



Geochemical modeling of systems affected by irrigation: The case of Lerma basin (Spain, 2004–2020)

J. Causapé^{a,c,*}, L. Auqué^{b,c}, M.J. Gimeno^{b,c}

^a Geological and Mining Institute of Spain, Spanish National Research Council, Residence CSIC Campus Aula Dei, Avda, Montañana 1005, 50059 Zaragoza, Spain

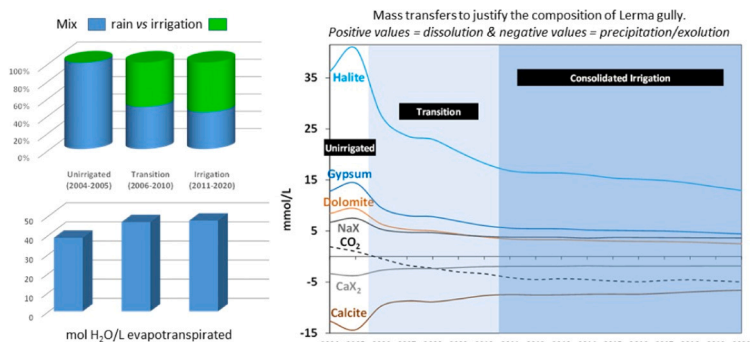
^b University of Zaragoza, Department of Earth Sciences (Geochemical Modelling Group), C/ Pedro Cerbuna 12, 50009 Zaragoza, Spain

^c IGME-CSIC/University of Zaragoza, Associated Unit in Earth Sciences, Zaragoza, Spain

HIGHLIGHTS

- Lerma gully (NE-Spain) evolution since irrigation land transformation
- Geochemical modeling of systems affected by irrigation
- Dissolution of halite, gypsum and dolomite. Calcite precipitation. Na—Ca exchange
- Irrigation accelerated natural processes but progressively slows down.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: José Virgílio Cruz

Keywords:

Irrigation agriculture
Irrigation return flow
Salinity
Environmental impact
PHREEQC temporal evolution

ABSTRACT

Geologically “saline” zones with scarce pluviometry, which are already susceptible to the salinization of natural drainage, can experience the acceleration of the salinization of the receiving water systems with the implementation of irrigation. The main objective of this paper is to analyze the geochemical processes that control the variations of the hydrosaline balance due to the implementation of irrigation of the Lerma basin (Spain) from the beginning of its transformation into irrigation land (2004) until the consolidation of irrigation (2020). The results of this study evidence the dissolution of some mineral phases, such as halite, gypsum, and dolomite, and the precipitation of others, such as calcite. Additionally, the final composition of the irrigation return flows cannot be explained without consideration of the Na—Ca exchange. Part of the dissolved Ca²⁺ is deposited in the soil, which, in turn, contributes with Na⁺ to the solution. These natural processes are accelerated with irrigation but progressively slow down as the soil salts are washed with time. Although less evident, there is an additional negative agroenvironmental effect associated with the precipitation of calcite and the possible formation of petrocalcic horizons in the soil. The results obtained herein indicate that studies focusing on the salinity of irrigated zones should go a step further and include the geochemical processes in quantifying the global mass of exported salts.

* Corresponding author at: Geological and Mining Institute of Spain, Spanish National Research Council, Residence CSIC Campus Aula Dei, Avda, Montañana 1005, 50059 Zaragoza, Spain.

E-mail address: j.causape@igme.es (J. Causapé).

URL: <https://www.jcausape.es> (J. Causapé).

<https://doi.org/10.1016/j.scitotenv.2023.166997>

Received 21 June 2023; Received in revised form 24 August 2023; Accepted 9 September 2023

Available online 22 September 2023

0048-9697/© 2023 Elsevier B.V. All rights reserved.

1. Introduction and objective

Irrigation can significantly impact the quality of the waters receiving the irrigation return flows. Geologically “saline” zones with low pluviometry levels are already prone to natural salinization of drainage, but this can be enhanced by the implementation of irrigation.

The studies based on hydrosaline balances of irrigated hydrological basins can quantify the mass of exported salts and establish the amount of dissolved salts by the difference between inputs and outputs (Causapé, 2009; García-Garizábal et al., 2012; Jiménez-Aguirre and Isidoro, 2018, ...). However, most of the existing research of this subject do not provide neither a deep geochemical study of the different ions involved (whose behavior can be either dissolution or precipitation) nor the information about the evolution of their behavior over the years due to irrigation.

In this sense, Causapé et al. (2004) started an investigation line based on the geochemical modeling of irrigation zones, which enabled the simulation of modernization scenarios for the Bardenas I irrigation zone and the verification of the environmental effects associated with the implementation of irrigation in Bardenas II. García-Garizábal et al. (2014) also successfully employed geochemical modeling to analyze the salinity dynamics of irrigation return flows associated with changes in irrigation management at the Irrigation Community n° V at Bardenas. Merchán et al. (2015) presented an initial assessment of the geochemical processes at a new irrigation zone of the Lerma basin (Fig. 1) and studied natural and anthropogenic factors. All these studies analyzed specific punctual situations that can vary throughout the evolution of the irrigation zone and the study of this evolution is the main objective of the approach made here.

Using the Lerma irrigation zone as a natural laboratory, Causapé et al. (2023) made a substantial advance by presenting a study on the salinization of a hydric system due to irrigation return flows that encompassed not only the overall salt balances but also the individual

balances for each major ion. The study goes a step further as it assesses the effect of irrigation in the long term (temporally dynamic, not static) and it is the second part of Causapé et al. (2023).

The study zone is also the Lerma basin (Spain), of which 48 % of its surface (352 ha) was included in the Sector XII irrigation transformation zone of Bardenas II. The geographic, climatic, geological, and agronomic description is presented in Causapé et al. (2023).

The methodology employed by Causapé et al. (2023) to determine the components of the hydrosaline balances consists of using the concentrations of each ion to obtain mean annual values (per hydrological year) representative of the water inputs (rain and irrigation), aquifer storage, and water outputs at the drainage of the irrigable area of Lerma (Fig. 2). These mean values are the required dataset for the geochemical modeling carried out afterwards.

The results of the hydrosaline balance highlight that the implementation of irrigation at the Lerma basin has doubled the mass of exported salts up to an average of 3177 kg/ha irrigable-year for the entire study period (2004–2020). 55 % (1816 kg/irrigable-year) correspond to a global process of salt dissolution, which is decreasing as the salts of the soil are being washed. The general pattern observed for most ions (SO_4^{2-} , Cl^- , Mg^{2+} , Na^+ , and K^+) was of more concentration in the outputs than in the inputs (an increase of the dissolved contents). However, HCO_3^- and Ca^{2+} , presented lower values in the outputs than in the inputs (decrease of their dissolved concentration).

Although directly related, the assumption of a unique effect of dissolution or precipitation processes for all ions can lead to significant errors. Therefore, the objective of this study is to characterize and quantify the geochemical processes that have taken place throughout 17 years of monitoring the Lerma irrigation area.

2. Methodology

Once the goodness of the hydrosaline balances of Causapé et al.

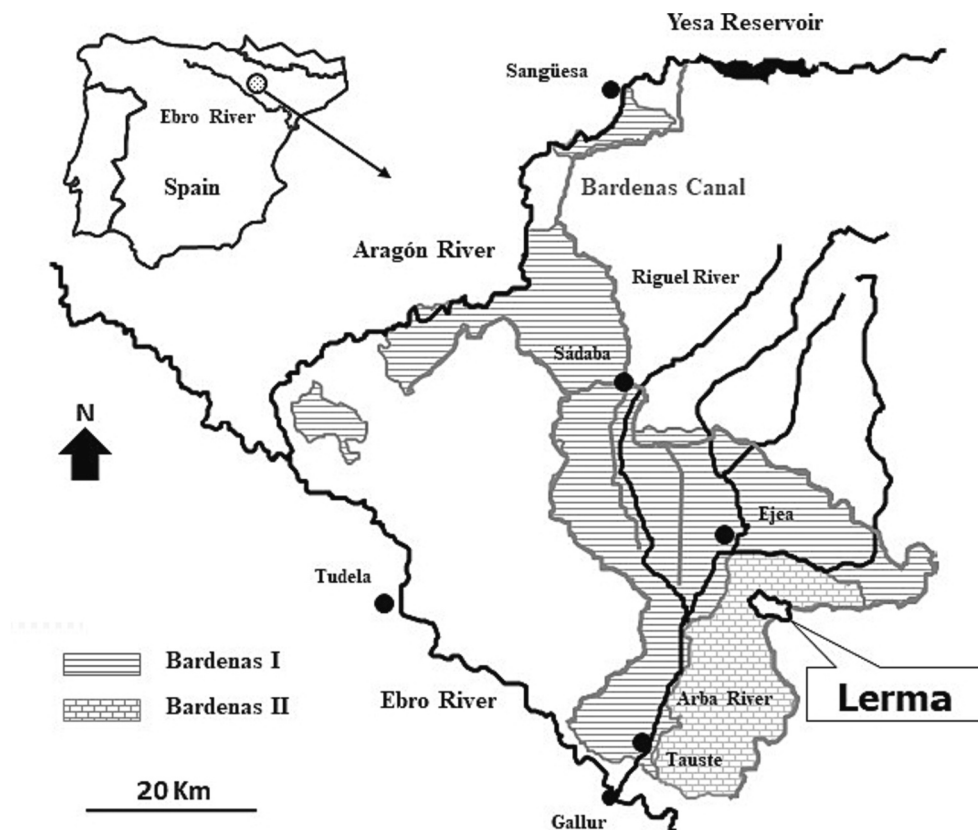


Fig. 1. Geographic location of the Lerma basin.

(2023) has been confirmed, the average annual concentrations calculated for the components will serve as input data for the geochemical models. These models aim to explain, year by year, the final chemical composition of the drainage water in the Lerma gully due to different geochemical processes affecting rainwater and irrigation water compositions.

The main controlling processes of the hydrogeochemical evolution were studied by evaluating the molar ratios between ions and from the geochemical modeling of the processes deduced from that analysis. The molar ratios were evaluated over the chemical analysis data of the 100 water samples collected at the Lerma gully over the years (Causapé et al., 2023) and considering the mineralogical data of the study zone.

Geochemical modeling calculations employed the PHREEQC code (Parkhurst and Appelo, 2013) and the WATEQ4F database. These calculations were performed in three steps (Fig. 3). The first two steps encompassed direct modeling (e.g., Zhu and Anderson, 2002) simulating the mixture of rainwater and irrigation water (Step 1) and its concentration after evapotranspiration of the plants in the proportions calculated for each year until obtaining an “intermediate” solution (Step 2). The third step was an inverse modeling (Zhu and Anderson, 2002) considering the mass balance between that intermediate solution, as the initial solution, and the composition of the drainage of the irrigable area as the final one. The results obtained with PHREEQC indicated the geochemical processes required to justify the dissolved contents in the final drainage water, from the initial concentrations of the inputs. The processes could include dissolution/precipitation of the main mineral phases of the system (calcite, dolomite, gypsum, and halite), ion exchange in the soil (CaX₂ and NaX), and CO₂ (gas) transfer.

3. Results and discussion

3.1. Ionic ratios

Fig. 4 shows some of the ionic ratios studied in the waters of the Lerma gully, considering the mineralogy of the studied zone. The values of Na⁺ and Cl⁻ are clearly related, although they are located above the 1:1 line (dissolution of halite, NaCl; Fig. 4), which indicates the need for an additional source of Na⁺ in the waters.

There is also a clear relationship between Ca²⁺ and SO₄²⁻ (Fig. 4B), although there is less calcium than expected from the gypsum dissolution (CaSO₄·2H₂O). The relationship between Ca²⁺ and HCO₃⁻ (Fig. 4C)

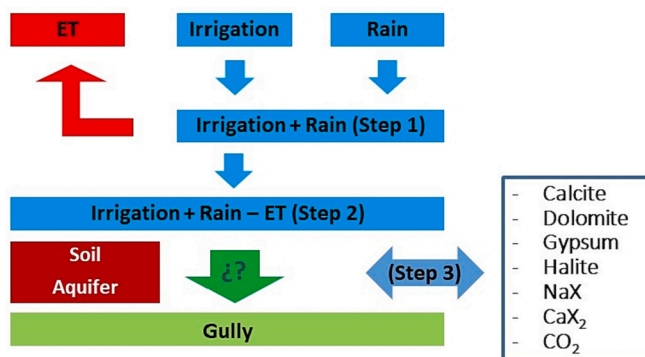


Fig. 3. Conceptual model of the processes simulated with PHREEQC from the supply of rain and irrigation (Step 1) to the arrival of the drainage to the gully, through the soil and aquifer (Step 3).

shows a more dispersed distribution, probably indicating the superposition of several processes, such as the interaction of waters with calcite and some other carbonate phase and/or gypsum.

When considering Mg²⁺ and simultaneously HCO₃⁻ + SO₄²⁻ (Fig. 4D), the relationship is much more linear and closer to the 1:1 line, but still does not justify the amount of dissolved Ca²⁺ and Mg²⁺. This means that an additional process, besides the interaction with gypsum, calcite, and dolomite, is required.

The excess of Na⁺ and deficiency of Ca²⁺ observed in the waters suggests a Na—Ca cationic exchange process that supplies Na⁺ to water and removes Ca²⁺ from it to a solid phase. This process has been previously mentioned in other geochemical studies in the zone (Causapé et al., 2004; García-Garizábal et al., 2014; Merchán et al., 2015).

From these established ionic ratios, it could be said that the main geochemical processes in the system include the dissolution/precipitation of halite, gypsum, calcite, and dolomite, and the Na—Ca cationic exchange. The geological characteristics of the area support the presence of these mineral phases and their possible dissolution. Even the possible participation of calcium carbonate is coherent with the reported presence of petrocalcic horizons locally called “mallacán”.

The processes deduced from these molar ratios and the transfer of CO₂ from and to the waters, are contemplated in the geochemical modeling presented in the next section.

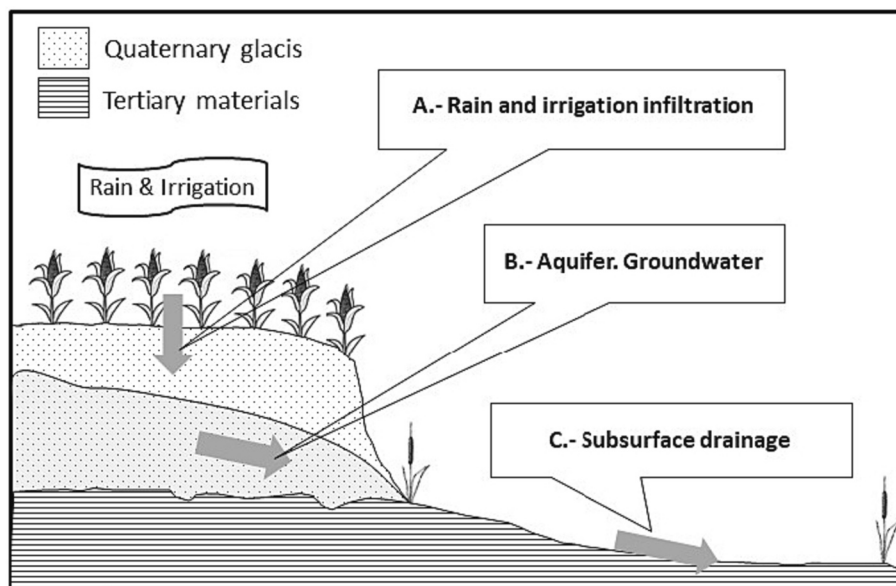


Fig. 2. Conceptual hydrological model (adapted from Merchán et al., 2015).

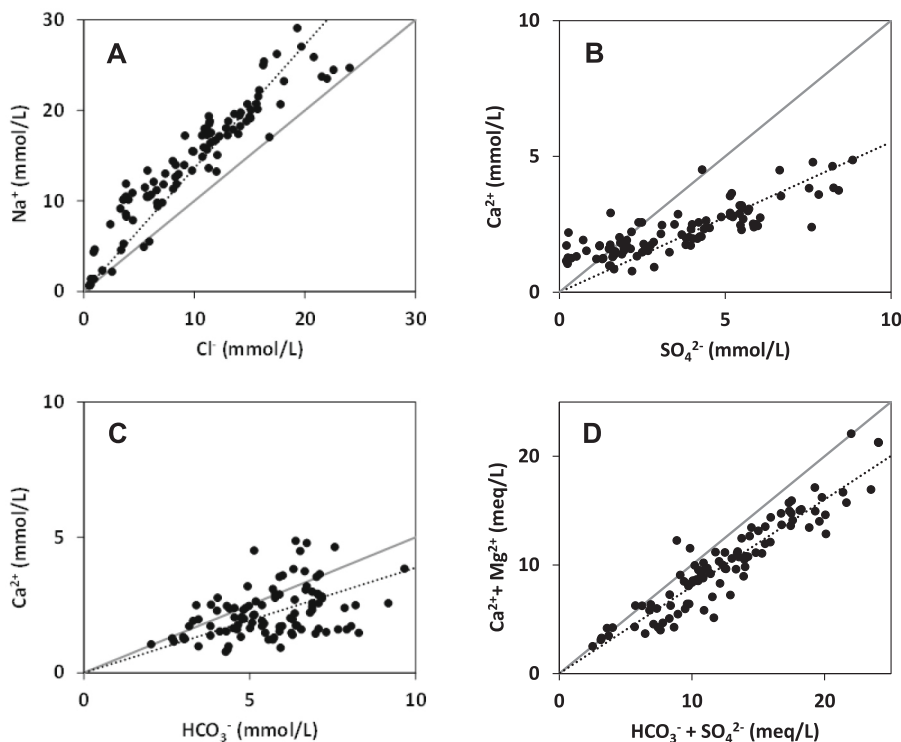


Fig. 4. Molar ratios for the waters of the Lerma gully. The solid lines represent the ratios typical for halite (A), gypsum (B), calcite (C), and for the combination of calcite, dolomite, and gypsum (D). The dotted lines represent the regression curves between variables.

3.2. Geochemical modeling

The geochemical modeling of the processes represented in the conceptual model of the system (Fig. 3) is partially based on the results obtained from the hydrosaline balances. Table 1 shows these results, which indicate that the percentage of water introduced with irrigation went from zero, at the beginning of the study period (2004), to 52 % for the entire study period.

Irrigated agriculture has also caused an increase in the percentage of evapotranspired water concerning the overall amount of water introduced by irrigation and rain. This increase has varied from 53 % during the first year to 84 % for the overall study period.

All ionic concentrations in the drainage water of Lerma have

decreased with the implementation of irrigation. In the beginning, the dilution of drainage water could have been due to the mixture with significant irrigation water volumes with lower salinity content. However, the global decrease during the final period would have depended more on the progressive consumption of the salts present in the soils due to the constant washing.

The chemical unbalances of the average annual cumulative concentrations were very low (under 3 %, Causapé et al., 2023), which validates the methodology employed and supports its use as input data in PHREEQC.

The direct modeling carried out in the first two steps highlights that the mixture of rainwater with irrigation water (Step 1) and the posterior evapotranspiration of the mixture (Step 2) produce an increment in the

Table 1 Percentage of Irrigation (I) in contrast with Rain (R) and percentage of evapotranspiration (ET). Average accumulated annual chemical concentration of the drainage at Lerma.

	I	ET	HCO ₃ ⁻	SO ₄ ²⁻	Cl ⁻	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	EB ^a
	%	%	mg/L			mg/L				%
2003–2004	0	53	543	1229	1281	216	206	1032	9	0.7
2003–2005	0	69	585	1385	1443	238	231	1158	10	0.2
2003–2006	11	73	483	932	973	174	161	805	9	1.8
2003–2007	24	78	454	801	836	155	141	703	8	2.2
2003–2008	33	79	449	786	821	153	139	690	8	1.9
2003–2009	38	81	427	709	741	142	126	627	8	1.9
2003–2010	42	81	411	632	661	131	115	568	8	2.3
2003–2011	45	83	401	588	615	124	108	533	8	2.4
2003–2012	47	84	400	581	608	123	107	528	8	2.4
2003–2013	48	83	398	578	605	123	106	526	8	2.3
2003–2014	49	83	395	563	589	121	104	513	8	2.2
2003–2015	50	84	392	551	577	119	102	504	8	2.2
2003–2016	51	84	391	545	571	118	101	500	8	2.1
2003–2017	51	84	388	535	560	117	100	491	7	2.1
2003–2018	51	83	384	517	541	114	97	477	7	2.2
2003–2019	51	84	379	494	518	111	93	460	7	2.3
2003–2020	52	84	375	474	497	108	90	444	7	2.4

^a Error Balance (%) = 200 · [(cations – anions) / (cations + anions)]. Concentrations in meq/L.

concentration of solutes in the resulting solutions (Table 2). The rainwater + irrigation water mixture also leads to an increase in pH until almost neutral values. Nevertheless, the simulation of evapotranspiration with proportional water loss to that obtained with hydric balances (considering that 1 l of water has 55.6 mol of H₂O) causes a slight decrease in the pH, to slightly acid values.

Analysis of the differences in the percentage of mixing and evapotranspiration shows that the most remarkable changes were produced in the first years of the implementation of irrigation (transition period 2006–2010). Once irrigation was consolidated (2011–2020), the increment of ions due to the mixture of waters and evapotranspiration was maintained, with a clear stabilization trend. The saturation states of the solutions obtained with PHREEQC show that initially, the rainwater was undersaturated in calcite, dolomite, gypsum, and halite. Irrigation water was undersaturated in gypsum and halite but slightly oversaturated in calcite and dolomite (Fig. 5). The mixture of both types of water and its posterior evapotranspiration maintains the saturation indices of these mineral phases mainly at negative values.

Remarkably, the implementation of irrigation produced a step-change in the evolution of the saturation indices, with a higher increase/decrease between the beginning (2004–2005) and the transition periods (2006–2010), than between the latter and the consolidated period (2011–2020). This increase between 2004–2005 and the transition period was so important that, once evapotranspiration is considered, calcite was already oversaturated, decelerating the oversaturation of dolomite when irrigation was consolidated.

The situation of the final water in the drainage shows that halite and gypsum are undersaturated for the three periods, while calcite and dolomite are oversaturated. There is a decreasing temporal trend for oversaturation in calcite and dolomite, and an increasing trend for the undersaturation degree of gypsum and halite, indicating a progressively lower availability of these minerals for dissolution.

Regarding CO₂ (gas), the logarithm of its partial pressure is closer to equilibrium with the atmosphere (–3.5) in the irrigation water than in the rainwater. Still, in both cases, the values are higher. Once these waters are mixed and evapoconcentrated, the final value is even higher and, therefore, farther from equilibrium with the atmosphere. However, as irrigation began to consolidate, the final drainage started to reach equilibrium with the atmospheric CO₂ (Fig. 6), indicating a lower content of dissolved CO₂.

The inverse models obtained with PHREEQC for each considered period show the accumulation of some mineral phases in the system (precipitation of calcite and decrease of Ca²⁺ in the solution due to ionic exchange) and the disappearance of others (dissolution of dolomite,

gypsum, and halite along with the increase in Na⁺ in the solution due to ionic exchange). It is also interesting to highlight that CO₂ (gas) starts increasing in the aqueous solution, but with irrigation, its concentration decreases.

The rest of the mineral phases start the evolution by increasing or decreasing (depending on the case) due to the rainy year 2004. Still, all phases change their increasing/decreasing evolution abruptly with the implementation of irrigation. The trends are progressively smoothed but they maintain the accumulation or loss character in the system (Fig. 7).

Other areas with changes in the use of their land (before and after irrigation modernization) quantify a decrease of 50–60 % in the mass of salts exported in the drainage (García-Garizábal et al., 2012; Jiménez-Aguirre and Isidoro, 2018), although their study began with already consolidated irrigation and they did not include the modeling of the possible geochemical processes.

Considering Lerma results, it would be expected that the transfers of all mineral phases should stabilize with progressively lower amounts of dissolved halite, gypsum, and dolomite and less precipitated calcite in the future. The same would occur with the Ca–Na ionic exchange and the CO₂ (gas) transfer under the new irrigation conditions.

4. Conclusions

This study highlights that the dynamics of irrigation return flows in the Lerma basin, depends on the dissolution of some mineral phases (halite, gypsum, dolomite) and the precipitation of other phases, such as calcite. Additionally, the Na–Ca ionic exchange seems necessary to justify the final composition of these return flows (part of the dissolved Ca²⁺ goes to the soil, which supplies Na⁺ to the solution). These natural processes were accelerated with the implementation of irrigation but smoothed out with time as the salts in the soil were progressively washed.

The dissolution of salts and their release to the final drainage contribute to the salinization of the systems that receive the irrigation return flows. Even in a hypothetical situation in which the irrigated zone only exported the salts introduced with irrigation, the salinity of the receiving system would increase due to the detraction of flows (the same amount of salts in a lower flow).

Another less evident negative environmental effect is the increase in salinity due to the precipitation of calcite and the possible formation of petrocalcic horizons. These precipitations hinder drainage, causing flooding and subsequent soil salinization as the salts introduced by irrigation are not being washed. Therefore, reducing the agro-environmental impact of irrigation requires minimizing the mass of

Table 2

Results of the direct modeling during the initial period (2004–2005), transition period (2006–2010), and consolidated irrigation (2011–2020) for the irrigable area of the Lerma basin. Step 1: Mixture of Rain (R) and Irrigation (I), step 2: water loss due to evapotranspiration.

Step 1	R vs I % - %	pH	HCO ₃ ⁻ mg/L	SO ₄ ²⁻	Cl ⁻	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺
Unirrigated 2004/2005	100-0	5.7	11.8	2.3	1.3	3.0	1.1	1.2	0.5
Transition 2006/2010	49-51	6.9	90.0	10.9	9.9	26.1	4.6	6.4	0.7
Consolidated 2011/2020	43-57	7.0	99.1	11.9	11.0	28.6	5.0	7.0	0.8
Step 2	H ₂ O mol/L	pH	HCO ₃ ⁻ mg/L	SO ₄ ²⁻	Cl ⁻	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺
Unirrigated 2004/2005	-38.5	5.7	38.5	7.5	4.2	9.5	3.6	4.1	1.6
Transition 2006/2010	-46.7	6.8	552.2	69.0	62.4	164.7	29.2	40.5	4.9
Consolidated 2011/2020	-47.5	6.9	667.5	83.2	76.1	200.7	34.9	48.9	5.6

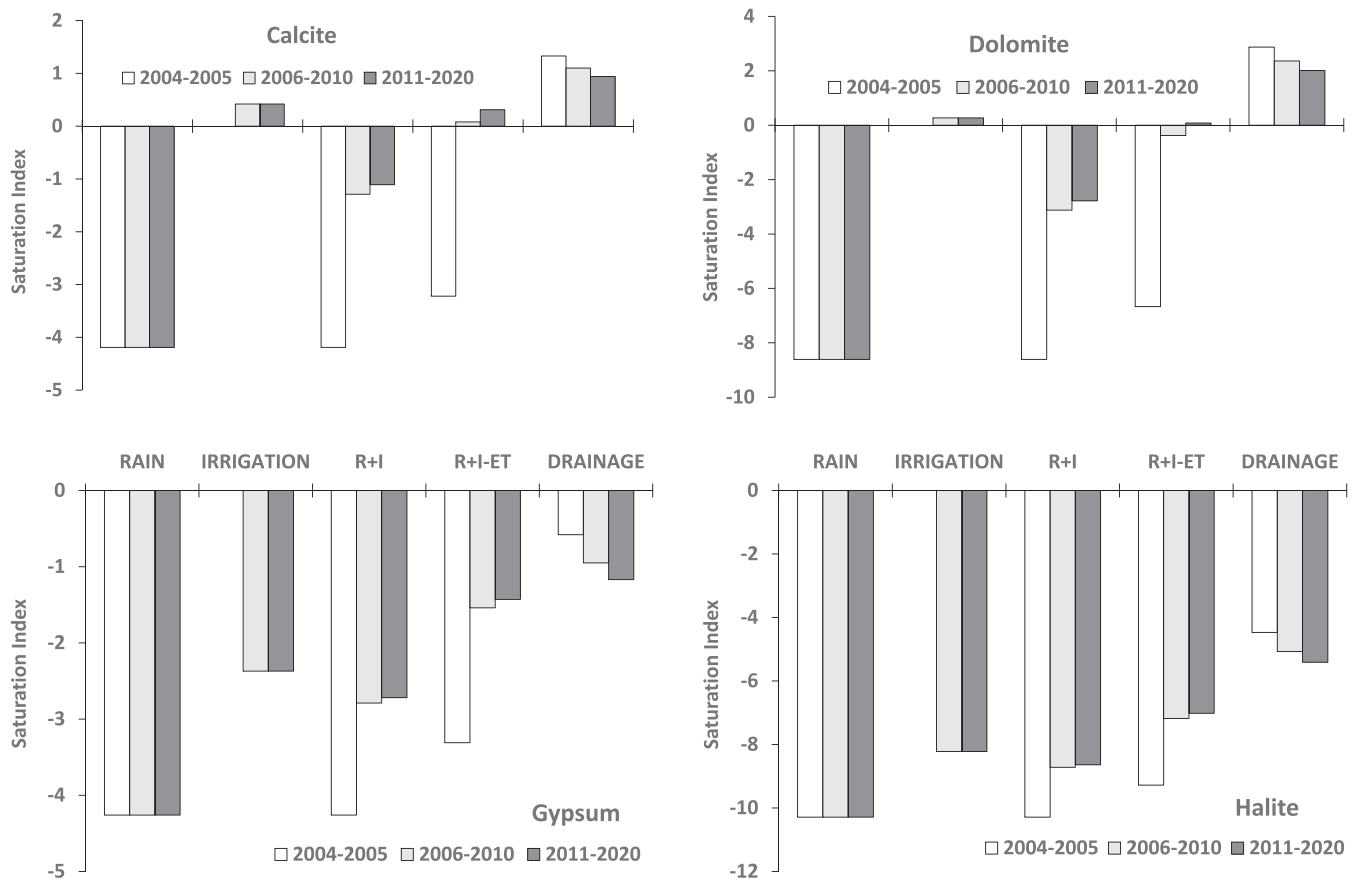


Fig. 5. Saturation indices for rainwater (R), irrigation (I), mixture of both (R + I), mixture minus evapotranspired water (R + I-ET), and drainage, concerning calcite, dolomite, gypsum, and halite for the three evaluated periods, initial (2004–2005), transition (2006–2010), and consolidated irrigation (2011–2020).

exported salts and avoiding the salinization of soils with hampered drainage.

The geochemical processes that cause the distribution of salts in the water cannot be reduced to a simple global dissolution of salts but should include combinations of processes that do not necessarily point in

the same direction. The analysis of these processes has been traditionally omitted in studies that focused on quantifying the exported salts in the final drainage flows of irrigated zones and the results obtained herein indicate the crucial and beneficial information that can be obtained from them.

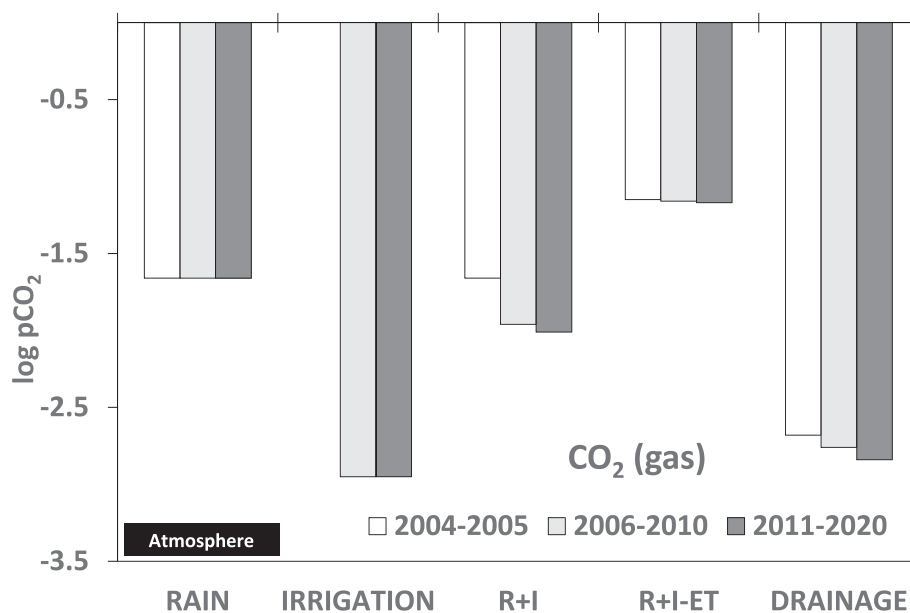


Fig. 6. Partial pressure of CO₂ in rainwater (R), irrigation (I), mixture of both (R + I), mixture minus evapotranspired water (R + I-ET), and drainage, concerning calcite, dolomite, gypsum, and halite for the initial periods (2004–2005), transition (2006–2010), and consolidated irrigation (2011–2020).

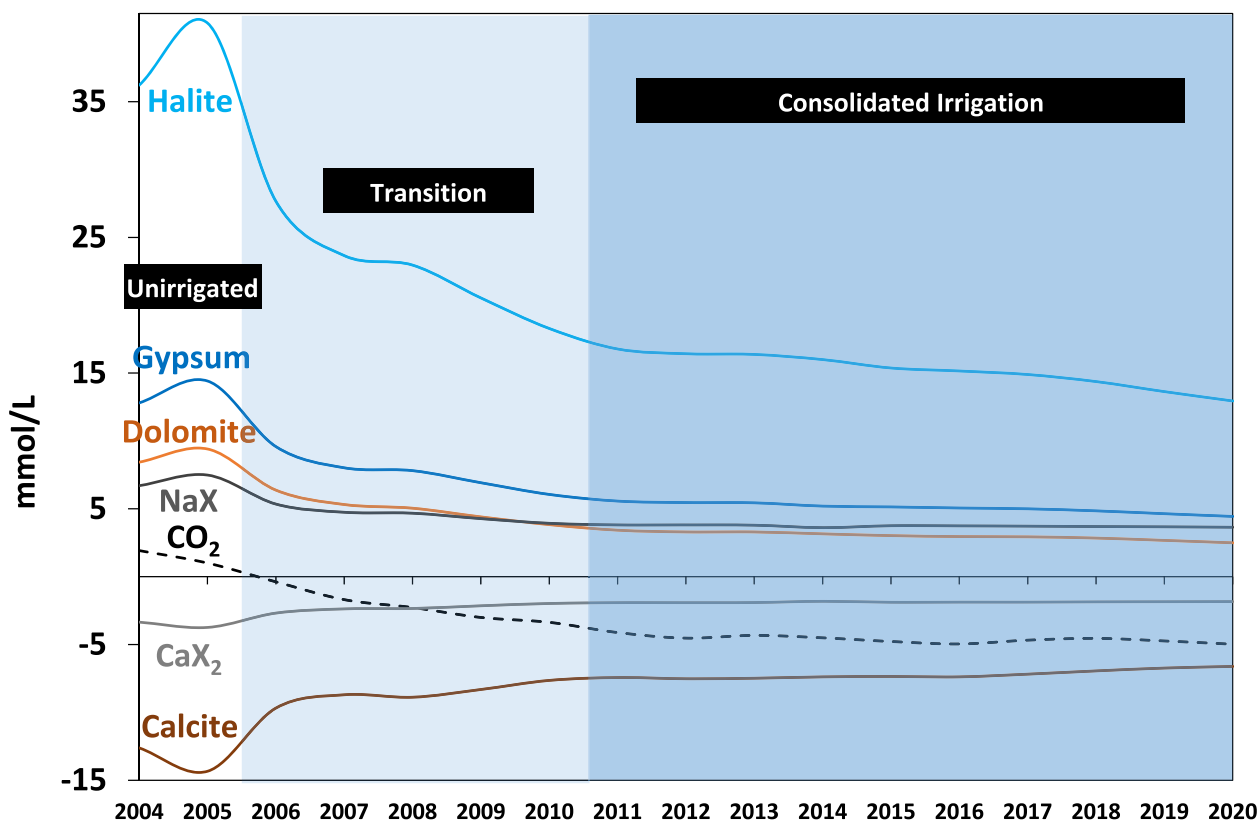


Fig. 7. Mass transfers (positive values indicate dissolution, negative values indicate precipitation) required to justify the composition of the waters of the Lerma gully due to the corresponding mixture of rainwater/irrigation and evapotranspiration.

Finally, monitoring the environmental impact of irrigated zones should be carried out in the long term and continuously, to analyze its evolution and possible effects in real-time. Salinity studies are recommended to go beyond quantifying the mass of exported salts and include the geochemical processes for an improved agroenvironmental diagnosis, such as the one presented herein.

CRediT authorship contribution statement

Jesús Causapé: Conceptualization, Methodology, Formal Analysis, Investigation, Writing – Original Draft, Visualization, Supervision, Project Administrator.

Luis Auqué: Conceptualization, Methodology, Resources, Data Curation, Writing – Review and Editing.

Ma José Gimeno: Conceptualization, Methodology, Resources, Data Curation, Writing – Review and Editing.

Funding

This study was possible thanks to Project AgroSOS (PID2019-108057RB-I00) funding by the Ministry of Science and Innovation – Feder EU Funds.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used is confidential.

References

- Causapé, J., 2009. Agro-environmental evaluation of irrigation land. II: pollution induced by Bardenas Irrigation District (Spain). *Agric. Water Manag.* 96 (2), 188–194. <https://doi.org/10.1016/j.agwat.2008.09.004>.
- Causapé, J., Auqué, L., Gimeno, M.J., Mandado, J., Quílez, D., Aragüés, R., 2004. Irrigation effects on the salinity of the Arba and Riguel rivers (Spain): present diagnosis and expected evolution using geochemical models. *Environ. Geol.* 45 (5), 703–715. <https://doi.org/10.1007/s00254-003-0927-6>.
- Causapé, J., Gimeno, M.J., Auqué, L., 2023. Hydrosaline balance evolution of an irrigated zone: the case of Lerma (Spain, 2004-2020). *Sci. Total Environ.* <https://doi.org/10.1016/j.scitotenv.2023.166996> (In review).
- García-Garizábal, I., Abrahão, R., Causapé, J., 2012. Irrigation management and pollution by salts and nitrate: floods vs pressurized system. *ITEA-Información Técnica Económica Agraria* 108 (4), 482–500.
- García-Garizábal, I., Gimeno, M.J., Auqué, L., Causapé, J., 2014. Salinity contamination response to changes in irrigation management. Application of geochemical codes. *Span. J. Agric. Res.* 12 (2), 376–387. <https://doi.org/10.5424/sjar/2014122-4694>.
- Jiménez-Aguirre, M.T., Isidoro, D., 2018. Hydrosaline balance in and nitrogen loads from an irrigation district before and after modernization. *Agric. Water Manag.* 208, 163–175.
- 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. *Sci. Total Environ.* 502, 330–343. <https://doi.org/10.1016/j.scitotenv.2014.09.041>.
- Parkhurst, D.L., Appelo, C.A.J., 2013. Description of input and examples for PHREEQC version 3. A computer program for speciation, batch reaction, one dimensional transport, and inverse geochemical calculations. In: *Techniques and Methods (U.S. Geological Survey, Ed.)*, Book 6, Chap. A43. U.S.
- Zhu, C., Anderson, G., 2002. *Environmental Applications of Geochemical Modeling*. Cambridge University Press (284 pp.).