Drainage water quality and end-member identification in La Violada irrigation district (Spain)

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Abstract

The identification of the different components in a water course is required to individualize and assess the actual contribution of irrigated agriculture to the pollution of the water course. This paper aimed at identifying and assessing the composition of the end-members in La Violada irrigation district (VID) and establishing a statistical procedure to reduce the sampling effort needed to establish drainage water quality. The quality of irrigation water, groundwater, and irrigated-land drainage water in VID was monitored during three hydrologic years to identify the components of flow in La Violada Gully, the natural exit course of VID. A network of sampling points in the secondary ditches and main drains of VID allowed identifying and separating those collecting irrigated-land drainage waters from those conveying high proportions of irrigation waters. Three end-member flows were identified in La Violada Gully during the irrigation season: (a) irrigation water arising from tail-waters, leakages and spills from the irrigation canals, very low in salts; (b) groundwater originating from the non-irrigated upper reaches of La Violada Gully watershed, high in Cl^- and Na^+; and (c) VID drainage water, high in SO_4^{2-} and Ca^{2+}. The overall VID drainage water quality was accurately assessed through a simplified sampling scheme of only four sampling points that produced low errors of 0.1 dS/m for EC and 0.1 $mmol_c/L$ for Cl^-. The separation of La Violada Gully flow in these three components is essential for estimating the actual contribution of irrigation in VID to the salt and nitrogen loads in La Violada Gully.

Keywords

Drainage, irrigation, water quality, salinity, end-member, Ebro River Basin

1. Introduction

Irrigated agriculture has increased crop's productivity in arid and semiarid areas of the world, but the irrigation return flows (IRF) are a major non-point contributor to the pollution of surface- and ground-water bodies (Aragüés and Tanji, 2003). Irrigation return flows consist of drainage waters, tail-waters from the irrigated land (runoff), and waters reaching the drainage network directly from the irrigation ditches (operational spills, gate leakage and canal seepage). The total flow in the drainage collectors of an irrigation system results from the contribution of these IRF's components plus other intercepted surface and groundwater lateral flows.

Diffuse pollution due to IRF's (both drainage and surface flows) is difficult to individualize from other natural or man-made contributions when it is part of the multi-component flow in a water course. Hydrograph separation techniques (originally intended to estimate the proportion of direct runoff and base flows in stream waters) consist in the quantification of the different flow components in a water course. Pinder and Jones (1969) used the differential chemical compositions of these flows to estimate their relative contributions to the overall stream flow (mixing model). In general, the contribution of *N* flow components to the total flow can be assessed from the mass balance equations for water and *N-1* conservative solutes, provided that the flows have different concentrations of the selected solutes (Durand and Juan Torres, 1996). The End Member Mixing Analysis assumes that the stream flow is composed of several contributing end-member flows of different chemical composition that may be sampled independently (Christophersen et al., 1990). Elsenbeer et al. (1995) discuss the main assumptions regarding the composition of the mixing flows, namely, that the tracers used in the separation are conservative and that the different tracer concentrations within a flow source are fairly uniform during the mixing event. EMMA has been successfully used in instances where the main flowpaths were known and the different flows could be sampled, such as in forested catchments (Katsuyama et al., 2001; Mulholland, 1993), agricultural catchments (Durand and Juan Torres, 1996) and tropical (Elsenbeer et al., 1995) and semi-arid (Sandström, 1996) environments.

This paper is part of an integrated work aimed at quantifying the salt and nitrogen exports from La Violada irrigation district (VID) in North East Spain. Since La Violada Gully, the natural outlet of VID drainage waters, also collects tail waters, leakages and spills from the irrigation canals, as well as lateral groundwater inflows originating from the non-irrigated upper reaches of the Gully's catchment, the proper adscription of the pollution solely induced by VID implies the identification and isolation of the different end-members contributing to the overall flow in La Violada Gully. Since the geologic features of La Violada catchment provide ground waters and drainage waters with distinct chemical compositions, the EMMA is a useful tool to quantify the different flow components in the gully. The results of that separation in 1995 and 1996 are discussed by Isidoro et al. (2006a). This paper expands on the identification of the end-members and presents a method to reduce the sampling effort necessary to establish VID drainage water quality. Reducing the amount of sampling for the EMMA will help the monitoring of VID required to assess the impact of the changes in the irrigation system currently taking place in VID on the flow paths in VID and the overall water quality in La Violada Gully.

Thus, this work focuses on (a) the chemical characterization of VID drainage waters; (b) the individualization of the end-members contributing to La Violada Gully flow; and (c) establishing a simplified sampling scheme that a allows for determining the quality of VID drainage waters from a reduced number of samples and that could be applied to other areas. The analysis is focused mainly on the irrigation season because our goal is to provide means to estimate the contribution of VID drainage waters to the salt and nitrogen loads in the Gully that take place mainly during the irrigation season.

2. Description of the study area

La Violada Gully is located in the middle Ebro River Basin in NE Spain (42º 01' N - 0º 35' W) (Fig. 1). The climate is dry subhumid and mesothermic, with mean annual values (period 1965-1998) of 469 mm (precipitation-P), 13.3ºC (temperature-T) and 1124 mm (Hargreaves-ETo). La Violada Gully drains 19637 ha upstream of the D-14 gauging station (Figure 1). The upper, dry-land reach of the watershed is used for winter crops (mainly wheat) and rangeland, whereas the lower reach comprises La Violada Irrigation District (VID), delimited by the Monegros (NE), La Violada (W) and Santa Quiteria (S) canals, and the D-14 Gully station (SW) (Fig. 1). VID has 3866 ha irrigated land (mean value of the study years) out of 5282 ha. The rest are non-irrigated agricultural lands (1109 ha), rangelands (166 ha), pine tree forests (109 ha) and non-productive lands (307 ha). Irrigation water is diverted from the Gállego River that flows from the Pyrenees, and presents high quality for irrigation (low salinity and sodicity).

The drainage network of VID consists of a dense net of secondary open ditches flowing into the main Valsalada and Artasona ditches that join upstream of gauging station D-14 to conform La Violada Gully. Three natural gullies (Las Pilas, Valdepozos, and Azud) drain the upper dry-land reaches of the watershed and flow under the Monegros Canal into the drainage network (Fig. 1).

The upper reaches of the basin upstream of Los Monegros Canal consist mainly of Tertiary calcareous rocks and clay deposits; the heights to the West and South of VID are composed mainly of tabular gypsum rocks; and the irrigated area consists mainly of Quaternary alluvial and colluvial deposits (ITGE, 1995). In the North-East of VID these deposits are rocky glacis and alluvial fans dominated by calcareous conglomerates, whereas gypsiferous colluvial deposits are found close to the W and S heights. The bottom of the valleys along the Artasona and Valsalada ditches are formed of alluvial silt, clay and gravel deposits, generally with limiting drainage conditions (Fig. 2).

The clays underlying the watershed are fairly impervious, preventing percolation to deeper regional aquifers and making the basin very appropriate for mass balance studies (Faci et al., 1985). Thus, groundwater flows take place mainly down the quaternary fills along the valleys of the main gullies. The boundary between the mainly calcareous upper La Violada basin and the lower basin (Quaternary deposits and Tertiary gypsum) runs roughly along Los Monegros canal (Fig. 2). The high gypsum (> 3%) and calcite (> 30%) contents in the parent materials and soils of VID provide flows relatively high in SO_4^{2-} and Ca^{2+}, whereas the high limestone, marl and clay deposits in the upper watershed provide flows relatively high in Cl^- and Na^+. In addition, low-salinity (EC = 0.38 dS/m) irrigation water is incorporated to the drainage network as tail-water and spills from the irrigation ditches and as canal leakage and direct releases from the gates of the Monegros Canal over the natural gullies (Fig. 2).

3. Materials and methods

A network of 31 sampling points was established to characterize the quality of VID waters draining into La Violada Gully upstream of D-14 (Fig. 1). The network includes (1) the outlets of 22 secondary drains (labelled D or I if draining to Valsalada or Artasona ditches, respectively), (2) five sampling points along the Valsalada ditch (from head to end: D-1, D-10, D-11, D-12, and D-13), (3) one sampling point at the end of Artasona ditch (I-9), (4) the VID outlet (D-14), (5) Los Monegros Canal (CMO), and

(6) the F3C (Fuente de los Tres Caños) spring that conveys the groundwater flows from the upper reaches of the watershed.

Network water sampling was performed on 41 dates from December 1994 to March 1997, approximately once a month during the non-irrigation season (NIS, October to March) and fortnightly during the irrigation season (IS, April to September). All samples were analysed for electrical conductivity (EC, dS/m 25ºC), chloride (Cl^-), sulphate (SO_4^{2-}) and nitrate (NO_3^-) concentrations.

In addition, the samples of 11 of these surveying dates (6 dates in the NIS and 5 dates in the IS of the hydrologic years 1994-95 and 1995-96) were also analysed for calcium (Ca^{2+}), magnesium (Mg^{2+}) and sodium (Na^+); HCO_3^- was estimated as the difference between cations and anions in $mmol_c$/L. The Total Dissolved Solids (TDS, mg/L) in these samples were calculated as the sum of all ions in mg/L.

The EC was measured with a Radiometer A/S CDM83 conductivity meter, Cl^-, SO_4^{2-} and NO_3^- with a Dionex-2000isp ion chromatograph, and Ca^{2+}, Mg^{2+} and Na^+ with a Perkin-Elmer 3030 atomic absorption spectrophotometer. The quality of VID drainage waters was studied with the data of the 11 sampling dates with full records of major cations and anions and EC. A few water samples showing a clear dilution (EC much lower than the mean drain EC) were excluded from this analysis. The drain waters were characterized by their ionic composition and grouped through cluster analysis to separate those collecting essentially irrigated-land drainage waters, which were used to define the quality of this end-member, from those receiving also irrigation water.

Three end-member flows in La Violada Gully were identified from the observed changes in the composition of La Violada Gully water (D-14) and the composition of the water samples in the area (CMO, VID drainage network and F3C): (1) irrigation waters (tail waters, leakages and spills from irrigation canals); (2) drainage waters from VID; and (3) groundwater inflows from the upper reaches of the watershed.

The EC and Cl^- were primarily selected as variables for the EMMA because they were quite different in each end-member among the variables sampled along the study period (EC, Cl^-, SO_4^{2-} and NO_3^-; from December 2004 to March 2007). Although EC is not a conservative parameter, it was selected as an EMMA variable because it has been used successfully for hydrograph separation (Matsubayashi et al., 1993) and had the most complete record. Cl^- was preferred as an EMMA variable over SO_4^{2-} and NO_3^- because of its lower correlation with EC in D-14, its lower variability in the three flow components, and its lower measurement uncertainty. Also, in this gypsum-rich environment EC is well correlated to SO_4^{2-}, preventing their use together for the EMMA; and NO_3^- showed a higher temporal variability (both in F3C and drainage water) induced by fertilization which made the EMMA results more sensitive to the sampling date.

3.1. Statistical analysis

Factor analysis (FA) was performed on the standardized Ca^{2+}, Mg^{2+}, Na^+, Cl^-, SO_4^{2-}, and NO_3^- concentrations by varimax rotation of the principal components (PC) solution (Harman, 1976). The observations used in this analysis were the average concentrations of the 11 sampling dates in 27 sampling points: CMO, F3C and 25 ditches (22 secondary drains plus the head (D-1) and end (D-12) points of Valsalada Ditch and the I-9 end point of Artasona Ditch).

The 25 drainage sampling points were clustered using the first three PC's as variables, the Euclidean distance between observations and the Ward clustering method (Dunn and Everitt, 1982). The first three PC's were not standardized, so that a given difference in the PC-1 (salinity) had a greater influence in the classification than the same difference in PC-2 and PC-3. In this way, the drains were classified according to their total salinity (PC-1) and not only to their ion concentrations. Differences in EC, SAR, TDS/EC ratio, Cl^- and NO_3^- between clusters were established with the Duncan multiple range test.

Because EMMA requires a quantification of the mean EC and Cl^- of the overall VID drainage waters, a procedure was devised to estimate these values from a reduced number of sampling points rather than sampling of the whole drainage network. For this purpose, all combinations of (a) any 4 sampling points taken from the 22 secondary ditches; or (b) one of the sampling points along the main ditches (i.e. D-1, D-10, D-11, D-12, D-13 and I-9) with any 3 of the secondary ditches were tested. Combinations of less than 4 sampling points were rejected because the influence of lost data upon their means was too high.

The mean EC and Cl^- of each 4-point combination (k) for each of the 41 sampling dates (t) were calculated (X^k_t, where X stands for either EC or Cl^-). The X^k_t estimates were compared to the mean EC and Cl^- of the 19 secondary ditches (X_t) by means of the average estimated bias [$\hat{\beta}(X^k)$] (Eq. 1) and the standard deviation [$\hat{\sigma}(X^k)$] (Eq 2) of the differences ($X^k{}_t$ -X_t):

$$\hat{\beta}(X^k) = \frac{1}{41}\sum_{t=1}^{41}\left(X^k{}_t - X_t\right) \quad [1]$$

$$\hat{\sigma}(X^k) = \sqrt{\frac{1}{40}\sum_{t=1}^{41}\left(X^k{}_t - X_t\right)^2} \quad [2]$$

The best *(k)* estimator should have the maximum accuracy: maximum precision (i.e. minimum $\hat{\sigma}(X^k)$) and minimum bias (i.e. minimum $\hat{\beta}(X^k)$) for both EC and Cl^-. For each variable, the 4-point estimators were ordered by increasing $\hat{\sigma}(X^k)$, so that the most precise estimates were written first. The estimators that ranked among the lowest $\hat{\sigma}(X^k)$ for both variables were selected as possible best estimators. All of them had a bias significantly different from 0 ($P < 0.05$; t-test for paired samples) that needed correction except one Cl^- estimator (Fig. 3).

In order to remove the bias from the $X^k{}_t$ estimates, the linear regressions between the differences ($X^k{}_t$ - X_t) and the $X^k{}_t$ estimates were calculated [$(X^k{}_t - X_t) = a^k + b^k \cdot X^k{}_t$] for each of the best estimators and used to obtain the unbiased estimators ($\hat{X}^k{}_t$) by means of Eq. 3. When the regressions were not significant, the unbiased EC and Cl^- ($\hat{X}^k{}_t$) were estimated subtracting the mean bias for that estimate (Eq. 4):

$$\hat{X}^k{}_t = X^k{}_t - (a_k + b_k \cdot X^k{}_t) \quad [3]$$

$$\hat{X}^k{}_t = X^k{}_t - \hat{\beta}^k \quad [4]$$

The bias-corrected estimates for both variables were evaluated in terms of the root mean square error (RMSE) and the mean absolute error (MAE) of ($\hat{X}^k{}_t - X_t$).

4. Results and discussion

4.1. Quality of VID drainage waters

The factor analysis performed on the average Ca^{2+}, Mg^{2+}, Na^+, Cl^-, SO_4^{2-}, and NO_3^- concentrations measured in irrigation water, groundwater inflows and the 25 points sampled in the VID drainage network yielded three factors that accounted for 97% of the total variance. Factor 1 was related to Ca^{2+}, Mg^{2+} and SO_4^{2-} (i.e., gypsum contribution); Factor 2, to Na^+ and Cl^- (i.e., halite contribution); and Factor 3, to NO_3^- (Table 1).

The 25 VID drainage sampling points were grouped into six clusters shown in Table 2 with their mean EC, sodium adsorption ratio (SAR), TDS/EC ratio, and Cl^- and NO_3^- concentrations. The areal distribution of the drains pertaining to each cluster is shown in Fig. 2. Cluster 1 includes most of the drains from the upper reaches of Valsalada Ditch and its end point. These drains are relatively high in EC and low in SAR. Cluster 2 includes the three drains receiving water from Los Monegros Canal. These diluted drains are the lowest in EC and Cl^-. Cluster 3 includes only drain D-3, the highest in SAR, Cl^- and NO_3^-. Clusters 4 and 5 include the most saline drains in VID, with mean EC values slightly below 3 dS/m. Cluster 4 incorporates the drains from the lower right Valsalada Ditch that drain soils developed on colluvial gypsiferous deposits, and drain D-17 that drains the south area of the district surrounded by gypsum heights (Fig. 2). Cluster 5 includes most drains from the upper Artasona Ditch, drain D-23 in the lower right Valsalada Ditch, and drain D-18 in the central area of the district. Cluster 5 differs from cluster 4 mainly in its higher NO_3^- (Table 2). Cluster 6 includes the less saline drains of VID after those of cluster 2: the Artasona Ditch (I-9), several secondary ditches in the central and upper Artasona, and drain D-19 in the upper Valsalada area. (Fig. 2).

The TDS/EC ratio varies with the ionic composition of the water. Only the diluted drains of cluster 2 show a TDS/EC close to 640 $(mg/L)\cdot(dS/m)^{-1}$, the usual ratio given by USSL (1954). The rest of clusters, except cluster 3 high in Na^+ and Cl^-, show higher TDS/EC ratios due to the dominance of divalent ions that form uncharged ion pairs.

The classification of these drains is presented in the graph of the two first factors along with CMO and F3C (Fig. 4). The six clusters show a greater scattering in Factor 1 (Ca^{2+}, Mg^{2+} and SO_4^{2-}) than in Factor 2 (Na^+, Cl^-). The three diluted drains of cluster 2 are the closest to the irrigation water (CMO). Cluster 3 (drain D-3) and groundwater (F3C) show the highest values of Factor 2, whereas the rest of clusters are more homogeneous and with Factor 2 values close to zero.

The ratios $(Ca^{2+}+Mg^{2+})/SO_4^{2-}$ and Cl^-/SO_4^{2-} versus EC are presented in Fig. 5. All the drains (except for the diluted drains of cluster 2) show $(Ca^{2+}+Mg^{2+})/SO_4^{2-}$ ratios close to one, suggesting that most of the sulphates derived from the dissolution of calcium and magnesium sulphates. In contrast, the irrigation water (CMO) has the highest ratio (3.86) (i.e., calcite-dominated waters), whereas groundwater inflow (F3C) is the only sample with a ratio lower than one (0.86) (Fig. 5 a). The Cl^-/SO_4^{2-} ratio is lower than 0.1 in all drains except D-3 and cluster 2 (Fig. 5 b), indicating that salinity is dominated by sulphates rather than chlorides. On the other hand, this ratio is close or higher than 0.2 in the drains of cluster 2, drain D-3 and groundwater inflow (F3C), and increases up to a value of 0.57 for the irrigation water (CMO). All the drains, except clusters 2 and 3 are fairly uniform in these ionic ratios.

All the analyses above (overall salinity, cluster and TDS/EC or ionic ratios) point to two types of waters in the drains of VID: (a) drains receiving relatively high proportions of irrigation water (cluster 2, with lower EC and TDS/EC ratio and higher Cl^-/SO_4^{2-}) and (b) drains that collect basically VID drainage water (clusters 1, 3, 4, 5, and 6). Drain D-3 (cluster 3) is also somewhat different from other drainage waters, but the difference can not be attributed to a contribution of canal water because, unlike cluster 2, its composition is not closer to CMO than the other drains. Thus, in each of the 41 sampling dates, the overall VID drainage water quality was calculated as the mean of all the secondary ditches sampled in that date excluding those that convey canal releases (D-2, I-1, and I-5), clearly identified by the cluster analysis.

Table 3 shows the mean EC, SAR and ion concentrations of the VID drainage waters in the non irrigation (NIS, 6 sampling dates) and the irrigation (IS, 5 sampling dates) seasons. Mean NO_3^- is higher in the IS (0.93 $mmol_c$/L) than in the NIS (0.67 $mmol_c$ /L) due to the high N fertilization inputs to the irrigated crops during the IS (Isidoro, 2006b). Mean EC is somewhat higher in the NIS (2.43 dS/m) than in the IS (2.29 dS/m) due to the higher concentrations of SO_4^{2-}, Na^+ and Mg^{2+} in the NIS. The sodicity hazard of VID drainage waters is very low (mean SAR < 0.6) due to the presence of gypsum deposits in the district.

Figure 6 shows the mean EC and Cl^-, SO_4^{2-} and NO_3^- concentrations measured in the 22 secondary drains of VID along the NIS and IS of the 1995 and 1996 hydrologic years. The mean EC showed a low variability between dates, it was slightly lower in the 1995 NIS, and reached the maximum values in the 1996 NIS. In contrast, the mean

NO_3^- is highly variable along the study period due to fertilization practices (Isidoro et al., 2006b), and the differences between drains within each date (the standard error bars) are the highest of the studied variables. The most stable ion between dates and between drains within each date is SO_4^{2-}, with concentrations in general close to gypsum saturation and slightly higher in NIS than in IS (Table 3). Chloride exhibits a higher variability than SO_4^{2-}, with contrasting results in the NIS and IS of the 1995 and 1996 hydrological years.

4.2. Identification of the end-members

The plot of EC vs. Cl^- for La Violada Gully waters sampled at D-14 during the hydrologic years 1995 and 1996 is presented in Fig. 7, along with the samples of F3C (groundwater inflows), CMO (irrigation water) and the mean VID drainage waters. The samples at D-14 during the IS are grouped between 1.5 dS/m and 2.3 dS/m (EC) and 0.5 $mmol_c$/L and 3.0 $mmol_c$/L (Cl^-). The D-14 samples during the NIS present a higher scattering: the more diluted samples are due to direct canal water releases to the Gully in periods of low flows, whereas the more concentrated samples occur during periods of high base-flows taking place after high rainfall events, when the Gully flow has a greater contribution of high-EC groundwater flows originating in the Violada Gully watershed.

Groundwater inflows (F3C) are consistently higher in EC and Cl^- than D-14 waters in both IS and NIS (Fig. 7). The VID drainage waters are generally higher in EC than the D-14 waters, while they are similar in Cl^- during the IS and can be higher or lower during the NIS. The irrigation waters (CMO) are always the lowest in EC and Cl^- (Fig. 7). This suggests that during the IS La Violada Gully flow is derived mainly from the mixing of irrigation and drainage waters, whereas during the NIS the higher-Cl^- D-14 waters are due to a higher contribution of high-Cl^- groundwater inflows and the lower-Cl^- D-14 waters derive from the mixing of irrigation and drainage water.

This end-member identification is confirmed by the evolution of EC and Cl^- in these components along the study period (Fig. 8). The EC in La Violada Gully waters at D-14 may be explained quite consistently during the IS through the mixing of irrigation and VID drainage waters. However, during the NIS the mixing of these two components cannot account for the Cl^- concentration in La Violada Gully (Fig. 8), since they are higher than Cl^- in the irrigation and VID drainage waters. Groundwater inflows high in

Cl^- are identified as the third end-member component of La Violada Gully flows that explain the higher Cl^- in D-14 waters. The distinct troughs in EC (also present, but not so conspicuous in Cl^-) during the NIS reflect episodes of high canal releases of lower salinity pointing to an important contribution of diluted canal water especially during the NIS (Fig. 8).

Surface runoff water from the upper dry-land area of La Violada Gully watershed may also contribute to the flow in the Gully, especially after heavy rainfall events in winter (i.e., in the NIS). However, this contribution was irrelevant during the IS (Isidoro et al., 2006a). Hence, three end-member flows are identified as the contributing sources to La Violada Gully flow during the irrigation season: irrigation water from Los Monegros Canal, groundwater inflows, and VID drainage waters. The main chemical characteristics of these end-members are presented in Table 4. The irrigation water is very low in salinity (mean EC = 0.38 dS/m) and sodicity (SAR = 0.43 $(mmolc/L)^{0.5}$). Groundwater and VID drainage water are relatively similar in salinity (mean EC = 2.7 and 2.4 dS/m, respectively), but quite different in their ionic compositions. Thus, VID drainage water was higher in Ca^{2+} and SO_4^{2-} and much lower in Cl^- and Na^+ than groundwater (Table 4). These differential ionic compositions are the basis for the EMMA.

4.3. Simplification of the sampling procedure for the overall characterization of VID drainage waters

Out of the 17 EC and Cl^- estimators analyzed using different combinations of VID drainage waters, 5 estimators with four sampling points were selected on the basis of their lowest root mean square errors (RMSE) and mean absolute errors (MAE) (Table 5). The best estimator, ranked first for both EC and Cl^-, is the combination of sampling points D-17 and D-29 (both in the Valsalada Ditch, cluster 4) and I-3 and I-7 (both in the Artasona Ditch, cluster 6), both in terms of RMSE and MAE. The next three best estimators include the drains D-20, D-29 and I-7 and one sampling point along the Valsalada Ditch (either D-10, D-12 or D-13) pointing to the stability of these sampling points as estimators of the mean EC and Cl^- in VID drainage waters. The fifth best estimator is formed by drains D-13, D-4, D-32 and I-7. However, RMSE and MAE of these estimators are in all cases 10% higher than those for the best estimator.

For the best four-point estimator, the EC estimate was corrected by regression and the Cl^- estimate by addition of the mean estimated bias because the regression was not significant ($P > 0.05$) (Fig. 9). This estimator enabled the determination of EC and Cl^- individual estimates of the mean VID drainage water (EC_t and Cl_t) with an expected error lower than 0.1 dS/m and 0.1 $mmol_c$/L, respectively, from the mean of the 4 point samples (D-17, D-29, I-3, and I-7) in that date [$EC^k{}_t$ and $Cl^k{}_t$] through the equations:

$$\begin{aligned} EC_t\,(dS/m) &= EC^k{}_t - \left[0.384 \cdot EC^k{}_t - 1.039\right] \\ Cl_t &= Cl^k{}_t + 0.112 \end{aligned} \qquad [5]$$

The use of this approach allows the determination of EC and Cl^- of VID drainage waters from only four sampling points, reducing the sampling effort needed to characterize this end-member. However, other ion concentrations of VID drainage waters are not necessarily well represented by the average of these four sampling points. The procedure presented is general enough to be applied to other areas provided that there is a long initial record of data to compare the means from the reduced sets of drains with the overall mean for each parameter of interest. The reduced set of drains need not be the same for each parameter (i.e., in our case the selection of drains for EC could be different from that for Cl^-). When so, either a set with very low bias in all the selected parameters should be chosen; or different sets could be chosen for several different parameters (or even for each parameter).

5. Conclusions and future research needs

La Violada Gully flow results from the mixing of three end-members: canal irrigation waters, Violada Irrigation District (VID) drainage waters, and groundwater inflows. These end-members clearly differ in their chemical composition, allowing for their use in the end member mixing analysis. Canal irrigation water is very low in salts (mean EC = 0.38 dS/m), whereas VID drainage water, relatively high in Ca^{2+} and SO_4^{2-}, and groundwater, relatively high in Na^+ and Cl^-, result from the geological environments where they originated

Factor and cluster analyses performed on VID drainage waters, complemented with the study of the Cl^-/SO_4^{2-} and $(Ca^{2+}+Mg^{2+})/SO_4^{2-}$ ionic ratios, identified the drains with substantial contributions of canal water and allowed to select the appropriate drains for characterizing irrigated-land VID drainage waters.

The long records of numerous drainage water sampling points within VID was the basis for identifying the minimum number of drains to be analyzed for an accurate estimation of the mean EC and Cl^- in VID drainage waters in a given date. Thus, a combination of only four drains produced EC and Cl^- errors lower than 0.1 dS/m and 0.1 $mmol_c$/L; reducing the sampling effort needed to characterize VID drainage water adequately.

The two points above involve in-depth study of the drainage ditches (including a greater deal of analytical work); but this study proved necessary (i) To ascertain the ditches that really contribute irrigation drainage water (i.e. to identify the ditches receiving canal releases and seepage) and especially (ii) To establish drainage water quality accurately from a reduced number of samples. In the long run, the simplified sampling scheme proposed reduces the sampling effort (and the analytical burden) considerably, reducing the amount of work necessary and paying for the initial sampling and analytical effort. This procedure for establishing a set of ditches representative for drainage water quality could be applied in other areas to reduce sampling requirements.

The evolution of water quality (EC and Cl^-) in La Violada Gully D-14 monitoring station was the basis for identifying the relative contributions of the three end-members. During the irrigation season (IS), EC and Cl^- in D-14 waters were essentially explained from the mixing of two end-members (low-salinity irrigation waters, and close to gypsum-saturated (VID drainage waters); showing that the gully flow consists mainly of IRF during the IS. During the non-irrigation season (NIS) a third end-member (relatively high Cl^- groundwater inflows) was required to explain the higher Cl^- D-14 waters.

In recent years, VID has been subject to an intensive modernization process consisting in the rebuild of La Violada Canal, the construction of several internal reservoirs, the reuse of drainage waters for irrigation, and the on-course transformation of gravity irrigation into sprinkle irrigation. These actions will modify the hydrology of VID, will change the relative contributions of the identified end-members to the gully flow, and will surely reduce off-site pollution loads.

The continuation of this work will provide insight on these issues and, in particular, on two aspects that need a thorough evaluation in the new scenario: (a) the validity of the proposed 4-point estimator for VID drainage water, for which an intensification of the sampling scheme will be required, and (b) the impact of the reduced seepage derived from the rebuild of La Violada Canal on the actual composition of end-member “canal irrigation water”, and its role as a diluting source for La Violada Gully.

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FIGURE CAPTIONS

Figure 1. Map of La Violada Gully watershed at D-14 and La Violada Irrigation District (VID) delimited by the Monegros, La Violada and Santa Quiteria canals. The secondary drains, the water quality sampling points and the three gullies (Las Pilas, Valdepozos and Azud) entering VID are also shown.

Figure 2. Cluster classification of the 25 secondary drains sampled in VID in relation to the lithology adapted from ITGE (1995).

Figure 3. Bias (b) in the estimates of EC and Cl concentration for the 17 four-point estimators that showed the highest accuracy for both variables. The bars represent one standard error of the estimated bias.

Figure 4. Classification of irrigation water (CMO), groundwater inflows (F3C) and the 25 secondary drains sampled in VID on the graph of the rotated factors. The depicted EC isolines were obtained giving fixed EC values in the regression equations of EC on Factors 1 and 2.

Figure 5. $(Ca^{2+}+Mg^{2+})/SO_4^{2-}$ (a) and Cl^-/SO_4^{2-} (b) ratios versus EC for irrigation water (CMO), groundwater inflows (F3C), and the 25 secondary drains sampled in VID.

Figure 6. Mean EC, Cl^-, SO_4^{2-} and NO_3^- concentrations measured in 22 secondary drains sampled in VID along the irrigation (IS) and non irrigation (NIS) seasons of the 1995 and 1996 hydrologic years. Bars indicate one standard error of the mean.

Figure 7. EC-Cl^- relationships in irrigation water (CMO), groundwater inflows (F3C), mean VID drainage waters (DES), and La Violada Gully waters sampled at D-14 in the irrigation and non irrigation seasons.

Figure 8. EC and Cl^- concentrations measured from December 1994 to April 1997 in irrigation water (CMO), groundwater inflows (F3C), mean irrigated-land drainage waters (DES) and La Violada Gully waters sampled at D-14. The irrigation (IS) and non irrigation (NIS) seasons are also shown.

Figure 9. Relationships between the estimated bias $[b(X^k_t) = X^k_t - X_t]$ and the estimated values $[X^k_t]$ of (a) EC and (b) Cl for the best four-point estimators (secondary drains D17-D29-I3-I7) and method used to remove bias in both variables: regression of $b(EC^k_t)$ upon EC^k_t and subtraction of the mean bias $(E[b(Cl^k_t)])$.

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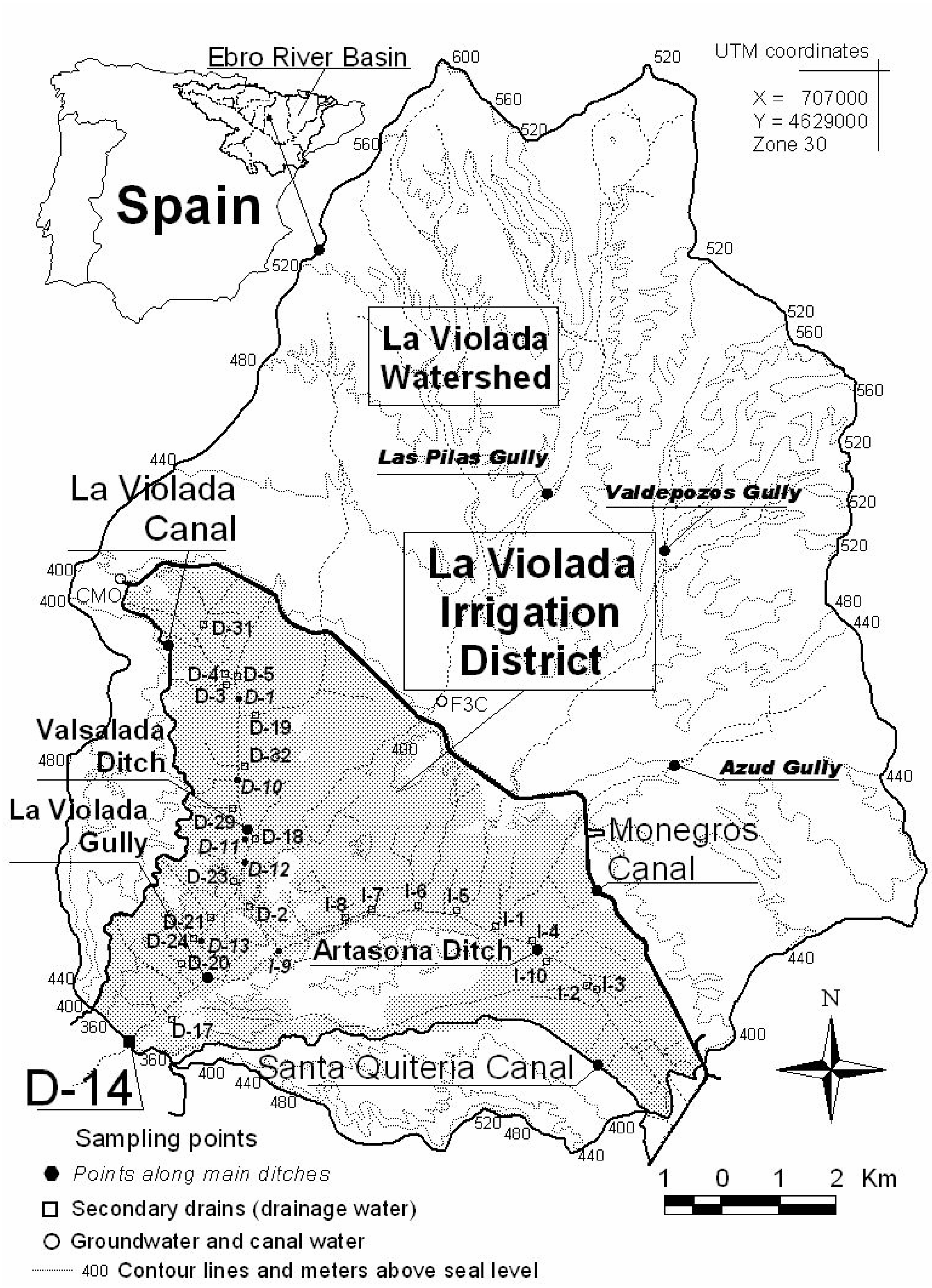
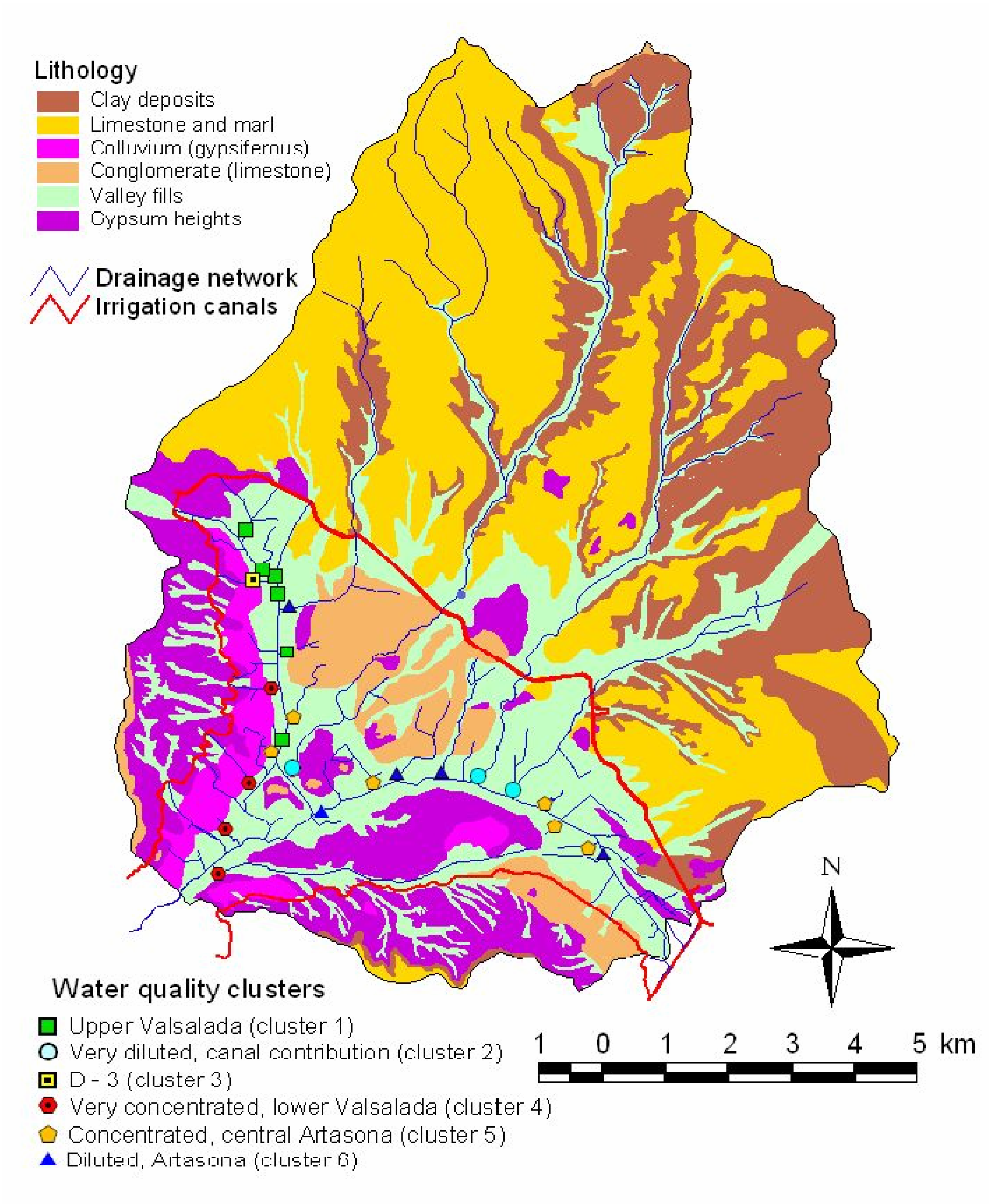
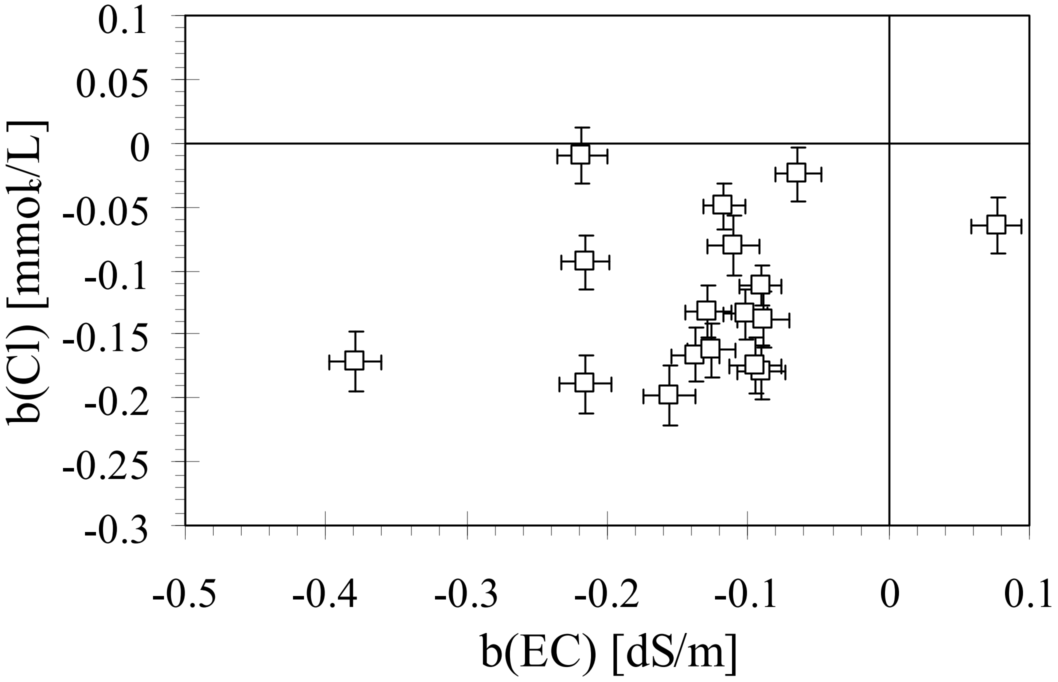
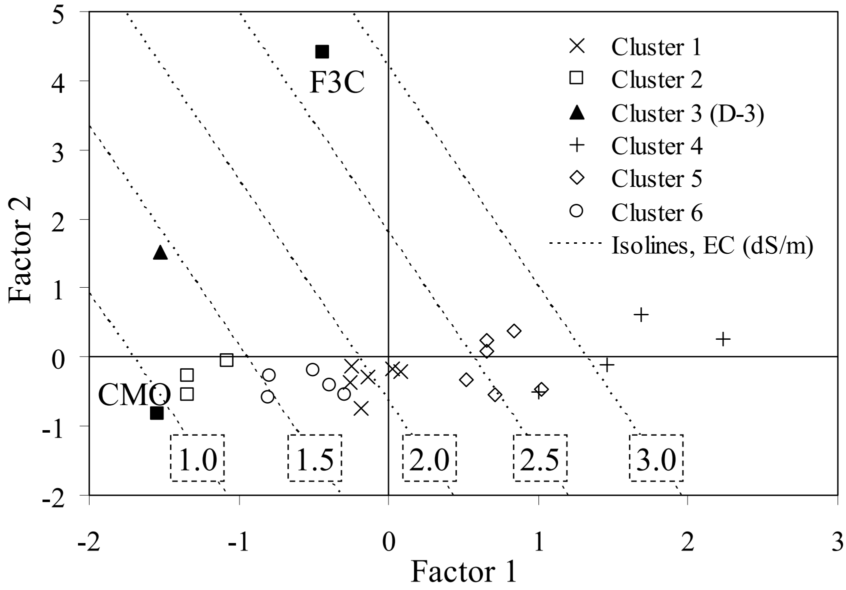


Ebro River Basin
Spain
UTM coordinates
X = 707000
Y = 4629000
Zone 30
La Violada Watershed
Las Pilas Gully
Valdepozos Gully
La Violada Canal
La Violada Irrigation District
CMO
F3C
Valsalada Ditch
La Violada Gully
Azud Gully
Monegros Canal
Artasona Ditch
Santa Quiteria Canal
D-14
N
1 0 1 2 Km
Sampling points
Points along main ditches
Secondary drains (drainage water)
Groundwater and canal water
400 Contour lines and meters above seal level

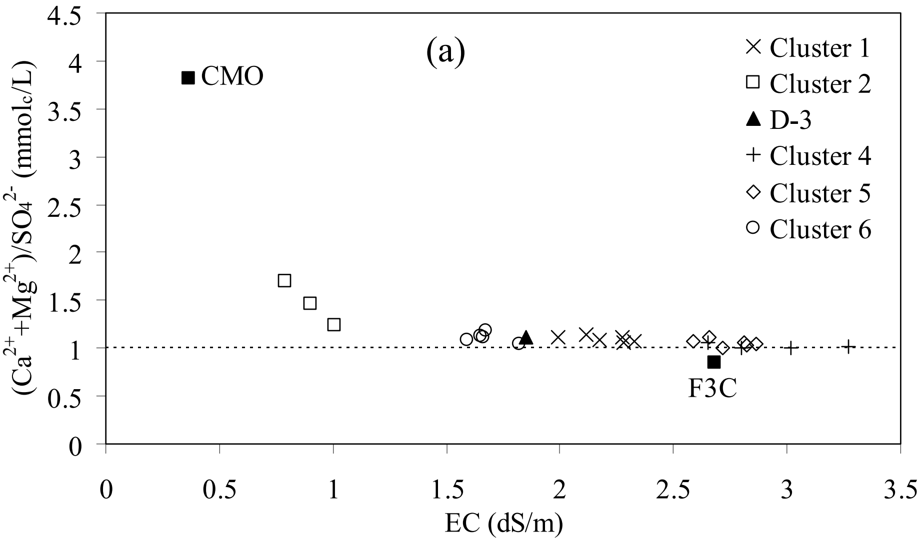

Lithology
Clay deposits
Limestone and marl
Colluvium (gypsiferous)
Conglomerate (limestone)
Valley fills
Gypsum heights
Drainage network
Irrigation canals
N
Water quality clusters
Upper Valsalada (cluster 1)
Very diluted, canal contribution (cluster 2)
D - 3 (cluster 3)
Very concentrated, lower Valsalada (cluster 4)
Concentrated, central Artasona (cluster 5)
Diluted, Artasona (cluster 6)
1 0 1 2 3 4 5 km

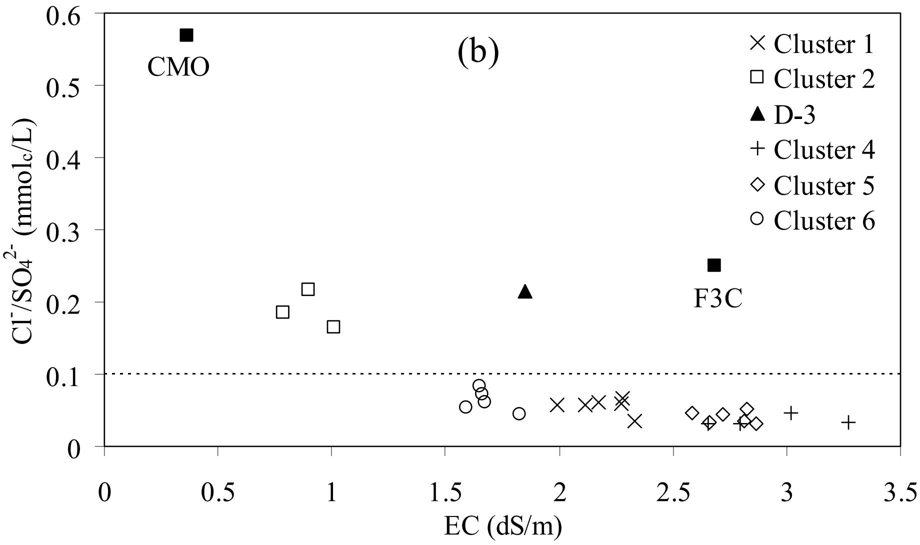


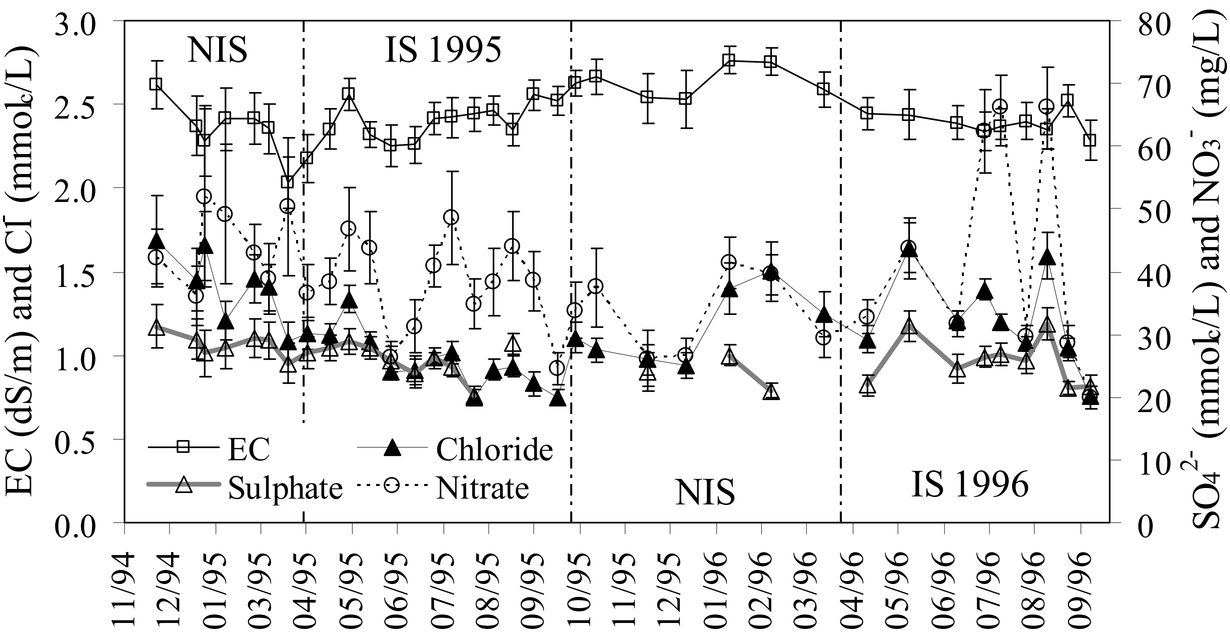
b(Cl) [mmol/L]
0.1
0.05
0
-0.05
-0.1
-0.15
-0.2
-0.25
-0.3
-0.5
-0.4
-0.3
-0.2
-0.1
0
0.1
b(EC) [dS/m]



F3C
CMO
Cluster 1
Cluster 2
Cluster 3 (D-3)
Cluster 4
Cluster 5
Cluster 6
Isolines, EC (dS/m)
1.0
1.5
2.0
2.5
3.0
Factor 2
Factor 1
5
4
3
2
1
0
-1
-2
-2
-1
0
1
2
3


(a)
CMO
F3C
Cluster 1
Cluster 2
D-3
Cluster 4
Cluster 5
Cluster 6
$(Ca^{2+}+Mg^{2+})/SO_4^{2-}$ (mmol$_c$/L)
EC (dS/m)
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5


(b)
CMO
F3C
Cluster 1
Cluster 2
D-3
Cluster 4
Cluster 5
Cluster 6
Cl^-/SO_4^{2-} (mmol$_c$/L)
EC (dS/m)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.5
1
1.5
2
2.5
3
3.5



EC (dS/m) and Cl⁻ (mmolc/L)
SO4 2- (mmolc/L) and NO3 - (mg/L)
NIS
IS 1995
NIS
IS 1996
EC
Chloride
Sulphate
Nitrate
3.0
2.5
2.0
1.5
1.0
0.5
0.0
80
70
60
50
40
30
20
10
0
11/94
12/94
01/95
03/95
04/95
05/95
06/95
07/95
08/95
09/95
10/95
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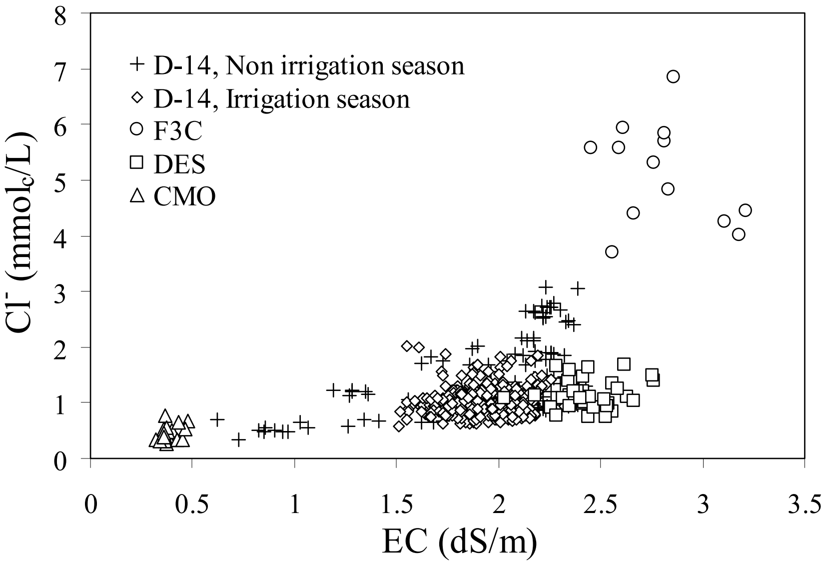
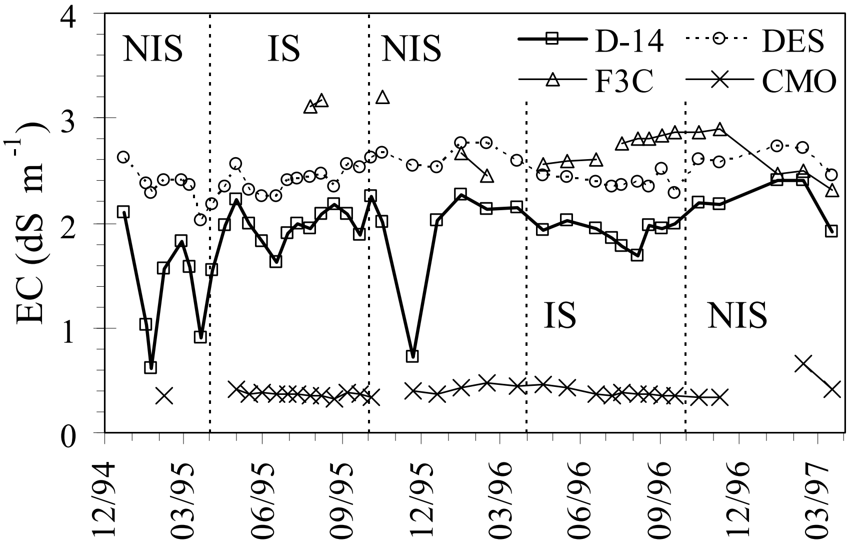
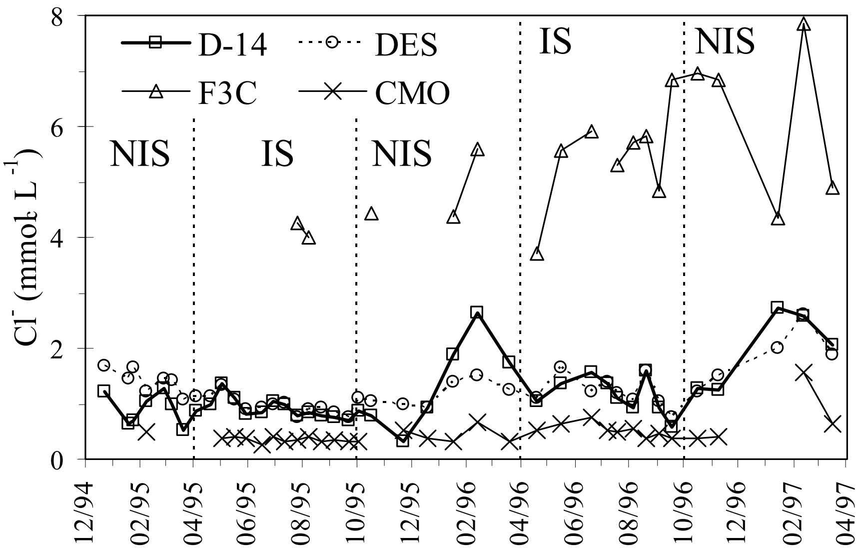
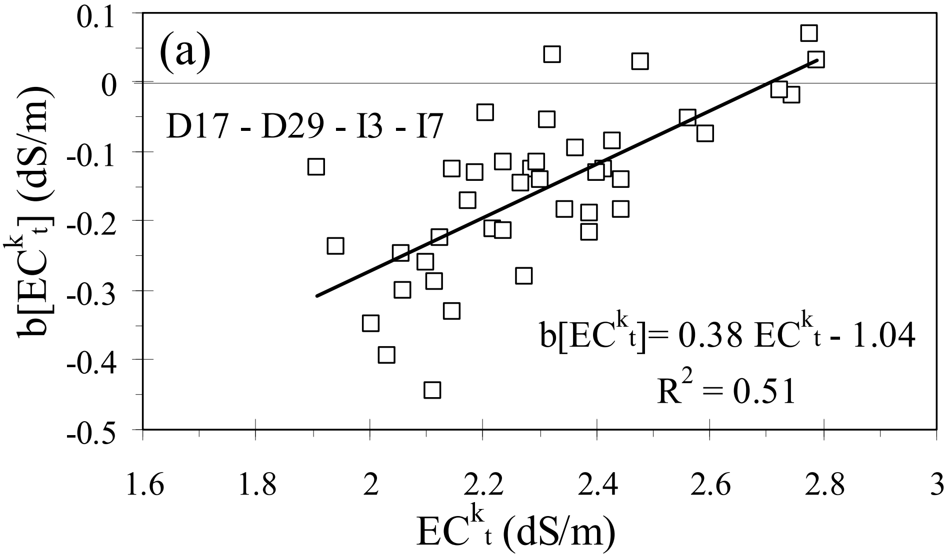
07/96
08/96
09/96



D-14, Non irrigation season
D-14, Irrigation season
F3C
DES
CMO
Cl⁻ (mmol$_c$/L)
EC (dS/m)
0
1
2
3
4
5
6
7
8
0
0.5
1
1.5
2
2.5
3
3.5


NIS
IS
NIS
IS
NIS
D-14
DES
F3C
CMO
EC (dS m-1)
0
1
2
3
4
12/94
03/95
06/95
09/95
12/95
03/96
06/96
09/96
12/96
03/97


D-14
DES
F3C
CMO
NIS
IS
NIS
IS
NIS
Cl- (mmol L-1)
0
2
4
6
8
12/94
02/95
04/95
06/95
08/95
10/95
12/95
02/96
04/96
06/96
08/96
10/96
12/96
02/97
04/97


(a)
D17 - D29 - I3 - I7
b[EC^k_t]= 0.38 EC^k_t - 1.04
R^2 = 0.51
b[EC^k_t] (dS/m)
EC^k_t (dS/m)
0.1
0
-0.1
-0.2
-0.3
-0.4
-0.5
1.6
1.8
2
2.2
2.4
2.6
2.8
3

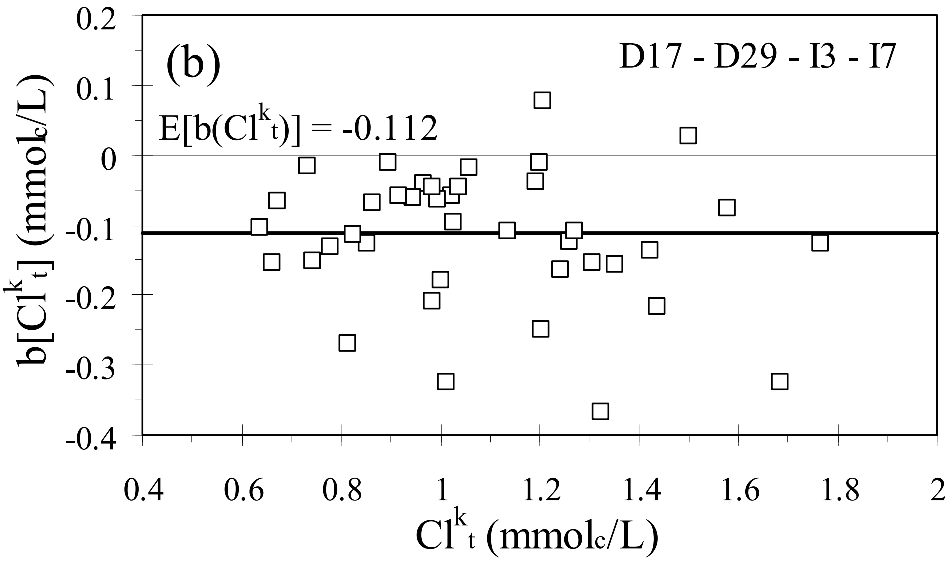

(b)
D17 - D29 - I3 - I7
E[b(Cl^k_t)] = -0.112
b[Cl^k_t] (mmolc/L)
Cl^k_t (mmolc/L)
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2

Table 1. Factor loadings of Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-}, SO_4^{2-} and NO_3^{-} concentrations after the varimax rotation of the principal components. Analysis performed on irrigation water (CMO), groundwater inflows (F3C) and the 25 points sampled in the VID drainage network. Loadings higher than 0.80 are presented in bold.

	Factor 1	Factor 2	Factor 3
Ca^{2+}	**0.8598**	-0.0885	0.4240
Mg^{2+}	**0.9554**	0.0969	0.0637
Na^{+}	0.0719	**0.9909**	0.0520
Cl^{-}	0.0032	**0.9844**	0.1170
SO_4^{2-}	**0.9577**	0.0746	0.2652
NO_3^{-}	0.3308	0.1618	**0.9195**

Table 2. Mean values of EC, SAR, TDS/EC ratio, Cl^- and NO_3^- for the 6 clusters established with the 25 points sampled in the VID drainage network. Within each column, values followed by the same letter do not differ significantly ($P > 0.05$).

Cluster (Drains)	EC (dS/m)	SAR $(mmol_c/L)^{0.5}$	TDS/EC (mg/L)/(dS/m)	Cl^- $(mmol_c/L)$	NO_3^- $(mmol_c/L)$
1. Upper Valsalada Ditch (D-1, D-4, D-5, D-12, D-31, D-32)	2.19 c	0.46 a	841 d	1.36 a	0.76 bc
2. Diluted drains (D-2, I-1, I-5)	0.90 a	0.80 b	637 a	1.04 a	0.25 a
3. D-3	1.85 b	2.08 c	709 b	2.85 b	1.30 d
4. Concentrated I (D-17, D-20, D-21, D-29)	2.94 d	0.61 ab	932 e	1.41 a	0.60 b
5. Concentrated II (D-18, D-23, I-2, I-4, I-8, I-10)	2.74 d	0.60 ab	915 e	1.39 a	1.07 cd
6. Artasona Ditch (D-19, I-3, I-6, I-7, I-9)	1.68 b	0.55 ab	786 c	1.05 a	0.57 ab

Table 3. Mean (± standard error), maximum and minimum values of the variables shown in the first column for the secondary drains sampled in VID along the irrigation (IS) and non irrigation (NIS) seasons of the 1995 and 1996 hydrologic years. Diluted drains (D-2, I-1 and I-5) and D-3 are excluded.

	Non Irrigation Season (NIS)			Irrigation Season (IS)		
	Mean	Max	Min	Mean	Max	Min
EC (dS/m)*	2.43±0.12	3.49	1.56	2.29±0.09	2.88	1.62
Cl^- ($mmol_c$/L)	1.3±0.1	2.0	0.8	1.2±0.0	1.5	0.8
SO_4^{2-} ($mmol_c$/L)*	29.7±2.2	50.9	13.7	26.4±1.4	37.1	16.0
NO_3^- ($mmol_c$/L)*	0.7±0.3	1.3	0.2	0.9±0.3	1.5	0.4
Ca^{2+} ($mmol_c$/L)	20.6±1.1	27.0	11.5	20.2±1.0	28.1	12.4
Na^+ ($mmol_c$/L)*	2.3±0.3	5.2	1.0	1.7±0.1	2.6	1.1
Mg^{2+} ($mmol_c$/L)*	11.0±1.2	25.7	3.6	7.8±0.6	13.4	4.3
SAR [$(mmol_c/L)^{0.5}$]*	0.58±0.05	1.19	0.28	0.47±0.02	0.66	0.28

* Significant differences between IS and NIS ($P < 0.05$)

Table 4. Mean values of the variables shown in the first column for the three end members: irrigation water, groundwater inflows and VID drainage waters. Standard deviations in brackets.

	Irrigation water	Ground water	VID drainage water
EC (dS/m)	0.38(0.04)	2.68 (0.24)	2.35 (0.50)
Cl^- ($mmol_c/L$)	0.43(0.12)	5.44 (1.14)	1.37 (0.43)
SO_4^{2-} ($mmol_c/L$)	0.78(0.22)	21.80(4.24)	27.60 (9.15)
NO_3^- ($mmol_c/L$)	0.05(0.03)	0.67 (0.40)	0.80 (0.29)
Ca^{2+} ($mmol_c/L$)	2.10(0.32)	11.50(1.49)	19.88 (5.03)
Na^+ ($mmol_c/L$)	0.50(0.37)	7.17 (0.87)	2.29 (1.09)
Mg^{2+} ($mmol_c/L$)	0.61(0.19)	10.89(0.76)	9.48 (4.55)
SAR [$(mmol_c/L)^{0.5}$]	0.43(0.31)	2.15 (0.27)	0.62 (0.37)

Table 5. Four-point estimators of the mean EC and Cl^- of VID drainage waters with best rankings after corrected by regression (EC) and bias subtraction (Cl^-): root mean square error (RMSE), mean absolute error (MAE), and ranking by smaller RMSE among the four-point estimators selected for both variables.

	EC			Cl^-		
Sampling points	RMSE	MAE	Rank	RMSE	MAE	Rank
D17-D29-I3-I7	0.082	0.063	1	0.099	0.076	1
D12-D20-D29-I7	0.091	0.075	2	0.134	0.104	9
D10-D20-D29-I7	0.094	0.079	5	0.133	0.100	8
D13-D20-D29-I7	0.096	0.081	8	0.126	0.090	6
D13-D4-D32-I7	0.096	0.076	7	0.127	0.092	7