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Salinity contamination response to changes in irrigation management. Application of geochemical codes

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Abstract

Salinity contamination caused by irrigation has been widely studied but the analysis of geochemical processes regarding agronomic variables has not adequately been considered yet. The research presented here analyzes the influence of changes in irrigation management on salinity contamination, through the use of geochemical modeling techniques, in an agricultural basin during the hydrological year of 2001 and within the period 2005-2008. The results indicate that the changes implemented in irrigation management reduced the masses of salts exported in 72%, although water salinity increased by 25% (this salinity level does not restrict its use for irrigation). The different ionic ratios in drainage water, the results of the salinity balances, and the results of geochemical calculations (mass balances and speciation-solubility) indicate, mainly, precipitation of calcite, dissolution of gypsum and halite and cation exchange. The salt contamination index decreased from approximately 70% to levels close to those presented in modern irrigation areas, indicating that the changes in irrigation management were effective. Petrocalcic genesis and punctual sodification of soils can constitute an agroenvironmental problem that requires adequate management of irrigation and drainage considering future modernization of irrigation areas.

Additional key words: water quality; irrigation return flows; salinization; salt balance; geochemical modeling.

Introduction

The supply of water and food to the world population converts water resource management into an important social issue. The agrarian sector is the greatest consumer of water, as three quarters of the planet's water is destined to irrigated agriculture, which allows higher yields and stabilization of food supply, especially in those regions where the development of crops is limited by rain (FAO, 2003).

Although the agrarian sector utilizes considerable amounts of water, at a global level only 50% of all extracted water is finally utilized by plants, with the remaining amount ending up as drainage and return flows in rivers and aquifers (FAO, 2003). This water that returns to hydric systems would help reducing the

impact of its extraction if its quality did not diverge significantly from the original (Beltrán, 1999; Tanji & Kielen, 2002; Subba Rao, 2008; García-Garizábal & Causapé, 2010).

Nevertheless, some zones present such high water necessities that although water quality is not optimal, management strategies are developed to use irrigation return flows as a resource (Beltrán, 1999), even at the expense of high investments. For example, in the American west coast, the necessity to use the waters of the Colorado River in agrarian environments resulted in the construction of the greatest desalinization plant in the world. The disposal of irrigation return flows along the course of the Colorado River has caused high salinity concentrations (Wichelns & Oster, 2006), therefore preventing the direct use of its water.

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Abbreviations used: D (soil water drainage); D&P (processes of dissolution and precipitation of minerals); EC (electrical conductivity); ECNI (EC of the drainage water in non-irrigated conditions); I (irrigation); IE (irrigation efficiency); IN (inputs); LSC (lateral subterranean contributions); OU (outputs); P (precipitation); S (mass of salts exported by the irrigation area); SAR (sodium adsorption rate); SCI (salt contamination index); SI (saturation index); ST (storage); STa (storage in the aquifer).

Water is not the only way to carry and store salts. Currently 10% of irrigated lands worldwide are affected by salinity due to the establishment of fields on saline materials and the inadequate management of agrarian irrigation and drainage (Tanji & Kielen, 2002), which causes decreases in agrarian yields and even the death of crops. In fact, it is estimated that between 250,000 and 300,000 ha are abandoned each year due to saline affections induced by irrigation (FAO, 2002), which highlights the obligation of eliminating salinity from the soil profile. Although salt leaching is carried out through the application of 'extra' water, it is recommended not to use irrigation while rain events are sufficient, optimizing the use of water (Beltrán, 1999; Caballero *et al.*, 2001). In any case, if the soil presents bad natural drainage conditions, leaching must be facilitated through the installation of artificial drains (Abrol *et al.*, 1988).

Serious water and soil salinity problems induced by irrigation have been found in numerous studies (Tedeschi *et al.*, 2001; Causapé *et al.*, 2004b,c; Isidoro *et al.*, 2006; Crosbie *et al.*, 2007; Duncan *et al.*, 2008). The studies based on mass balances in hydrological basins are highlighted, allowing for the quantification of the salts exported in irrigation return flows and the association with physical and agronomic characteristics of the irrigation area studied.

However, although the aforementioned studies have provided valuable information on salinity contamination generated by irrigated areas, few studies have developed balances for each of the main ions. Deeper analysis on the geochemical processes produced during the interaction between water and geological materials in contact with water also remains underexplored.

Geochemical modeling through the use of geochemical codes generates profound knowledge of the processes occurring in natural environments. After validation, these codes constitute a powerful prediction tool for the possible effects originated by simulated scenarios.

Although it has been widely used in many geoscientific areas (Zhu & Anderson, 2002; Bethke, 2008; Furian *et al.*, 2011), it is still underused in the agro-environmental problems. Therefore, it is interesting to check whether these tools are effective and if they can be applied to studies focused on the sustainability of the agrarian environment.

The dynamics of salinity contamination is analyzed here in relation to the changes implemented in irrigation management. Geochemical modeling calculations

and annual balances were developed for the main ions and applied to an irrigated hydrological basin during the hydrological year of 2001 and the period 2005-2008.

Material and methods

Description of study zone

The study zone includes the hydrological basin of drainage ditch D-XIX-6 (95 ha) of Bardenas Canal Irrigation District n° V, located in Northeast Spain (Fig. 1). Flood irrigation dominates 96% of the surface of the basin, with good quality waters coming from the Yesa reservoir (Pyrenees Mountains).

The climate of the study area is classified as Mediterranean warm weather, with rain concentrated during autumn/spring months and a higher evapotranspirative demand in summer (Fig. 2). The time period studied here (2001 and 2005-2008) encompassed the climatic variability of the zone, including one hydrological rainy year (2001: 526 mm), one dry year (2005: 211 mm), and three years with intermediate records (2006: 450 mm; 2007: 372 mm; 2008: 305 mm) that are closer to the historical average (460 mm yr⁻¹; <http://www.oficinaregante.aragon.es>).

Geologically (ITGE, 1995), 75% of the basin is located on a glaciais of gravel with loamy matrix (maximum thickness 5.5 m), constituting a free aquifer with a saturated thickness of up to 4 m. This introduces lateral subterranean contributions (LSC) into the basin from the Northwest as detected by the hydrological gradient obtained from the piezometer network of the zone (Fig. 1B). The LSC are added to the water introduced into the basin by irrigation and rain and are evacuated by the ditch that circulates from North to South, which affects the glaciais by forming a valley where tertiary substratum appears in surface.

An apparent electrical conductivity (EC) characterization of the soils of the basin was carried out from 25,600 readings by an electromagnetic sensor (Amézketa, 2007; Figs. 1D and 1E), indicating low salinity values (0.16 dS m⁻¹ with minimum values of 0.05 dS m⁻¹ on the soils developed on the glaciais; Calcixerollic Xerochrept; Soil Survey Staff, 1992). Maxima of 1.28 dS m⁻¹ were found for the soils developed on the tertiary valley (Typic Xerofluvent;

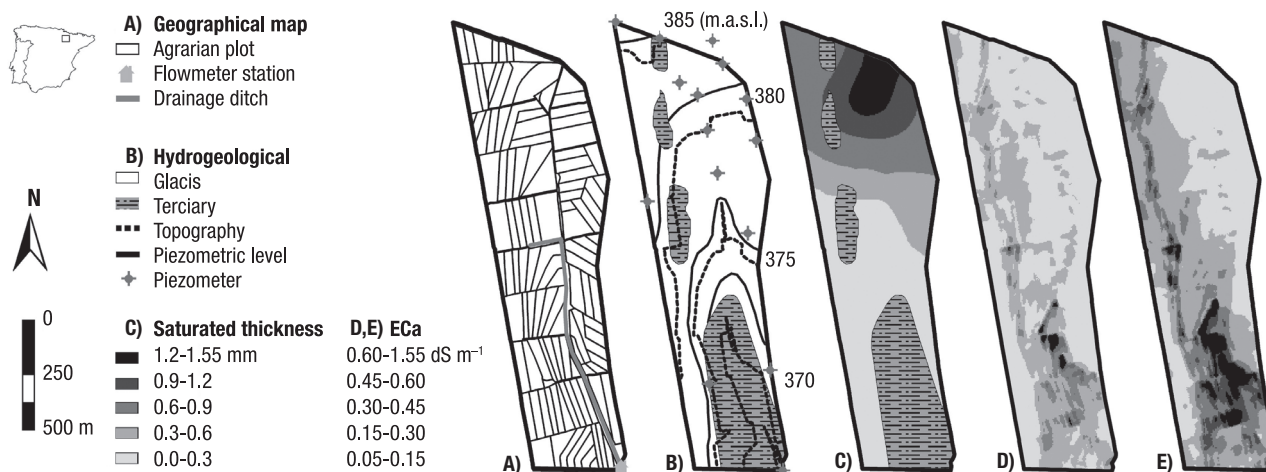


Figure 1. Location of the hydrological basin drained by the D-XIX-6 ditch: (A) Distribution of agrarian plots, gauging station and D-XIX-6 drainage ditch; (B) Geology, topography, piezometric level and piezometer distribution; (C) Average saturated thickness in the aquifer; (D) Map of soil apparent electrical conductivity (ECa) at 1 m depth; (E) Map of soil ECa at 2 m depth.

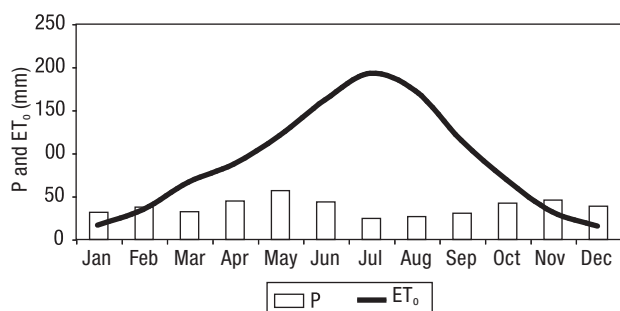


Figure 2. Historical monthly precipitation (P) and reference evapotranspiration (ET₀) in the area (Cinco Villas, Zaragoza, Spain). Source: <http://servicios.aragon.es/oresa/>

Soil Survey Staff, 1992). The higher average apparent EC (Figs. 1D and 1E) obtained at a greater depth demonstrates that the source of salts is located in the tertiary substratum.

Regarding the flood irrigation management of the study zone, García-Garizabal *et al.* (2011) quantified the benefits of the changes implemented by the irrigation district (assignment of irrigation allowances, on-demand flood irrigation system instead of rotation flood irrigation, and creation of water consumption accounts). The authors concluded that, between 2001 and the period 2005-2008, the changes implemented in the irrigation management resulted in a better use of water resources (efficiency increased by 26%), with water consumption better adjusted to the water requirements of the crops. The quantitative response of salinity contamination to the higher irrigation

efficiency (IE; percentage of irrigation water used by the crops) was the main goal of García-Garizabal *et al.* (2011).

Methods

Hydrochemical characterization

Hydrochemical characterization of the irrigation and drainage water of the agrarian basin of drainage ditch D-XIX-6 was carried out. Three samples of water were collected from the Bardenas canal and eight were collected at drainage ditch D-XIX-6, including the variation ranges of EC.

On-site EC at 25°C, temperature and pH were measured for the 11 samples. At the laboratory the concentrations of the main elements (CO₃²⁻, HCO₃⁻, SO₄²⁻, Cl⁻, Ca⁺², Mg⁺², Na⁺ and K⁺) were analyzed, obtaining errors of less than 5% in the charge balances, demonstrating the good quality of the chemical analysis.

Hydrochemical characterization of rain water was carried out from data registered by the Logroño measurement station (Spain) from the European Monitoring and Evaluation Program network (EMEP, 2009), that is located close to the study zone (100 km).

The data obtained was represented in a Piper-Hill-Langelier diagram, the main molar reactions were analyzed, and speciation-solubility calculations were

performed with the help of the geochemical modeling program PHREEQC (Parkhurst & Appelo, 1999).

Salinity balance

On the basis of the water balances developed by García-Garizábal *et al.* (2011), annual balances were carried out for the main chemical elements for the hydrological year 2001 and the period 2005-2008. In order to do this, concentrations were assigned to the different members of the water balance developed by García-Garizábal *et al.* (2011), except for evapotranspiration (assumed as pure water) and water stored in the soil (due to its difficult quantification and extremely low contribution to the water balance). The addition of the different chemical elements allowed establishing a general salt balance, resulting in the following balance equation:

$$\begin{aligned} \text{Inputs (IN)} - \text{Outputs (OU)} - \text{Storage (ST)} &= \text{D\&P} \\ (\text{I} + \text{P} + \text{LSC}) - (\text{D-XIX-6}) - (\text{STa}) &= \text{D\&P} \end{aligned} \quad [1]$$

where the inputs through irrigation (I), precipitation (P), lateral subterranean contributions (LSC), minus the outputs through the ditch (D-XIX-6), minus storage in the aquifer (STa), equal the processes of dissolution and precipitation of minerals (*D&P*).

The concentration of irrigation water was obtained, due to its low variability, from the average concentration in three water samples collected at the Bardenas canal. The concentration of rain water was obtained from the 1988-2000 average values registered by the network EMEP (2009) gauging station in Logroño (Spain). For the other three members (LSC, D-XIX-6, STa) the concentrations were assigned based on EC data and the relationships obtained with the different chemical elements in the eight drainage water samples analyzed for the basin, due to the low variability in the quality of drainage water:

$$\text{CO}_3^{2-} (\text{mg L}^{-1}) = 0 \quad [2]$$

$$\text{HCO}_3^- (\text{mg L}^{-1}) = 325 \quad [3]$$

$$\text{SO}_4^{2-} (\text{mg L}^{-1}) = 149.46 \text{ EC (dS m}^{-1}) - 49.02; R^2 = 0.56; p < 0.05 \quad [4]$$

$$\text{Cl}^- (\text{mg L}^{-1}) = 15.57 \text{ EC (dS m}^{-1}) - 57.61; R^2 = 0.80; p < 0.01 \quad [5]$$

$$\text{Ca}^{+2} (\text{mg L}^{-1}) = 53.23 \text{ EC (dS m}^{-1}) + 53.70; R^2 = 0.74; p < 0.01 \quad [6]$$

$$\text{Mg}^{+2} (\text{mg L}^{-1}) = 17.07 \text{ EC (dS m}^{-1}) + 4.37; R^2 = 0.83; p < 0.01 \quad [7]$$

$$\text{Na}^+ (\text{mg L}^{-1}) = 80.69 \text{ EC (dS m}^{-1}) - 8.40; R^2 = 0.63; p < 0.05 \quad [8]$$

$$\text{K}^+ (\text{mg L}^{-1}) = 0.38 \text{ EC (dS m}^{-1}) + 0.65; R^2 = 0.06; p > 0.1 \quad [9]$$

The concentration of D-XIX-6 was determined from the average EC measured in water samples collected daily by an automatic sampler (model ISCO 3600) installed in the gauging station, at the final point of the ditch (Fig. 1A). The concentration of the LSC was determined from monthly EC values at the entry zone of subterranean water (piezometer located at the Northwest vertex of the basin; Fig. 1B).

Finally, the salt content of the groundwater in the initial and final stages of this study (necessary for the estimation of storage) was obtained from the average EC of the groundwater through geostatistical techniques (Kriging) applied to the entire data from the piezometer network.

Geochemical modeling

Modeling calculations were focused on an inverse problem approach, in which knowledge on the composition of the input and output waters of the basin and on the mineral phases possibly present allow for the deduction of the mixture proportions of waters and the mass transfers associated with the water-rock interactions, resulting in the determination of the final composition.

Starting from annual volumes and masses, the average concentrations of rain water, irrigation, LSC and drainage from ditch D-XIX-6 were obtained for each study year.

Given the impossibility of dealing with representative sampling of the soil drainage concentration for the entire irrigated hydrological basin, annual average concentrations were estimated with the aid of the geochemical modeling program PHREEQC (Parkhurst & Appelo, 1999). Irrigation and rain water mixtures were simulated according to the annual contributions and the mixture was concentrated according to a factor defined by the proportion of the irrigation water contribution plus precipitation and drainage volume proceeding from the soil water balance calculated by García-Garizábal *et al.* (2011).

The resulting water and the annual average concentrations of the LSC were introduced in the program NETPATH (Plummer *et al.*, 1994), which is a specific geochemical modeling code that carries out mass balance calculations (inverse modeling). From the compositional data of the aforementioned waters and a set of mineral phases present in the system, the code obtains the mixture proportions and the magnitude of

the dissolution/precipitation and cation exchange processes necessary to obtain the concentration of the D-XIX-6 ditch waters.

In order to perform calculations with NETPATH, C, S, Cl, Ca, Mg and Na were introduced as chemical elements involved in the mass balances (restrictions). Calcite, dolomite, gypsum, halite, and CO₂ as well as NaX as cation exchanger, were introduced as mineral phases according to the chemical and mineralogical information of the materials of the zone (Causapé *et al.*, 2004a). Validation of results was accomplished through the comparison of the mixture proportions obtained by NETPATH with the mixture proportions deduced from the water balance carried out in GarcíaGarizábal *et al.* (2011).

Salinity produced by irrigation

The mass of salts exported by the irrigation area studied (S) was calculated as the difference between the salts transported through output water flows of the basin in ditch DXIX6 and the inputs through the LSC:

$$S = \text{D-XIX-6} - \text{LSC} \quad [10]$$

The salt contamination index (SCI; Causapé, 2009) was calculated to compare the impact on the study area with other irrigation areas under different natural conditions. The SCI corrects the exported masses by the EC of the drainage water in non-irrigated conditions (EC_{NI}), representative of the “natural” salinity conditions of each irrigation area.

$$\text{SCI} = S / \text{EC}_{\text{NI}} \quad [11]$$

Results and discussion

Hydrochemical characterization

The rain water presented very low mineralization (EC = 0.03 dS m⁻¹), and was classified as sulphate-chloride calcium-sodium water (based on EMEP: <http://www.nilu.no/projects/ccc/>). Irrigation water was classified as calcium-bicarbonate water (Fig. 3). Its mineralization (between 0.33 and 0.38 dS m⁻¹) and its sodium adsorption rate (SAR between 0.2 and 0.5) were low, with no restrictions for use as irrigation water (Ayers & Westcot, 1994).

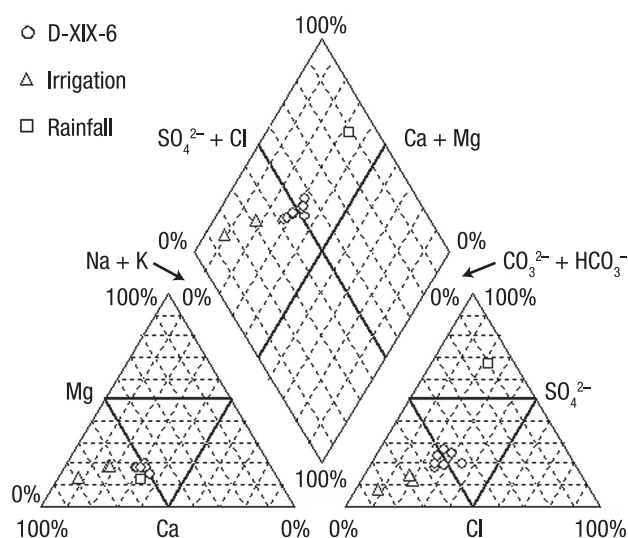


Figure 3. Piper-Hill-Langelier diagram with the samples of drainage water (eight samples; circles), irrigation (three samples; triangles) and precipitation (square; average data). Source: <http://www.nilu.no/projects/ccc/>

Irrigation and rain waters shifted compositions throughout drainage, towards bicarbonate-chloride calcium-sodium waters (Fig. 3), increasing mineralization (2-3 times for irrigation water) and SAR (EC_{max} = 1.28 dS m⁻¹ – SAR = 1.8; SAR_{max} = 2.2 – EC = 1.13 dS m⁻¹) up to levels that, according to Ayers & Westcot (1994), do not restrict the use as irrigation water.

The chemical dynamics of drainage water are controlled by the behavior of irrigation and rain water evapotranspiration, lithology, geochemical reactions, and anthropic activities that might have been developed in the area (Jalali, 2007).

— Molar ratio mNa⁺/mCl⁻: Molar ratio of drainage waters varies between 0.87 and 1.54, with values higher than 1 with the exception of one sample with the highest EC (Fig. 4A). The dissolution process of halite incorporates Na⁺ and Cl⁻ with a 1:1 relationship, which suggests the existence of a supplementary source of Na⁺ to explain such values over 1. In low-salinity waters, the excess of Na⁺ in comparison with Cl⁻ indicates the possible feldspar alteration or cation exchange processes in the soil (Nkotagu, 1996; Mahlknecht *et al.*, 2004). Considering that feldspar is not abundant in the materials of the zone, the cation exchange between Na⁺ and Ca⁺²-Mg⁺² would be the most suitable supplementary source.

— Molar ratio mMg⁺²/mCa⁺²: Molar ratio in the drainage water varies between 0.30 and 0.39,

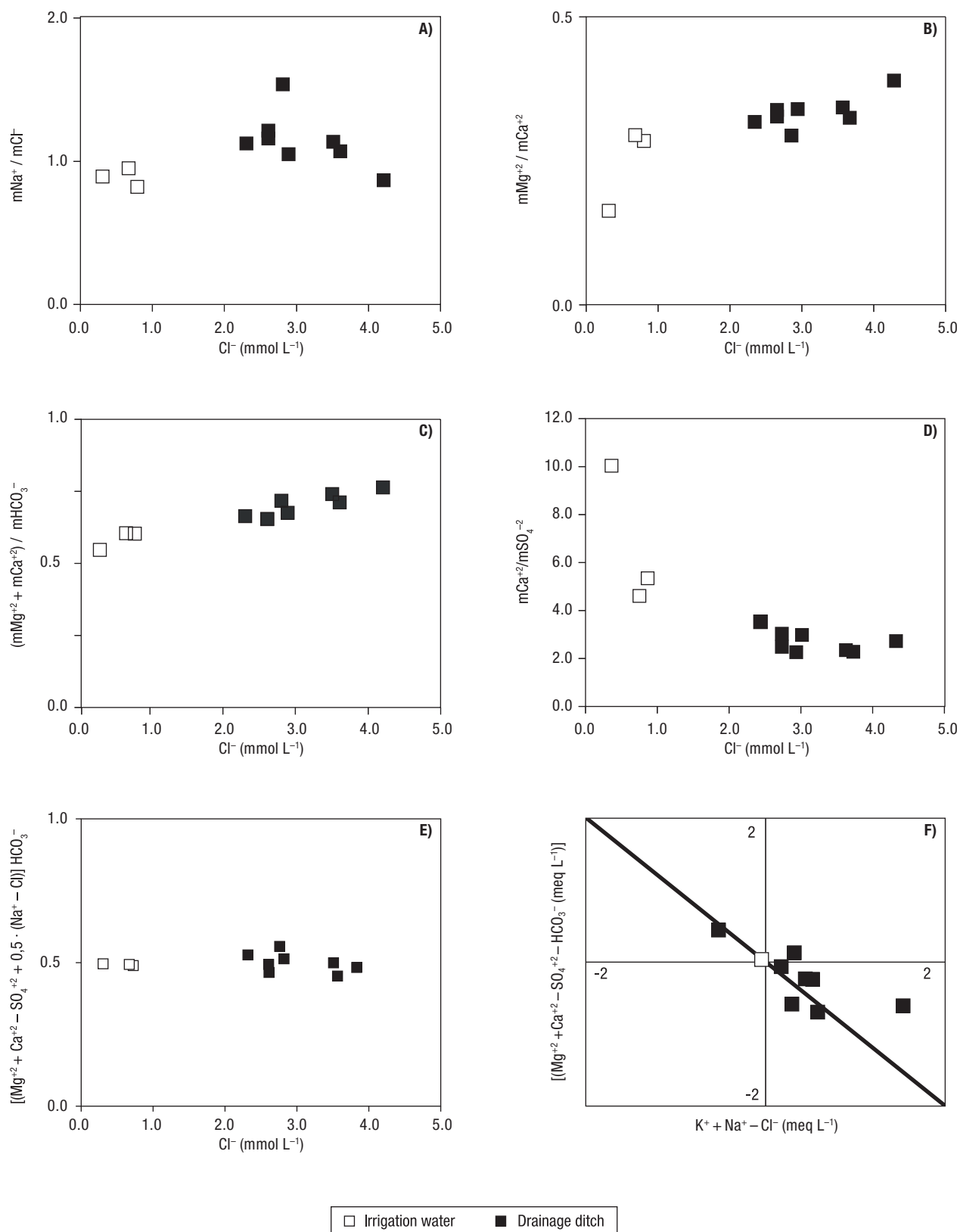


Figure 4. Dynamics of molar relationships (A-E) and $(\text{Mg}^{2+} + \text{Ca}^{2+} - \text{SO}_4^{2-} - \text{HCO}_3^-)$ vs. $(\text{K}^+ + \text{Na}^+ - \text{Cl}^-)$ (F) diagram in the three samples of irrigation water and eight samples of the drainage ditch.

increasing with salinity (Fig. 4B), indicating that either Ca^{+2} is incorporated in a smaller amount than Mg^{+2} or that Ca^{+2} exits the aqueous system. These behaviors can be related to the dissolution of carbonate-sulfate-chloride magnesium-calcium minerals, $\text{Na}^{+}\text{-Ca}^{+2}$ cation exchange processes (Nkotagu, 1996) or the precipitation of Ca^{+2} minerals (Andreo *et al.*, 1999).

— Molar ratio $(\text{mMg}^{+2} + \text{mCa}^{+2})/\text{mHCO}_3^-$: Molar ratio in the waters of D-XIX-6 varies between 0.60 and 0.77, increasing with salinity (Fig. 4C), for which either $\text{mMg}^{+2} + \text{mCa}^{+2}$ is incorporated into the waters in a higher proportion than HCO_3^- (through the dissolution of gypsum, for example, $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$), or HCO_3^- exits the solution, as the dissolution of carbonate itself would present a ratio of 0.5 (Nkotagu, 1996).

— Molar ratio $\text{mCa}^{+2}/\text{mSO}_4^{2-}$: Molar ratio in the drainage waters varies between 2.01 and 3.28, decreasing with salinity (Fig. 4D). Gypsum is the main source of Ca^{+2} and SO_4^{2-} , which are released with a 1:1 rate. Therefore $\text{mCa}^{+2}/\text{mSO}_4^{2-} > 1$ would be an indication of a Ca^{+2} contribution through the dissolution of carbonate in rain water in the collection zone of irrigation water (carbonate materials from the head basin). The decrease of $\text{mCa}^{+2}/\text{mSO}_4^{2-}$ with the increase of salinity can be explained by the precipitation of calcite (Lorite-Herrera *et al.*, 2008). Nevertheless, the presence of other sulfated mineral phases (different from gypsum) in fertilizers and phytosanitary products used in agrarian activities (Liñan, 2009) could release SO_4^{2-} to the solution, resulting in $\text{mCa}^{+2}/\text{mSO}_4^{2-}$ ratios lower than those obtained through mineral dissolution.

— Molar ratio $[(\text{mMg}^{+2} + \text{mCa}^{+2} - \text{mSO}_4^{2-} + 0.5(\text{mNa}^{+} - \text{mCl}^{-})) / \text{mHCO}_3^-]$: Molar ratio varies between 0.47 and 0.58 (Fig. 4E). Such a proximity to 0.5 indicates that HCO_3^- can originate from the dissolution of carbonates, as the incorporation of HCO_3^- due to the dissolution of plagioclases only occurs in low proportions (Nkotagu, 1996; Mahlkecht *et al.*, 2004).

— Scatter plot $(\text{Mg}^{+2} + \text{Ca}^{+2} - \text{SO}_4^{2-} - \text{HCO}_3^-)$ vs. $(\text{K}^{+} + \text{Na}^{+} - \text{Cl}^{-})$: Fig. 4F provides information on the origin of Ca^{+2} , Mg^{+2} , Na^{+} and K^{+} and on the existence of cation exchange processes. Therefore $\text{Na}^{+} + \text{K}^{+} - \text{Cl}^{-}$ represents the amount of $\text{Na}^{+} + \text{K}^{+}$ gained or lost, relative to that provided by chloride salts dissolution (mostly halite dissolution). $\text{Ca}^{+2} + \text{Mg}^{+2} - \text{SO}_4^{2-} - \text{HCO}_3^-$ represents the amount of Ca^{+2} and Mg^{+2} gained or lost, relative to that provided by gypsum, calcite and dolomite dissolution (Jalali, 2007).

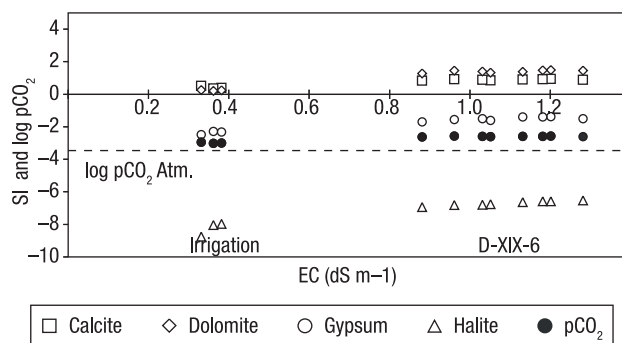


Figure 5. Partial pressure of CO_2 ($\log \text{pCO}_2$) and Saturation Index (SI) for calcite, dolomite, gypsum and halite in the three samples of irrigation water (Irrigation) and eight samples of the drainage ditch (D-XIX-6).

The situation of the waters on the -1 inclination line (Fig. 4F) is an indication that the chemical concentrations are explained by cation exchange processes, and in the absence of these reactions, all data should plot close to the origin (García *et al.*, 2001; Jalali, 2007). In this way, irrigation waters are located close to the origin while drainage waters are closer to the -1 slope line (Fig. 4F).

The speciation-solubility results demonstrate that irrigation water is in equilibrium with calcite, dolomite and at a CO_2 partial pressure very close to atmospheric values ($\log \text{pCO}_2 = -3.5$; Fig. 5). Nevertheless, drainage waters are clearly oversaturated with respect to calcite and dolomite and present higher CO_2 partial pressures due to its circulation through the subsoil, increasing its disequilibrium with the atmosphere (Drever, 1997).

The analyzed waters are undersaturated with respect to gypsum and halite. Its progressive mineralization only increases slightly the saturation indices, given the scarce presence of these minerals in the subsoil of the basin.

Therefore, given the ionic relationships and the speciation-solubility results, it can be deduced that the study zone is undergoing a process of calcite precipitation, as evidenced by the presence of petrocalcic in the soils (Lecina *et al.*, 2005), dissolution of gypsum and halite, and cation exchange processes.

Salinity balance

The study of the masses of the major elements has allowed the establishment of global salinity balances

Table 1. Volume of water and mass of salts in inputs [precipitation (P), irrigation (I) and lateral subterranean contributions (LSC)], outputs (D-XIX-6) and aquifer storage (STa) in the year 2001 and during the period 2005-2008

Year	Balance	Inputs			Output (D-XIX-6)	Storage (STa)	IE ¹ (%)
		P	I	LSC			
2001	Water ¹ (mm)	526	1139	561	1105	—	56
	Salts (kg ha ⁻¹)	49	3224	3120	7631	-138	
...							
2005	Water ¹ (mm)	211	570	270	359	—	89
	Salts (kg ha ⁻¹)	20	1613	1452	2479	-430	
2006	Water ¹ (mm)	450	567	332	417	42	84
	Salts (kg ha ⁻¹)	42	1604	1769	2786	509	
2007	Water ¹ (mm)	372	512	291	469	4	82
	Salts (kg ha ⁻¹)	35	1448	1522	3091	-98	
2008	Water ¹ (mm)	305	559	291	451	-16	78
	Salts (kg ha ⁻¹)	28	1583	1470	2936	-135	

IE: irrigation efficiency. ¹ Source: García-Garizábal *et al.* (2011).

Table 2. Annual balances of major elements (D&P) for the year 2001 and during the period 2005-2008

Year	D&P (kg ha ⁻¹ yr ⁻¹)							Total	IE ¹ (%)
	HCO ₃ ⁻	SO ₄ ²⁻	Cl ⁻	Ca ⁺²	Mg ⁺²	Na ⁺	K ⁺		
2001	199	-453	-446	-28	-42	-338	7	-1100	56
...									
2005	885	-44	-58	239	28	-18	6	1036	89
2006	542	-189	-201	94	-4	-128	5	120	84
2007	273	-111	-115	59	-3	-95	4	12	82
2008	475	-110	-114	107	4	-86	5	280	78

IE: irrigation efficiency. ¹ Source: García-Garizábal *et al.* (2011).

for the five studied years (Table 1). Irrigation and LSC introduce the majority of salts in the agrarian basin, as rain accounted for less than 1% of the salts introduced. Although presenting low mineralization, the mass of salts introduced with irrigation is similar to that of the LSC (smaller volume but higher concentration).

The mass of salts exported through ditch D-XIX-6 was conditioned by the irrigation volumes and the corresponding IE. The smaller irrigation volumes during 2005-2008 along with the increase in IE (up to an average of 83%; García-Garizábal *et al.*, 2011) resulted in that the mass of salts exported through D-XIX-6 (2.8 Mg ha⁻¹ yr⁻¹) was 63% lower than in 2001 (IE = 56%; García-Garizábal *et al.*, 2011). The lowest mass of salts exported occurred in 2005 (2.5 Mg ha⁻¹)

due to an intense water shortage that in turn produced an annual salt evacuation of 0.4 Mg ha⁻¹ (14% of inputs). It was back into normality at the end of 2006 when the aquifer registered a salt storage in the order of 0.5 Mg ha⁻¹.

The result of the salinity balance in 2001 was negative (-1100 kg ha⁻¹ yr⁻¹), indicating that dissolution processes were higher than precipitation. Analyzing individual element balances (Table 2), it was detected that HCO₃⁻ produced a positive balance, suggesting the precipitation of carbonates (calcite). For SO₄²⁻, Ca⁺², Cl⁻, and Na⁺ the balance result was negative indicating the possible dissolution of gypsum and halite. The quantities of Mg⁺² and K⁺ were sensibly lower than those of the remaining elements, and its

interpretation would be related to possible balance errors.

For the remaining years, and in special 2005 (climatically very dry), the HCO_3^- balance was higher, indicating a greater proportion of precipitated calcite due to higher irrigation water evapotranspiration (increment in the mineral saturation index; SI) caused by an increase in IE. During 2005-2008 the balance result for Ca^{+2} changed its trend to positive values, suggesting that calcite precipitation could predominate over gypsum dissolution. Finally, the quantities of SO_4^{2-} , Cl^- and Na^+ dissolved, especially for 2005, decreased significantly due to lower drainage flows in the soil. Therefore the global result of the salinity balances during 2005-2008 was positive (predominant precipitation over dissolution), reaching $1036 \text{ kg ha}^{-1} \text{ yr}^{-1}$ in 2005.

Geochemical modeling

The mixing proportions of soil drainage and LSC obtained by NETPATH are similar to those obtained from the water balance in García-Garizábal *et al.* (2011), especially for the four years in the period 2005-2008 (Fig. 6). The difference in 2001 values was interpreted as being associated with a greater error in water balances (García-Garizábal *et al.*, 2011). Nevertheless, the models are considered sufficiently valid to explain the geochemical processes in the system under study.

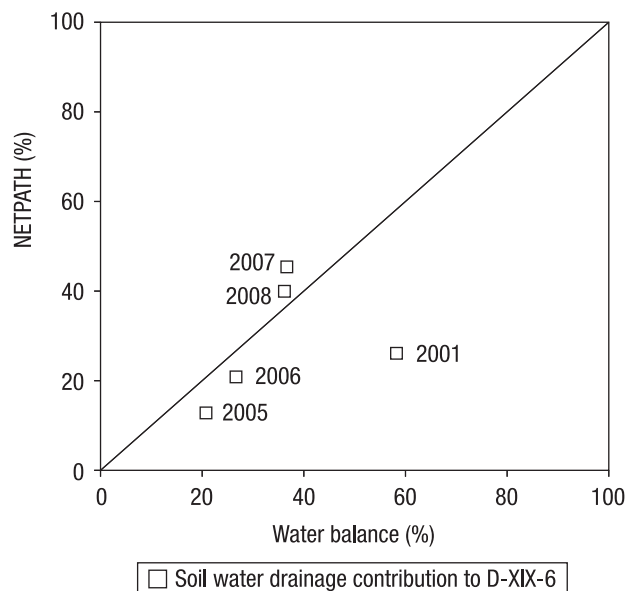


Figure 6. Comparison of the soil drainage contribution in the basin for the five study years (2001 and period 2005-2008): according to the water balance results (García-Garizábal *et al.*, 2011) vs. obtained by NETPA.

The results obtained with NETPATH (Table 3) indicate calcite precipitation for all years, ranging between 0.26 mmol L^{-1} in 2001 (lower concentration factor) and 0.89 mmol L^{-1} in 2005, with a higher concentration factor due to water scarcity and the correspondent increase in IE. During 2005-2008, a decrease was found in the concentration factor of the drainage water, decreasing the amount of precipitated calcite but not reaching 2001 levels.

Table 3. Mixture proportion of precipitation (P) – Irrigation (I) and concentration factor (Fc) introduced into PHREEQC to obtain water drainage concentration. Mixture proportions of soil water drainage (D) and lateral subterranean contributions (LSC), as well as the amount of calcite, dolomite, gypsum, halite, Na, and CO_2 obtained with NETPATH to explain the water concentration in the drainage ditch from irrigation-rain waters and its mixture with LSC in the year 2001 and during the period 2005-2008. The negative values of NETPATH indicate mineral precipitation or output of the solution and positive values indicate mineral dissolution or incorporation of the element into the solution

Year	PHREEQC			NETPATH						
	P ¹ (%)	I ¹ (%)	Fc ¹	D/LSC (%)	Calcite (mmol L ⁻¹)	Dolomite (mmol L ⁻¹)	Gypsum (mmol L ⁻¹)	Halite (mmol L ⁻¹)	Na (mmol L ⁻¹)	CO ₂ (mmol L ⁻¹)
2001	32	68	2.1	26/74	-0.26	0.24	0.49	1.33	—	0.06
...										
2005	27	73	11.0	12/88	-0.89	—	0.35	0.97	-0.07	-1.20
2006	44	56	8.4	21/79	-0.77	—	0.29	0.85	0.01	-0.83
2007	42	58	5.2	45/55	-0.76	—	0.29	0.81	0.21	-0.63
2008	35	65	5.2	40/60	-0.84	—	0.29	0.81	0.18	-0.86

¹ Source: García-Garizábal *et al.* (2011).

Table 4. Irrigation efficiency (IE), drainage from the hydrological basin (D), mass of salts exported with drainage (S), concentration of drainage (S/D), electrical conductivity during non-irrigated period (EC_{NI}) and salt contamination index (SCI) in the hydrological basin for the year 2001 and during 2005-2008

Year	IE ¹ (%)	D ¹ (mm)	S (Mg ha ⁻¹)	S/D (mg L ⁻¹)	EC _{NI} (dS m ⁻¹)	SCI (Mg ha ⁻¹ dS ⁻¹ m yr ⁻¹)
2001	56	544	4.5	829	1.05	4.3
...						
2005	89	89	1.0	1154	1.05	1.0
2006	84	85	1.0	1196	1.05	1.0
2007	82	178	1.6	881	1.05	1.5
2008	78	160	1.5	916	1.05	1.4

¹ Source: García-Garizábal *et al.* (2011).

From these results the presence of precipitated calcite in the soil profile can be deduced for the year 2001, with a lower IE (56%; García-Garizábal *et al.*, 2011). This fact has generated the petrocalcic levels with progressively increasing thickness that could produce limitation of root depth, reducing the water holding capacity of soils along with hydraulic conductivity, which could result in serious agronomic issues (FAO, 2009).

Another result from NETPATH for 2001 is that dolomite dissolution is possible. Apparently this result is incoherent with the oversaturation state obtained for irrigation and ditch D-XIX-6 waters (Fig. 5). However, it could be justified by the water flow across the soil and the incorporation of CO₂ (Drever, 1997) that only occurs in the 2001 model and therefore water could be undersaturated, producing dissolution.

The results of the balance indicate greater dissolutions of gypsum and halite in 2001 than in the period 2005-2008, as in 2001 the soil drainage was more diluted due to a lower IE. Therefore the increment in the mass of salts exported with low IE is not only due to a greater drainage volume but also to a greater dissolution capacity of low-concentration drainage waters.

Regarding sodium, possibly affected by cation exchange processes in the soil, the storage recorded in 2005 is remarkable due to the intense evapoconcentration of waters. From the model results, this fact indicates the existence of sodification episodes in the soils, which could produce structural deterioration and motivate air and water circulation issues (Abrol *et al.*, 1988).

Actually, the results seem to indicate that the punctual accumulation of sodium is being solved by its leaching during the years with lower IE. The possible establishment of high-efficiency systems must

be considered, which requires adequate planning with short- and medium-term measures to prevent soil sodification.

In summary, the results obtained with NETPATH are coherent with the elemental ratios of the waters in the ditch D-XIX-6 as well as with the results of the annual individual mass balances developed in the agrarian basin.

Salinity produced by irrigation

The low salinity of the geological materials present in the zone favored low-moderate salinity levels in the drainage waters and in the mass of salts exported by irrigation (Table 4). The increase in IE contributed to a greater evapoconcentration of drainage (smaller mass of salts in also a smaller volume). The year 2001 presents the lowest salinity concentrations (829 mg L⁻¹), which increases in 2005 and 2006 until its maximum value (1196 mg L⁻¹). The slight decrease in IE in 2007 and 2008 (Table 4) favored low-concentration return flows (881 and 916 mg L⁻¹ respectively), however not reaching salinity levels registered in 2001 due to a sensibly higher IE in these last study years.

The increase in IE contributed to a decrease in the mass of salts exported, from 4.5 Mg ha⁻¹ in 2001 to 1.0-1.6 in the period 2005-2008. The mass of salts exported in 2001 was of the same order as that measured by Causapé *et al.* (2004b) in two other small basins in the same irrigation district (4.7 and 3.4 Mg ha⁻¹ yr⁻¹) or in irrigation areas of the USA with low-moderate IE (approximately 50%; Duncan *et al.*, 2008). Likewise, salt exports were of the same order of those measured by Roman *et al.* (1999) and

Caballero *et al.* (2001) in two experimental plots in Madrid (5.2 and 3.9 Mg ha⁻¹ yr⁻¹) with higher salinities (EC_{NI} = 9.7 and 12.9 dS m⁻¹) and higher efficiencies (IE = 73 and 82%).

Other high-salinity irrigation areas of the medium Ebro valley (EC_{NI} = 8.4 dS m⁻¹; Tedeschi *et al.*, 2001) and Australia (EC_{NI} = 14.8 dS m⁻¹; Duncan *et al.*, 2008) export a greater quantity of salts (13.5 and 11.4 Mg ha⁻¹ yr⁻¹) although with higher IE (85% and 88%, respectively). Irrigated areas with a high content of gypsum in the medium Ebro valley (EC_{NI} = 1.8 dS m⁻¹; Isidoro *et al.*, 2006) with low-moderate IE (48%) can provide export values of up to 15 times the amount exported by the agrarian basin of the ditch after implementation of irrigation management changes.

The SCI calculation indicates that the contamination in the agrarian basin of ditch D-XIX-6 decreased after implementation of changes in irrigation management, from 4.3 Mg ha⁻¹ dS⁻¹ m yr⁻¹ in 2001 to between 1 and 1.5 Mg ha⁻¹ dS⁻¹ m yr⁻¹ during 2005-2008.

After implementation of management changes, the SCIs of this basin are slightly superior or of the same order of those registered in experimental plots in Madrid (0.4 Mg ha⁻¹ dS⁻¹ m yr⁻¹) or in efficient irrigation systems of the medium Ebro valley (1.6 Mg ha⁻¹ dS⁻¹ m yr⁻¹). Nevertheless, the SCIs are inferior to those presented in irrigation areas of the United States (1.9 Mg ha⁻¹ dS⁻¹ m yr⁻¹), in two small basins of the same irrigation district (3.2 and 7.5 Mg ha⁻¹ dS⁻¹ m yr⁻¹), and in other medium Ebro valley irrigated areas (11.4 Mg ha⁻¹ dS⁻¹ m yr⁻¹) with low-moderate IE (approximately 50%).

Therefore the changes in irrigation management produced an increase in drainage salinity but a decrease in the mass of salts exported, in such a way that the salt contamination index decreased approximately by 70%, reaching values of the same order of those presented in modern well-managed irrigated areas.

The use of geochemical codes for the study of salinity contamination processes in water and soils has been proved to be a powerful tool to study the impact of agrarian activities on the natural environment. Furthermore, the development of studies evaluating the impact, on water and soils, of changes in irrigation management under high-efficiency water use scenarios is necessary in this area considering the future modernization of this irrigation district, currently in the project phase.

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