managed irrigated soils of the Ebro Basin, no leaching in fine soils and high leaching in coarse soils were reported (Arauzo and Valladolid, 2013). This corroborates observations made in other countries, with lower leaching values for clay-textured soils than for sandy soils (Kyllmar et al., 2014).

Therefore the optimization of water and fertilization managements along with, when needed, some additional measures (such as the usage of cover crops) should be implemented in order to decrease agro-environmental impacts on water bodies receiving irrigation return flows.

5. Conclusions

Dissolution processes were the main source of exported salts in the Lerma Basin, and these processes predominated over precipitation (1.76 Mg ha^{-1} $year^{-1}$) in the salt balance. These exported salts evolved from 1.89 Mg ha^{-1} $year^{-1}$ under unirrigated conditions to 3.51 Mg ha^{-1} $year^{-1}$ under irrigated conditions, increasing with a rate of 0.23 Mg ha^{-1} $year^{-2}$. The salt contamination index was almost three times higher during the irrigated period (0.96 [Mg ha^{-1} $year^{-1}$]/[dS m^{-1}]) in comparison with the unirrigated period (0.36 [Mg ha^{-1} $year^{-1}$]/[dS m^{-1}]). Due to progressive salt washing of the study zone, lower increases were verified in comparison with the exported salts.

Regarding nitrate exports, increases were verified from 9.1 kg NO_3^--N ha^{-1} $year^{-1}$ under unirrigated conditions to 30.8 kg NO_3^--N ha^{-1} $year^{-1}$ during the irrigated period. Nitrate contamination indices have increased with irrigation implementation until reaching a stable value of 0.12, being this value more than double of that obtained in the first years of irrigation.

Despite SCI and NCI are within the threshold considered for the more sustainable irrigated areas (SCI < 2.0 [Mg ha^{-1} $year^{-1}$]/[dS m^{-1}] and NCI < 0.2), it would be advisable to improve irrigation management to increase water use and decrease leaching. Additionally, complementary measures such as adjusting fertilization rates to temporal crop necessities or the use of catch crops may prove useful.

Acknowledgements This work was performed within project CGL2012-32395 (Spanish Ministry of Economy and Competitiveness – Feder-EU Funds) and benefited from grant BES2010-034124 (Spanish Ministry of Economy and Competitiveness). Dr. Iker García-Garizábal was supported by the PROMETEO grant from SENESCYT-Ecuador. Thanks are also extended to the Irrigation Authority XI of Bardenas Irrigation Scheme, for facilitating irrigation data and providing help in several field-related issues.

REFERENCES

Arauzo, M., Valladolid, M., Martínez-Bastida, J.J., 2011. Spatio-temporal dynamics of nitrogen in river-alluvial aquifer systems affected by diffuse pollution from agricultural sources: Implications for the implementation of the Nitrates Directive. Journal of Hydrology 411: 155-168. doi: 10.1016/j.agwat.2011.01.004

Arauzo, M., Valladolid, M., 2013. Drainage and N-leaching in alluvial soils under agricultural land uses: Implications for the implementation of the EU Nitrates Directive. Agriculture, Ecosystems and Environment 179: 94– 107. doi: 10.1016/j.agee.2013.07.013

Arbat, G., Roselló, A., Domingo Olivé, F., Puig-Bargués, J., González Llinàs, E., Duran-Ros, M., Pujol, J., Ramírez de Cartagena, F. (2013). Soil water and nitrate distribution under drip irrigated corn receiving pig slurry. Agricultural Water Management 120: 11-22. doi: 10.1016/j.agwat.2012.08.001

Andrés, R., Cuchí, J.A., 2014. Salt and nitrate exports from the sprinkler-irrigated Malfarás creek watershed (Ebro river valley, Spain) during 2010. Environmental Earth Science 72(7): 2667-2682. doi: 10.1007/s12665-014-3174-0

Barros, R., Isidoro, D., Aragüés, R., 2012a. Three study decades on irrigation performance and salt concentrations and loads in the irrigation return flows of La Violada irrigation district (Spain). Agriculture, Ecosystems and Environment 151: 44-52. doi: 10.1016/j.agee.2012.02.003

Barros, R., Isidoro, D., Aragüés, R., 2012b. Irrigation management, nitrogen fertilization and nitrogen losses in the return flows of La Violada irrigation district (Spain). Agriculture, Ecosystems and Environment 155: 161-171. doi: 10.1016/j.agee.2012.04.004

BOA, 2009. Orden de 11 de diciembre de 2008, del Consejero de Agricultura y Alimentación, por la que se designan y modifican las zonas vulnerables a la contaminación de las aguas por nitratos procedentes de fuentes agrarias en la Comunidad Autónoma de Aragón. Boletín Oficial de Aragón 1, de 02 de Enero de 2009 (in Spanish). www.boa.aragon.es (accessed 27.06.14).

Casalí, J., Gastesi, R., Álvarez-Mozos, J., De Santisteban, L.M., Del Valle de Lersundi, J., Giménez, R., Larrañaga, A., Goñi, M., Agirre, U., Campo, M.A., López, J.J., Donézar, M., 2008. Runoff, erosion, and water quality of agricultural watersheds in central Navarre (Spain). Agricultural Water Management 95: 1111-1128. doi: 10.1016/j.agwat.2008.06.013

Casalí, J., Giménez, R., Díez, J., Álvarez-Mozos, J., Del Valle de Lersundi, J., Goñi, M., Campo, M.A., Chahor, Y., Gastesi, R., López, J., 2010. Sediment production and water quality of watersheds with contrasting land use in Navarre (Spain). Agricultural Water Management 97: 1683-1694. doi: 10.1016/j.agwat.2010.05.024

Castellanos, M.T., Tarquis, A.M., Ribas, F., Cabello, M.J., Arce, A., Cartagena, M.C., 2013. Nitrogen fertigation: An integrated agronomic and environmental study. Agricultural Water Management 120: 46-55. doi: 10.1016/j.agwat.2012.06.016

Causapé, J., 2009. A computer-based program for the assessment of water-induced contamination in irrigated lands. Environmental Monitoring Assessment 158: 307-314. doi: 10.1007/s10661-008-0584-z

Causapé, J., Quílez, D., Aragües, R., 2004a. Assessment of irrigation and environmental quality at the hydrological basin level II: Salt and nitrate loads in irrigation return flows. Agricultural Water Management 70: 211-228. doi: 10.1016/j.agwat.2004.06.006

Causapé, J., Auqué, L., Gimeno, M.J., Mandado, J., Quílez, D., Aragües, R., 2004b. Irrigation effects on the salinity of the Arba and Riguel Rivers (Spain): present diagnosis and expected evolution using geochemical models. Environmental Geology 45: 703-715. doi: 10.1007/s00254-003-0927-6

Causapé, J., Clavería, I., Abrahão, R., García-Garizabal, I., 2009. Cartografía edáfica mediante un Sensor Electromagnético Móvil Georreferenciado (SEMG). XXVII Reunión Científica del Suelo. Sociedad Española de la Ciencia del Suelo. Huesca.

Cavero, J., Beltrán, A., Aragües, R., 2003. Nitrate exported in drainage waters of two sprinkler-irrigated watersheds. Journal of Environmental Quality 32 (3): 916-926.

Custodio, E., Llamas, M., 1983. Hidrología Subterránea. Ediciones Omega, Barcelona, Spain.

Duncan, R.A., Bethune, M.G., Thayalakumaran, T., Christen, E.W., McMahon, T.A., 2008. Management of salt mobilization in the irrigated landscape – A review of selected irrigation regions. Journal of Hydrology 351: 238-252. doi: 10.1016/j.jhydrol.2007.12.002

Gabriel, J.L., Almendros, P., Hontoria, C., Quemada, M., 2012a. The role of cover crops in irrigated systems: Soil salinity and salt leaching. Agriculture, Ecosystems and Environment 158: 200-207. doi: 10.1016/j.agee.2012.06.012

Gabriel, J.L., Muñoz-Carpena, R., Quemada, M., 2012b. The role of cover crops in irrigated systems: Water balance, nitrate leaching and soil mineral nitrogen accumulation. Agriculture, Ecosystems and Environment 155: 50-61. doi: 10.1016/j.agee.2012.03.021

García-Garizábal, I., 2012. Dynamics of an aquifer and water quality in a traditional irrigated land in the Ebro river basin. ITEA Informacion Técnica Economica Agraria 108(2): 115-130.

García-Garizábal, I., Causapé, J., Abrahão, R., 2012. Nitrate contamination and its relationship with flood irrigation management. Journal of Hydrology 442-443: 15-22. doi: 10.1016/j.jhydrol.2012.03.017

García-Garizábal, I., Gimeno, M.J., Auqué, L.F., Causapé, J., 2014. Salinity contamination response to changes in irrigation management. Application of geochemical codes. Spanish Journal of Agricultural Research 12(2): 376-387. doi: 10.5424/sjar/2014122-4694

Gaydon, D.S., Meinke, H., Rodriguez, D., 2012. The best farm-level irrigation strategy changes seasonally with fluctuating water availability. Agricultural Water Management 103: 33-42. doi: 10.1016/j.agwat.2011.10.015

He, J., Dukes, M.D., Hochmuth, G.J., Jones, J.W., Graham, W.D., 2012. Identifying irrigation and nitrogen best management practices for sweet corn production on sandy soils using CERES-Maize model. Agricultural Water Management 109: 61-70. doi: 10.1016/j.agwat.2012.02.007

Helsel, D.R., Hirsch, R.M., 2002. Statistical methods in water resources. Techniques of water resources investigations, Book 4, Chapter A3. Reston, VA: US Geological Survey.

Höring, H., Chapman, D., 2004. Nitrates and Nitrites in Drinking Water. In: World Health Organization Drinking Water Series. IWA Publishing, London.

Howden, N.J.K., Burt, T.P., Mathias, S.A., Worrall, F., Whelan, M.J., 2011. Modelling long-term diffuse nitrate pollution at the catchment-scale: Data, parameter and epistemic uncertainty. Journal of Hydrology 403: 337-351. doi: 10.1016/j.jhydrol.2011.04.012

ITGE (Instituto Tecnológico GeoMinero de España), 1988. Mapa Geológico de España, Ejea de los Caballeros (map and memory) no. 284 27-12. Madrid.

Kyllmar, K., Stjernman Forsberg, L., Andersson, S., Martensson, K., 2014. Small agricultural monitoring catchments in Sweden representing environmental impact. Agriculture, Ecosystems and Environment 198: 25-35. doi: 10.1016/j.agee.2014.05.016

Lassaletta, L., García-Gómez, H., Gimeno, B.S., Rovira, J.V., 2009. Agriculture-induced increase in nitrate concentrations in stream waters of a large Mediterranean catchment over 25 years (1981-2005). Science of the Total Environment 407: 6034-6043. doi: 10.1016/j.scitotenv.2009.08.002

Letey, J., Hoffman, G.J., Hopmans, J.W., Grattan, S.R., Suarez, D., Corwin, D.L., Oster, J.D., Wu, L., Amrhein, C., 2011. Evaluation of soil salinity leaching requirement guidelines. Agricultural Water Management 98: 502-506. doi: 10.1016/j.agwat.2010.08.009

Merchán, D., Causapé, J., Abrahão, R., 2013. Impact of irrigation implementation on hydrology and water quality in a small irrigated agricultural area in Spain. Hydrological Sciences Journal 58: 1400-1413. doi: 10.1080/02626667.2013.829576

Merchán, D., Otero, N., Soler, A., Causapé, J., 2014. Main sources and processes affecting dissolved sulphates and nitrates in a small irrigated basin (Lerma Basin, Zaragoza, Spain): Isotopic characterization. Agriculture, Ecosystems and Environment 195: 127–138. doi: 10.1016/j.agee.2014.05.011

Merchán, D., Auqué, L.F., Acero, P., Gimeno, M.J., Causapé, J., 2015. Geochemical processes controlling water salinization in an irrigated basin in Spain: Identification of natural or anthropogenic influence. Science of the Total Environment 502: 330-343. doi: 10.1016/j.scitotenv.2014.09.041

Merchán, D., Causapé, J., Abrahão, R., García-Garizábal, I., COMPANION. Assessment of a newly implemented irrigated area (Lerma Basin, Spain) over a 10-year period. I: Water Balances and Irrigation Performance. Accepted in Agricultural Water Management.

Nielsen, D.L., Brock, M.A., Rees, G.N., Baldwin, D.S., 2003. Effects of increasing salinity on freshwater ecosystems in Australia. Australian Journal of Botany 51: 655-665. doi: 10.1016/j.agwat.2012.03.011

Oliver, D.P., Kookana, R.S., 2012. Minimising agricultural pollution to enhance water quality in the Philippines and Australia. Agricultural Water Management 106: 1-2. doi: 10.1016/j.agwat.2011.12.009

Orús, F., Sin, E., 2006. El balance del nitrógeno en la agricultura. In: Andreu, J., Betrán, J., Delgado, I., Espada, J.L., Gil, M., Gutiérrez, M., Iguácel, F., Isla, R., Muñoz, F., Orús, F., Pérez, M., Quílez, D., Sin, E., Yagüe, M.R., (Eds.), Fertilización nitrogenada. Guía de actualización. Informaciones Técnicas. Gobierno de Aragón, Zaragoza, Spain.

Plata, J.L., 2011. Informe sobre la determinación de la potencia de glacis en el barranco de Lerma (Zaragoza) mediante Sondeos Eléctricos Verticales. Informe IGME Centro de Documentación nº 64098 (in Spanish).

Quemada, M., Baranski, M., Nobel-de Lange, M.N.J., Vallejo, A., Cooper, J.M., 2013. Meta-analysis of strategies to control nitrate leaching in irrigated agricultural systems and their effects on crop yield. Agriculture, Ecosystems and Environment 174: 1-10.

Salama, R.B., Farrington, P., Bartle, G.A., Watson, G.D., 1993. Salinity trends in the wheatbelt of Western Australia: results of water and salt balance studies from Cuballing catchment. Journal of Hydrology 145: 41-63.

Stigter, T.Y., Carvalho Dill, A.M.M., Ribeiro, L., Reis, E., 2006. Impact of the shift from groundwater to surface water irrigation on aquifer dynamics and hydrochemistry in a semi-arid region in the south of Portugal. Agricultural Water management 85: 121-132. doi: 10.1016/j.agwat.2006.04.004

Sutton, M.A., Howard, C.M., Erisman, J.W., Billen, G., Bleeker, A., Grennfelt, P., van Grisven, H., Grizzetti, B., 2011. The European Nitrogen Assessment: Sources, Effects and Policy Perspectives. Cambridge University Press, Cambridge.

Tedeschi, A., Beltrán, A., Aragüés, R., 2001. Irrigation management and hydrosalinity balance in a semi-arid area of the middle Ebro river basin (Spain). Agricultural Water Management 49: 31-50.

Thayalakumaran, T., Bethune, M.G., McMahon, T.A., 2007. Achieving a salt balance-Should it be a management objective? Agricultural Water Management 92: 1-12. doi: 10.1016/j.agwat.2007.05.004

Thayalakumaran, T., Bristow, K.L., Charlesworth, P.B., Fass, T., 2008. Geochemical conditions in groundwater systems: Implications for the attenuation of agricultural nitrate. Agricultural Water Management 95: 103-115. doi: 10.1016/j.agwat.2007.09.003

Urdanoz, V., Amezketa, E., Clavería, I., Ochoa, V., Aragües, R., 2008. Mobile and georeferenced electromagnetic sensors and applications for salinity assessment. Spanish Journal of Agricultural Research 6(3): 469-478.

Wang, R., Kang, Y., Wan, S., Hu, W., Liu, S., Jiang, S., Liu, S., 2012. Influence of different amounts of irrigation water on salt leaching and cotton growth under

drip irrigation in an arid and saline area. Agricultural Water Management 110: 109-117. doi: 10.1016/j.agwat.2012.04.005

CHAPTER IX

DISCUSSION AND CONCLUSIONS

IX. DISCUSSION AND CONCLUSIONS

This PhD Thesis has studied the impacts of irrigated agriculture over water bodies receiving irrigation return flows, basically with respect to their salinization and nitrate pollution, two relevant environmental problems of irrigated agriculture in general and, specifically, in some irrigated areas of the Ebro Basin. The main points covered in the research correspond to the five published (or accepted for publication) papers included in the work. In this chapter, the joint discussion of the results and the relationships between the independent works are presented, followed by the main PhD Thesis conclusions.

9.1. Joint Discussion

The transformation to irrigated land in the Lerma Basin has produced hydrological changes regarding quantity and quality of water. This final discussion deals with the integrated results of the different aspects studied in this work and described in the papers. The references to the published papers included in the framework of this thesis are made following the notation used throughout the dissertation (e.g., Paper I).

9.1.1. Water balance and irrigation performance

The implementation of irrigation produced an important shift in the water balance of the Lerma Basin. While during unirrigated conditions precipitation was the only water input in the study area (with an average of 382 mm), the implementation of irrigation greatly increased the inputs at the basin level, raising them up to 574 mm (382 mm from precipitation, 192 mm from irrigation). This shift was even more acute if we consider only the irrigated surface, so that the average inputs rose from 382 mm (only precipitation) to 783 mm (382 mm of precipitation and 401 mm of irrigation, Paper IV).

In general, the irrigation performance of the Lerma Basin is within the observed values for other pressurized irrigated areas in the Ebro Basin. Irrigation efficiency reached 76.1%, while the losses of efficiency where due to evaporation and wind drift losses (13.5%) and drainage fraction (10.4%). A water deficit of 17.8% was estimated. The irrigation efficiency increased (1.05% year^{-1}) while irrigation drainage fraction decreased

(0.95% year^{-1}), through the period 2006-2013. No significant changes in evaporation and wind drift losses of sprinkler irrigation were detected. Despite these facts, an improvement in irrigation performance was not guaranteed, as water deficit has also increased (0.95% year^{-1}; Paper IV).

It is necessary to improve irrigation management in order to obtain higher irrigation efficiency, while decreasing evaporation and wind drift losses, drainage fraction and water deficit. Provided irrigation infrastructure allows for it, irrigation events should be adjusted to crops water requirements in order to obtain an optimal water use (Paper IV).

In the period during which groundwater was accessible, a great dependence on the applied irrigation was observed, with sharp increases at the end of the irrigation season (Paper IV). This is probably due to certain delay caused by the unsaturated zone. Water applied over the necessities of the crops has to bring the soil to field capacity and afterwards drainage from soil or groundwater recharge is expected. However, once the irrigated season ended, the saturated thickness in the aquifer declined during the whole year until a new sharp rise at the end of the next irrigation season. Soils or aquifer storage were accounted for but negligible in comparison with other components of the water balance (Paper IV).

Groundwater discharge occurred in the contact between Tertiary and Quaternary materials, feeding the network of gullies. During unirrigated conditions, these gullies constituted ephemeral streams, only active in wet periods or after important storms (farmer's pers. comm.). The water stored in the aquifer was probably minimal over that period. With the implementation of irrigation, a significant amount of water stores in the aquifer and it drains slowly all around the year making the gullies to become perennial streams (Paper I). Diffuse surface flow occurs from the seepage in the Quaternary-Tertiary contact to the gullies, with numerous springs with minimal, non-gaugeable, discharge.

Consequently, the discharge in the outlet of the Lerma Basin increased after irrigation implementation. The increase was quantified in 3.1 L s^{-1} year^{-1} (Paper I) and was mainly related to increases in specific seasons, coupled with the seasonality in the irrigation inputs. No significant trend was detected for precipitation in the same period. In addition, a higher influence of irrigation water over precipitation water was detected through the Lerma Basin waters isotopic signature (Paper II). However, at the end of the study period, a decreasing trend in Lerma Gully's flow was detected, possibly related to the detected decreasing trends in irrigation drainage fraction (Paper IV).

During the period 2004-2013, discharge in the Lerma Gully constituted 22% of outputs, being the actual evapotranspiration the main input (71%). Evaporation and wind drift

losses of sprinkler irrigation were a significant output (7% of the outputs; Paper IV). Differences between inputs and outputs for the period 2004-2013 were minimal, with an average of -1.2% (Paper IV).

As indicated above, the implementation of irrigation has modified the hydrology of the Lerma Basin. The addition of irrigation water greatly increased the actual evapotranspiration, but also caused higher levels in aquifers and higher discharge in the gully.

9.1.2. Salinization processes

Salinization processes of ground- and surface waters in the Lerma Basin were related to the evapotranspiration of recharge water and the dissolution of salts, mainly gypsum and halite available in the Tertiary substrate (Paper III). Since irrigation water was saturated in calcite, the dissolution of gypsum causes the precipitation of calcite and the concomitant dissolution of dolomite (Paper III). Cationic exchange was a significant process, providing Na^+ and removing Ca^{2+} from Lerma waters (Paper III). Consequently, a preponderance of dissolution processes over precipitation was found for the salt balance in the Lerma Basin, which constituted the main source for the exported salts (Paper V).

Sulphate was used as the primary solute indicator of salinization processes for two reasons: it increased more substantially from groundwater to surface waters than any other anion typically associated with salinization (e.g., chloride), and also allowed for investigation using isotopic methods. Mixing soil sulphate with the local gypsum sulphate explains the isotopic composition of most samples, pointing to minor influence of land use in the water salinization processes (Paper II).

The more saline soils of the study area are located over the Tertiary materials, especially close to the gullies, where soil salinity profiles were inverted. Therefore, water salinization occurred mainly in the diffuse flow over the Tertiary materials, with small increases in salinity in the groundwater flow, but great increases in the diffuse surface flow (Papers II and III). A clear evolution from low salinity Ca^{2+}-HCO_3^- type in the input water to Na^+-mixed-to-Cl^- water type with increasing salinity was observed in water samples collected in the Lerma Basin (Paper III).

The salinity in the outlet of the basin was modified during the study period, with estimated decreasing trends of 0.38 mS cm^{-1} $year^{-1}$, what was mainly explained by a dilution effect (since more water was available) and by the successive wash out of the more accessible salts present in soils and geological materials (Paper I). This trend had a clear seasonal pattern, with higher and more significant trends for the irrigated period, i.e., when more water was available and higher flow and dilution effects occurred.

Despite the decreasing trend in water salinity, an increase in exported salt loads of 0.27 Mg ha^{-1} $year^{-2}$ was observed, which was related to the higher influence of discharge rather than water quality in the exported loads (Paper I). This fact suggests the importance of achieving an adequate water management to control pollution loads to downstream sensitive waters.

The exported salts evolved from 1.89 Mg ha^{-1} $year^{-1}$ under rainfed conditions to 3.51 Mg ha^{-1} $year^{-1}$ under irrigated conditions; values that fall within those reported for other pressurized irrigation systems in the Ebro Basin (Paper V). The salt contamination index was almost three times higher during the irrigated period that during the unirrigated period (0.96 and 0.36 [Mg ha^{-1} $year^{-1}$]/[dS m^{-1}], respectively) with lower increase than that of the exported salts as a consequence of the progressive salt washing of the study zone (Paper V).

The main conclusion was that salinization processes are controlled by natural causes, i.e., it is a natural, on-going process. However, the anthropogenic impact of irrigated agriculture enhances this natural problem since it increases the recharge significantly and therefore, the salt loads to downstream water bodies. Therefore, the potential for remediation is slight and mainly related to a better management of irrigation water.

9.1.3. Nitrate pollution processes

Nitrate was the predominant form of the dissolved nitrogen, accounting for 90% 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 concentrations were lower. The proportion of NO_3^--N in total-N in groundwater was significantly higher than in surface water. Among different samples, nitrate accounted for 69–98% of all detected nitrogen (Paper II).

According to available isotopic data, the origin of nitrate in the Lerma Basin is related to inorganic fertilization, with higher influence of ammonia/urea fertilizers than of nitrate fertilizers (Paper II). Ammonia and urea fertilizers are the main kind of fertilization used for maize (farmer's surveys), which is the main crop present in the study zone (Paper IV). Nitrate fertilizers were also detected but they have lower influence in the nitrate concentrations of ground- and surface waters (Paper II). Organic fertilizers such as pig slurry or manure were not detected in the isotopic data, what is coherent with the minimal application reported by the farmers in the Lerma Basin.

Nitrate concentration was higher in groundwater than in surface water. In the groundwater flow lines nitrate increased (Paper II, III). Denitrification likely accounted for low nitrate concentrations in the groundwater-fed surface diffuse pathway to the

gullies, with higher activity levels during summer's irrigated season, as temperature limited biological denitrification activity during winter in these weather-exposed sites (Paper II). However, the reduction of N content from groundwater to surface water was mainly due to dilution from low-N waters coming from upper reaches.

As a consequence of the practice of rainfed agriculture previous to irrigation implementation, nitrate concentration in the gully at the outlet of the basin was already high in the study zone before the implementation of irrigation. At the beginning of the implementation works for irrigation there was a pause in the fertilization of the agricultural plots in the zone. This was observed in the gully with a significant delay, since soil N was available for leaching and aquifer nitrate-rich groundwater seeped to the gullies. With time, NO_3^- in soils and aquifers depleted and concentration in the gully decreased (Paper I).

With the implementation of irrigation, nitrate concentrations in the gully increased again. Trends in nitrate in the gully of 5.4 mg L^{-1} $year^{-1}$ were estimated for the period 2004-2011, associated mainly to the summer months, what was related to the periods in which fertilizers application was higher (Paper I). The increase observed in flow and the increasing trend in nitrate concentration greatly increased the mass of nitrate exported by the Lerma Gully, with an estimated value of 2.63 kg NO_3^--N ha^{-1} $year^{-2}$ (Paper I). The increase in discharge had higher influence than the increase in nitrate concentration.

Nitrate exported from the irrigable area increased from 9.1 kg NO_3^--N ha^{-1} $year^{-1}$ under unirrigated conditions to 30.8 kg NO_3^--N ha^{-1} $year^{-1}$ during the irrigated period, which falls in the range of the values reported for other pressurized irrigation systems in the Ebro Basin (Paper V). Nitrate contamination indexes have increased with irrigation implementation up to a stable value of 0.12 which is more than double compared with the first years of irrigation (Paper V).

The main conclusion is that nitrate pollution processes are controlled by the input of inorganic fertilizers and some influence of the natural attenuation capacity of the study area. An adequate management of both irrigation water and fertilizers can minimize nitrate pollution to downstream waters bodies. Besides, the enhancement of the natural attenuation capacity may be a useful tool to decrease nitrate leaching from irrigated areas.

9.1.4. Relationships between water quantity and quality

Environmental impacts of agriculture management are often considered isolated but, in fact, they are highly interrelated. Each issue has been treated separately so far in this chapter but the aim of this section is to provide the relationships detected between

water use, salinization and nitrate pollution processes in the Lerma Basin. In this sense, no significant relationships were found between precipitation and other hydrological variables of interest. However, significant relationships were found between irrigation volumes and flow and exported loads of salt and nitrate, highlighting irrigation as a controlling factor of the observed changes (Paper I).

Salinization and nitrate pollution were found to be independent. While salinization was related to the presence of soluble salts, nitrate pollution was associated to agricultural land use in the study zone (Paper III). Despite the fact that salt contamination index (0.96 [Mg ha^{-1} $year^{-1}$]/[dS m^{-1}]) and nitrate contamination index (0.12) were inside the threshold considered for the more sustainable irrigated areas (SCI <2.0 [Mg ha^{-1} $year^{-1}$]/[dS m^{-1}] and NCI <0.2), an improvement in the irrigation management would be advisable in order to increase the water use and decrease the leaching. Additionally, complementary measures such as adjusting fertilization rates to temporal crop necessities or the use of catch crops may prove useful (Paper V).

9.1.5. Future work

Salinization and nitrate pollution are really challenging problems in irrigated areas. However, there are other environmental issues that have not been directly addressed in this study. For instance, the impacts of phosphorous, pesticides or heavy metals are out of the scope of this research, but they present interesting and relevant environmental problems of irrigated areas that should be addressed in future works.

Long term monitoring seems to be a paramount requirement to fully understand the impact of different land uses over water quality, since short data series are not representative due to the climatic variability and management differences. Therefore, it is important to continue the monitoring of agricultural basins in order to estimate long-term pollution rates and trends.

9.2. Final Conclusions

- Irrigation implementation produced increasing trends in gully flow and nitrate concentration, whereas the salintiy decreased over the study period. The loads of salts and nitrate increased over time, since they were mainly controlled by discharge volume rather than by solute concentrations.
- Irrigation had a higher influence than precipitation in the hydrology of the basin, controlling groundwater and surface water quantity and quality.
- Salinization and nitrate pollution processes were found to be independent, with differences in the controls of low-salinity high-nitrate groundwaters and higher-salinity lower-nitrate surface waters.
- Salinization is a natural process controlled by the dissolution of halite and gypsum, and cationic exchange. However, the presence of irrigation water favoured higher loads of salts leaving the basin via the Lerma Gully.
- Nitrate pollution is controlled by the input of ammonia and urea fertilizers. Groundwater presented higher nitrate concentrations than surface water as a consequence of dilution from upper reaches water and, in some degree, denitrification in the diffuse surface flow.
- Irrigation performance slightly increased over the study period, but there is a wide margin of improvement that could be reached with a more adequate irrigation management.
- The mass of salts exported from the irrigable area has multiplied by a factor of three from rainfed to irrigated conditions. However, salt pollution was in the lower range of those reported for other irrigated areas in the Ebro Basin.
- The mass of nitrogen exported from the irrigable area has multiplied by a factor of three from rainfed to irrigated conditions. Nitrate loads were in the lower range of those reported for irrigated areas in the Ebro Basin.

REFERENCES

Listed references are those included in chapters I, II, III and IX. Chapters IV, V, VI, VII and VIII (published papers) have their own reference section.

References

Abrahão, R., 2010. *Impactos ambientales del riego: La transformación de la cuenca de Lerma (Zaragoza, España).* PhD Dissertation, Universidad de Zaragoza, 143 pp. [Spanish]

Abrahão, R., Causapé, J., García-Garizábal, I., Merchán, D., 2011a. Implementing irrigation: Water balances and irrigation quality in the Lerma basin (Spain). *Agricultural Water Management* 102: 97-104.

Abrahão, R., Causapé, J., García-Garizábal, I., Merchán, D., 2011b. Implementing irrigation: Salt and nitrate exported from the Lerma basin (Spain). *Agricultural Water Management* 102: 105-112.

Abrahão, R., Causapé, J., Moreno-Mateos, D., Comín, F., 2013. Nitrate and salt water contamination associated with the transition of an agrarian basin into an irrigated area. *Water Environment Research* 85(2): 105-112.

Acero, P., Gutiérrez, F., Galve, J.P., Auqué, L.F., Carbonel, D., Gimeno, M.J., Gómez, J.B., Asta, M.P., Yechieli, Y., 2013. Hydrochemical characterization of an evaporite karst area affected by sinkholes (Ebro Valley, NE Spain). *Geologica Acta* 11(4): 389-407.

AEMET (Agencia Estatal de Meteorología), 2011. *Atlas climático ibérico. Temperatura del aire y precipitación (1971-2000).* Agencia Estatal de Meteorología – Ministerio de Medio Ambiente y Medio Rural y Marino, Instituto de Meteorologia de Portugal. [Spanish]

Allen, R.G., Pereira, L.S., Raes, D., Smith, M., 1998. *Crop Evapo-Transpiration: Guidelines for Computing Crop Water Requirements.* United Nations Food and Agriculture Organization, Rome, Italy (FAO Irrigation and Drainage Paper No. 56).

Andrade, A.I.A.S.S., Stigter, T.Y., 2009. Multi-method assessment of nitrate and pesticide contamination in shallow alluvial groundwater as a function of hydrogeological setting and land use. *Agricultural Water Management* 96: 1751-1765.

Appelo, C.A.J., Postma, D., 2005. *Geochemistry, groundwater and pollution* (2nd edition). Leiden, The Netherlands, 649pp.

Arauzo, M., Valladolid, M., Martínez-Bastida, J.J., 2011. Spatio-temporal dynamics of nitrogen in river-alluvial aquifer systems affected by diffuse pollution from agricultural sources: Implications for the implementation of the Nitrates Directive. *Journal of Hydrology* 411: 155-168.

Arauzo, M., Valladolid, M., 2013. Drainage and N-leaching in alluvial soils under agricultural land uses: Implications for the implementation of the EU Nitrates Directive. *Agriculture, Ecosystems and Environment* 179: 94-107.

Barros, R., Isidoro, D., Aragüés, R., 2012a. Three study decades on irrigation performance and salt concentrations and loads in the irrigation return flows of La Violada irrigation district (Spain). *Agriculture, Ecosystems and Environment* 151: 44-52.

Barros, R., Isidoro, D., Aragüés, R., 2012b. Irrigation management, nitrogen fertilization and nitrogen losses in the return flows of La Violada irrigation district (Spain). *Agriculture, Ecosystems and Environment* 155: 161-171.

Battle-Aguilar, J., Orban, P., Dassargues, A., Brouyère, S., 2007. Identification of groundwater quality trends in a chalk aquifer threatened by intensive agriculture in Belgium. *Hydrogeology Journal* 15: 1615-1627.

Beltrán, A., 1986. *Estudio de suelos de la zona regable de Bardenas. II. Sectores: VIII, XI, X, XII y XIII.* Instituto Nacional de Reforma y Desarrollo Agrario, Ministerio de Agricultura, Pesca y Alimentación, España. [Spanish]

BOA, 2009. Orden de 11 de diciembre de 2008, del Consejero de Agricultura y Alimentación, por la que se designan y modifican las zonas vulnerables a la contaminación de las aguas por nitratos procedentes de fuentes agrarias en la Comunidad Autónoma de Aragón. *Boletín Oficial de Aragón* 1, de 02 de Enero de 2009. [Spanish]

Bouza-Deaño, R., Ternero-Rodríguez, M., Fernández-Espinosa, A.J., 2008. Trend study and assessment of surface water quality in the Ebro River (Spain). *Journal of Hydrology* 361: 227-239.

Casalí, J., Gastesi, R., Álvarez-Mozos, J., De Santisteban, L.M., Del Valle de Lersundi, J., Giménez, R., Larrañaga, A., Goñi, M., Agirre, U., Campo, M.A., López, J.J., Donézar, M., 2008. Runoff, erosion, and water quality of agricultural watersheds in central Navarre (Spain). *Agricultural Water Management* 95: 1111-1128.

Casalí, J., Giménez, R., Díez, J., Álvarez-Mozos, J., Del Valle de Lersundi, J., Goñi, M., Campo, M.A., Chahor, Y., Gastesi, R., López, J., 2010. Sediment production and water quality of watersheds with contrasting land use in Navarre (Spain). *Agricultural Water Management* 97: 1683-1694.

Causapé, J., 2009a. Agro-environmental evaluation of irrigation land. I: Water use in Bardenas irrigation district (Spain). *Agricultural Water Management* 96: 179-187.

Causapé, J., 2009b. A computer-based program for the assessment of water-induced contamination in irrigated lands. *Environmental Monitoring Assessment* 158: 307-314.

Causapé, J., Quílez, D., Aragües, R., 2004a. Assessment of irrigation and environmental quality at the hydrological basin level. I: Irrigation quality. *Agricultural Water Management* 70: 195-209.

Causapé, J., Quílez, D., Aragües, R., 2004b. Assessment of irrigation and environmental quality at the hydrological basin level. II: Salt and nitrate loads in irrigation return flows. *Agricultural Water Management* 70: 211-228.

CHE (Confederación Hidrográfica del Ebro), 2006. *Control de los retornos de las actividades agrarias de la cuenca del Ebro: evaluación de tendencias en la calidad del agua, control experimental de los retornos y propuesta de red de control.* Available from: www.chebro.es [Accessed 25 May 2012] [Spanish]

CHE, 2009a. *Situación actual de la cuenca.* Available from: www.chebro.es [Accessed 25 May 2012]. [Spanish]

CHE, 2009b. *Análisis de tendencias de masas exportadas en la Cuenca del Ebro.* Available from: www.chebro.es [Accessed 25 May 2012] [Spanish]

Corwin, D.L., Rhoades, J.D., Šimůnek, J., 2007. Leaching requirement for soil salinity control: Steady-state versus transient models. *Agricultural Water Management* 90: 165-180.

Custodio, E., 2002. Aquifer overexplotation: what does it mean? *Hydrogeology Journal* 10: 254-277.

Custodio, E., Llamas, M., 1983. *Hidrología Subterránea.* Ediciones Omega, Barcelona, Spain, 2 Vol., 2359 pp. [Spanish]

Dougherty, T.C., Hall, A.W., 1995. *Environmental Impact assessment of irrigation and drainage projects.* United Nations Food and Agriculture Organization, Rome, Italy (FAO Irrigation and Drainage Paper No. 53).

Duncan, R.A., Bethune, M.G., Thayalakumaran, T., Christen, E.W., McMahon, T.A., 2008. Management of salt mobilisation in the irrigated landscape – A review of selected irrigation regions. *Journal of Hydrology* 351: 238-252.

Durand, P., Breuer, L., Johnes, P.J., 2011. Nitrogen processes in aquatic ecosystems. In: *The European Nitrogen Assessment, Sources, Effects and Policy Perspectives.* Eds:

Sutton, M.A., Howard, C.M., Erisman, J.W., Billen, G., Bleeker, A., Grennfelt, P., van Grisven, H., Grizzetti, B. Cambridge University Press, Cambridge, UK, 612 pp.

Elmi, A.A., Madramootoo, C., Egeh, M., Hameo, C., 2004. Water and fertilizer nitrogen management to minimize nitrate pollution from a cropped soil in southwestern Quebec, Canada. *Water, Air, and Soil Pollution* 151: 117–134.

Fan, A.M., Steinberg, V.E., 1996. Health implications of nitrate and nitrite in drinking water: an update on methemoglobinemia occurrence and reproductive and developmental toxicity. *Regulatory Toxicology and Pharmacology* 23 (1): 35–43.

FAO, 2003a. *Unlocking the Water Potential of Agriculture.* United Nations Food and Agriculture Organization, FAO, Rome, Italy, XXX pp.

FAO, 2003b. *World Agriculture Towards 2015/2030. A FAO Perspective.* United Nations Food and Agriculture Organization, FAO, Rome, Italy, XXX pp.

FAO, 2013. FAO Statistical Year Book 2013, World Food and Agriculture. United Nations Food and Agriculture Organization, FAO, Rome, Italy, XXX pp.

Farre, I, Faci, J.M., 2006. Comparative response of maize (Zea mays L.) and sorghum (Sorghum bicolor L. Moench) to deficit irrigation in a Mediterranean environment. *Agricultural Water Management* 83: 135-143.

Farre, I., Faci, J.M., 2009. Deficit irrigation in maize for reducing agricultural water use in a Mediterranean environment. *Agricultural Water Management* 96: 383-394.

García-Garizábal, I., Causapé, J., Abrahão, R., 2012. Nitrate contamination and its relationship with flood irrigation management. *Journal of Hydrology* 442-443: 15-22.

García-Garizábal, I., Gimeno, M.J., Auqué, L.F., Causapé, J., 2014. Salinity contamination response to changes in irrigation management. Application of geochemical codes. *Spanish Journal of Agricultural Research* 12(2): 376-387.

García-Ruíz, J.M., López-Bermúdez, F.L., 2009. *La erosión del suelo en España.* Sociedad Española de Geomorfología. Zaragoza, 441 pp. [Spanish]

Gaydon, D.S., Meinke, H., Rodríguez, D., 2012. The best farm-level irrigation strategy changes seasonally with fluctuating water availability. *Agricultural Water Management* 103: 33-42.

Graf, W.L., 2006. Downstream hydrologic and geomorphic effects of large dams on American rivers. *Geomorphology* 79: 336-360.

He, J., Dukes, M.D., Hochmuth, G.J., Jones, J.W., Graham, W.D., 2012. Identifying irrigation and nitrogen best management practices for sweet corn production on sandy soils using CERES-Maize model. *Agricultural Water Management* 109: 61-70.

Helsel, D.R., Hirsch, R.M., 2002. *Statistical methods in water resources.* Techniques of water resources investigations, Book 4, Chapter A3. Reston, VA: US Geological Survey.

Höring, H., Chapman, D., 2004. *Nitrates and Nitrites in Drinking Water.* In: World Health Organization Drinking Water Series. IWA Publishing, London.

Ibrahikmovik, M., Martius, C., Lamers, J.P.A., Tischbein, B., 2011. The dynamics of groundwater table and salinity over 17 years in Khorezm. *Agricultural Water Management* 101: 52-61.

Isaaks, E., Srivastava, R.M., 1989. *An introduction to applied geostatistics.* Oxford University, Nueva York, US, 561 pp.

Isidoro, D., Quílez, D., Aragües, R., 2006. Environmental Impact of Irrigation in La Violada District (Spain): I. Salt Export Patterns. *Journal of Environmental Quality* 35: 766-775.

ITGE (Instituto Tecnológico GeoMinero de España), 1988. *Mapa Geológico de España, Ejea de los Caballeros* (map and memory) no. 284 27-12. Madrid, Spain. [Spanish]

Jia, Z., Wu, Z., Luo, W., Xi, W., Tang, S., Liu, W.L., Fang, S., 2013. The impact of improving irrigation efficiency on wetland distribution in an agricultural landscape in the upper reaches of the Yellow River in China. *Agricultural Water Management* 121: 54-61.

Kendall, M.G., 1975. *Rank correlation methods.* London: Griffin.

Klaus, J., Zehe, E., Elsner, M., Palm, J., Schneider, D., Schröder, B., Steynbeiss, S., van Schaik, L., West, S., 2014. Controls of event-based pesticide leaching in natural soils: A systematic study based on replicated field scale irrigation experiments. *Journal of Hydrology* 512: 528-539.

Koh, D-C., Ko, K-S., Kim, Y., Lee, S-G., Chang, H-W., 2007. Effect of agricultural land use on the chemistry of groundwater from basaltic aquifers, Jeju Island, South Korea. *Hydrogeology Journal* 15: 727-743.

Kume, T., Akca, E., Nakano, T., Nagano, T., Kapur, S., Watanabe, T., 2010. Seasonal changes of fertilizer impacts on agricultural drainage in a salinized area in Adana, Turkey. *Science of the Total Environment* 408: 3319-3326.

Kurunc, A., Yurekli, K., Okman, C., 2005. Effects of Kilickaya Dam on concentration and load values of water quality constituents in Kelkit stream in Turkey. *Journal of Hydrology* 317: 17-30.

Kyllmar, K., Stjernman Forsberg, L., Andersson, S., Martensson, K., 2014. Small agricultural monitoring catchments in Sweden representing environmental impact. *Agriculture, Ecosystems and Environment* 198: 25-35.

Lassaletta, L., García-Gómez, H., Gimeno, B.S., Rovira, J.V., 2009. Agriculture-induced increase in nitrate concentrations in stream waters of a large Mediterranean catchment over 25 years (1981-2005). *Science of the Total Environment* 407: 6034-6043.

Letey, J., Hoffman, G.J., Hopmans, J.W., Grattan, S.R., Suarez, D., Corwin, D.L., Oster, J.D., Wu, L., Amrhein, C., 2011. Evaluation of soil salinity leaching requirement guidelines. *Agricultural Water Management* 98: 502-506.

Lorente, C., Causapé, J., Glud, R.N., Hancke, K., Merchán, D., Muñiz, S., Val, J., Navarro, E., 2014. Impacts of agricultural irrigation on nearby freshwater ecosystems: The seasonal influence of triazine herbicides in benthic algal communities. *Science of the Total Environment* 503-504: 151-158.

Lorite-Herrera, M., Jiménez-Espinosa, R., Jiménez-Millán, J., Hiscock, K.M., 2008. Integrated hydrochemical assessment of the Quaternary alluvial aquifer of the Guadalquivir River, southern Spain. *Applied Geochemistry* 23: 2040-2050.

MAAMA (Ministerio de Agricultura, Alimentación y Medio Ambiente), 2014. http://www.magrama.gob.es/es/agua/temas/gestion-sostenible-de-regadios/ [Accessed 31 July 2014] [Spanish]

Mann, H.B., 1945. Nonparametric test against trend. Econometrica 13: 245-259.

MMARM (Ministerio de Medio Ambiente y Medio Rural y Marino), 2011. Resolución de 24 de marzo de 2011 de la Dirección General del Agua, por la que se determinan las aguas afectadas por la contaminación, o en riesgo de estarlo, por aportación de nitratos de origen agrario en las cuencas hidrográficas intercomunitarias. Available from: www.marm.es [Accessed 7 December 2011]. [Spanish]

Nielsen, D.L., Brock, M.A., Rees, G.N., Baldwin, D.S., 2003. Effects of increasing salinity on freshwater ecosystems in Australia. Australian Journal of Botany 51: 655-665.

Novotny, V., 1999. Diffuse pollution from agriculture – A worlwide outlook. *Water Science and Technology* 39 (3): 1-13.

OJEC (Official Journal of European Communities), 1991. Directive 1991/676/CEE concerning the protection of waters against pollution caused by nitrates from

agricultural sources. *Official Journal of the European Communities* L 375 (31.12.1991): 1-8.

OJEC, 2000. Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy. *Official Journal of the European Communities* L 327 (22.12.2000): 1-72.

OJEU (Official Journal of the European Union), 2006. Directive 2006/118/EC of the European Parliament and of the Council of 12 December 2006 on the protection of groundwater against pollution and deterioration. *Official Journal of the European Union* L 372 (27.12.2006): 19-31.

Parkhurst, D.L., Appelo, C.A.J., 1999. *User's guide to PHREEQC (version 2.0) – A Computer Program for Speciation, Batch-reaction, One-dimensional Transport, and Inverse Geochemical Calculations.* Vol. Water-Resources Investigations Report 99-4259. US Geological Survey, Denver, Colorado, USA, 326 pp.

Peck, A.J., Hatton, T., 2003. Salinity and the discharge of salts from catchments in Australia. *Journal of Hydrology* 272: 191-202.

Plata, J.L., 2011. *Informe sobre la determinación de la potencia de glacis en el barranco de Lerma (Zaragoza) mediante Sondeos Eléctricos Verticales.* Informe IGME Centro de Documentación nº 64098. [Spanish]

Quemada, M., Baranski, M., Nobel-de Lange, M.N.J., Vallejo, A., Cooper, J.M., 2013. Meta-analysis of strategies to control nitrate leaching in irrigated agricultural systems and their effects on crop yield. *Agriculture, Ecosystems and Environment* 174: 1-10.

Richter, B.C., Kreitler, C.W., 1991. *Identification of sources of ground-water salinization using geochemical techniques.* U.S. Environmental Protection Agency. Ada, Oklahoma, 273 pp.

Rivett, M.O., Buss, S.R., Morgan, P., Smith, J.W.N., Bemment, C.D., 2008. Nitrate attenuation in groundwater: A review of biogeochemical controlling processes. *Water Research* 42: 4215-4232.

Schepers, J.S., Varvel, G.E., Watts, D.G., 1995. Nitrogen and water management strategies to reduce nitrate leaching under irrigated maize. *Journal of Contaminant Hydrology* 20: 227-239.

Scott, J., Rosen, M.R., Saito, L., Decker, D.L., 2011. The influence of irrigation water on the hydrology and lake water budgets of two small arid-climate lakes in Khorezm, Uzbekistan. *Journal of Hydrology* 410: 114-125.

Sen, P.K., 1968. Estimates of the regression coefficient based on Kendall's tau. *Journal of the American Statistics Association* 63: 1379-1389.

Skhiri, A.B.H., 2011. *Dinámica y procesos de contaminación difusa de las aguas superficiales por el fósforo en los regadíos de Aragón.* PhD Dissertation, Universidad de Zaragoza, 211 pp.

Skhiri, A., Dechmi, F., 2012. Impact of sprinkler irrigation management on the Del Reguero river (Spain). I: Water balance and irrigation performance. *Agricultural Water Management* 103: 120-129.

Soil Survey Staff, 2014. Keys to Soil Taxonomy (12th edition). United States Department of Agriculture – Natural Resources Conservation Service. 359 pp.

Soto-García, M., Martínez-Álvarez, V., García-Bastida, P.A., Alcon, F., Martin-Gorriz, B., 2013. Effect of water scarcity and modernisation on the performance of irrigation districts in south-eastern Spain. *Agricultural Water Management* 124: 11-19.

Stålnacke, P., Grimvall, A., Libiseller, C., Laznik, M., Kokorite, I., 2003. Trends in nutrient concentrations in Latvian rivers and the response to the dramatic change in agriculture. *Journal of Hydrology* 283: 184-205.

Statpoint Technologies, 2009. *Statgraphics Centurion XVI, User Manual.* StatPoint Technologies Inc., 297 pp.

Stigter, T.Y., Carvalho Dill, A.M.M., Ribeiro, L., Reis, E., 2006. Impact of the shift from groundwater to surface water irrigation on aquifer dynamics and hydrochemistry in a semi-arid region in the south of Portugal. *Agricultural Water Management* 85: 121-132.

Stoate, C., Boatma, N.D., Borralho, R.J., Rio Carvahlo, C., de Snoo, G.R., Eden, P., 2001. Ecological impacts of arable intensification in Europe. *Journal of Environmental Management* 63: 337-365.

Stockle, C.O., 2001. *Environmental impact of irrigation: A review.* Department of Biological Systems Engineering Newsletter, Washington State University. From http://www.swwrc.wsu.edu/newsletter/fall2001/IrrImpact2.pdf [Accessed 15 November 2010].

Sutton, M.A., Howard, C.M., Erisman, J.W., Billen, G., Bleeker, A., Grennfelt, P., van Grisven, H., Grizzetti, B., 2011. The European Nitrogen Assessment: Sources, Effects and Policy Perspectives. Cambridge University Press, Cambridge, UK, 612 pp.

Tan, D., Jiang, L., Tan, S., Zheng, F., Xu, Y., Cui, R., Wang, M., Shi, J., Li, G., Liu, Z., 2013. An in situ study of inorganic nitrogen flow under different fertilization treatments

on a wheat-maize rotation system surrounding Nansi. *Agricultural Water Management* 123: 45-54.

Tanji, K., 1990. Agricultural salinity assessment and management. *American Society of Civil Engineers* vol. 71, 619 pp.

Tanji, K.K., Kielen, N.C., 2002. *Agricultural Drainage Water Management in Arid and Semi-arid Areas.* United Nations Food and Agriculture Organization, Rome, Italy (FAO Irrigation and Drainage Paper No. 61).

Tedeschi, A., Beltrán, A., Aragüés, R., 2001. Irrigation management and hydrosalinity balance in a semi-arid area of the middle Ebro river basin (Spain). *Agricultural Water Management* 49: 31-50.

Thayalakumaran, T., Bethune, M.G., McMahon, T.A., 2007. Achieving a salt balance-Should it be a management objective? *Agricultural Water Management* 92: 1-12.

Thayalakumaran, T., Bristow, K.L., Charlesworth, P.B., Fass, T., 2008. Geochemical conditions in groundwater systems: Implications for the attenuation of agricultural nitrate. *Agricultural Water Management* 95: 103-115.

US EPA (Unites States Environmental Protection Agency), 1992. Managing non-point source pollution. Washington, DC: EPA, Office of Water.

Van der Kooij, S., Zwarteveen, M., Boesveld, H., Kuper, M., 2013. The efficiency of drip irrigation unpacked. *Agricultural Water Management* 123: 103-110.

Wahl, T., 2000. *Winflume User's Manual.* United States Department of the Interior.

Weight, W.D., 2008. *Hydrogeology Field Manual* (2nd edition). McGraw-Hill Companies Inc, USA, 751 pp.

Yuce, G., Pinarbasi, A., Ozcelik, S., Ugurluoglu, D., 2006. Soil and water pollution derived from anthropogenic activities in the Porsuk River Basin, Turkey. *Environmental Geology* 49: 359-375.

ATACHMENT A

Acceptation letters of the non-published papers.

- Paper IV: Merchán, D., Causapé, J., Abrahão, R., García-Garizábal, I. ASSESSMENT OF A NEWLY IMPLEMENTED IRRIGATED AREA (LERMA BASIN, SPAIN) OVER A 10-YEAR PERIOD. I: WATER BALANCES AND IRRIGATION PERFORMANCE. *Agricultural Water Management* (Accepted on April 24th 2015).

- Paper V: Merchán, D., Causapé, J., Abrahão, R., García-Garizábal, I. ASSESSMENT OF A NEWLY IMPLEMENTED IRRIGATED AREA (LERMA BASIN, SPAIN) OVER A 10-YEAR PERIOD. II: SALTS AND NITRATE EXPORTED. *Agricultural Water Management* (Accepted on April 24th 2015).

View Letter

Close

Date: Apr 24, 2015
To: "Daniel Merchan" d.merchan@igme.es,eremad@hotmail.com
From: "Agricultural Water Management" agwat@elsevier.com
Subject: Your Submission

Ref.: Ms. No. AGWAT6718R2
ASSESSMENT OF A NEWLY IMPLEMENTED IRRIGATED AREA (LERMA BASIN, SPAIN) OVER A 10-YEAR PERIOD. I: WATER BALANCES AND IRRIGATION PERFORMANCE
Agricultural Water Management

Dear Mr. Merchan,

I am pleased to tell you that your work has now been accepted for publication in Agricultural Water Management. The manuscript will be transferred to our production site for preparation for press. I will be your contact person during the production process of the paper towards the final publication on the web (Science Direct) and on paper (in the printed-on-paper issue).

Proofs will be sent to you in due course.

If there were any comments from the Editor and/or Reviewers, they can be found below.

When your paper is published on ScienceDirect, you want to make sure it gets the attention it deserves. To help you get your message across, Elsevier has developed a new, free service called AudioSlides: brief, webcast-style presentations that are shown (publicly available) next to your published article. This format gives you the opportunity to explain your research in your own words and attract interest. You will receive an invitation email to create an AudioSlides presentation shortly. For more information and examples, please visit http://www.elsevier.com/audioslides.

Thank you for submitting your work to this journal.

With kind regards,

Pallavi Das
Agricultural Water Management
agwat@elsevier.com

Comments from the Editors and Reviewers:

Dear Dr. Merchan,

I am pleased to accept your manuscript entitled "ASSESSMENT OF A NEWLY IMPLEMENTED IRRIGATED AREA (LERMA BASIN, SPAIN) OVER A 10-YEAR PERIOD. I: WATER BALANCES AND IRRIGATION PERFORMANCE" in its current form for publication in Agricultural Water Management.

Thank you for your fine contribution. On behalf of the Editors of Agricultural Water Management, we look forward to your continued contributions to the Journal.

Kind regards,

J. E. Fernández
Editor-in-Chief

Close

View Letter

Close

Date: Apr 24, 2015
To: "Daniel Merchan" d.merchan@igme.es,eremad@hotmail.com
From: "Agricultural Water Management" agwat@elsevier.com
Subject: Your Submission

Ref.: Ms. No. AGWAT6719R2
ASSESSMENT OF A NEWLY IMPLEMENTED IRRIGATED AREA (LERMA BASIN, SPAIN) OVER A 10-YEAR PERIOD. II: SALTS AND NITRATE EXPORTED
Agricultural Water Management

Dear Mr. Merchan,

I am pleased to tell you that your work has now been accepted for publication in Agricultural Water Management. The manuscript will be transferred to our production site for preparation for press. I will be your contact person during the production process of the paper towards the final publication on the web (Science Direct) and on paper (in the printed-on-paper issue).

Proofs will be sent to you in due course.

If there were any comments from the Editor and/or Reviewers, they can be found below.

When your paper is published on ScienceDirect, you want to make sure it gets the attention it deserves. To help you get your message across, Elsevier has developed a new, free service called AudioSlides: brief, webcast-style presentations that are shown (publicly available) next to your published article. This format gives you the opportunity to explain your research in your own words and attract interest. You will receive an invitation email to create an AudioSlides presentation shortly. For more information and examples, please visit http://www.elsevier.com/audioslides.

Thank you for submitting your work to this journal.

With kind regards,

Pallavi Das
Agricultural Water Management
agwat@elsevier.com

Comments from the Editors and Reviewers:

Dear Mr. Merchán,

I am pleased to accept your manuscript entitled "ASSESSMENT OF A NEWLY IMPLEMENTED IRRIGATED AREA (LERMA BASIN, SPAIN) OVER A 10-YEAR PERIOD. II: SALTS AND NITRATE EXPORTED" in its current form for publication in Agricultural Water Management.

Thank you for your fine contribution. On behalf of the Editors of Agricultural Water Management, we look forward to your continued contributions to the Journal.

Kind regards,

J. E. Fernández
Editor-in-Chief

Close

ATACHMENT B

Rejection of other co-authors to use the papers in other PhD dissertations

According to Zaragoza's University regulation, those co-authors participating in any of the included publications who do not hold a PhD degree have to explicitly reject to their right to use them in any other PhD dissertation ("Acuerdo de 20/12/2013 del Consejo de Gobierno de la Universidad de Zaragoza relativo al Reglamento sobre Tesis Doctorales").

In this case, all the co-authors hold a PhD degree previous to the development of the work conducting to the publications included in this dissertation, and therefore such a rejection is not required.

The shift from rainfed to irrigated agriculture modifies the water balance along with the leaching of salts and nitrogen in agricultural areas. This thesis evaluated the hydrological effects of irrigation implementation in a semi-arid small basin in Spain. Trends detection and quantification, stable isotopes analysis, hydrogeochemical characterization, assessment of the use of water in irrigation, and quantification of the mass of exported pollutants from the irrigable area were used to deep in the knowledge of the hydrological processes involved. The implementation of irrigation imposed relevant hydrological changes in the basin, increasing its mass of exported pollutants. Several natural and management factors may influence these processes, and their understanding is important in order to achieve a more efficient use of water and fertilizers, and an environmental friendly irrigated agriculture.

Daniel Merchán Elena received his graduate education at the Geological Survey of Spain and Earth Sciences Department (Zaragoza's University). He holds a M.Sc. degree in Water Resources and Environment and a B.Sc. degree in Environmental Science, both from Málaga's University, Spain.