

Irrigation management, Nitrogen fertilization and Nitrogen losses in the return flows of La Violada irrigation district (Spain)

R. Barros, D. Isidoro*, R. Aragüés

Centro de Investigación y Tecnología Agroalimentaria de Aragón (CITA), Diputación General de Aragón (DGA), Unidad de Suelos y Riegos (Unidad Asociada EEAD-CSIC), Avenida Montañana 930, 50059 Zaragoza, España.

**Corresponding author.* Tel.: +34 976716393; fax: +34 976716335. E-mail address: disidoro@aragon.es (D. Isidoro).

ABSTRACT

Nitrogen (N) pollution induced by irrigated agriculture is a significant environmental problem. The main N inputs and outputs were measured or estimated in the semi-arid La Violada irrigation district (Spain). Data on two periods (1995-98 and 2006-08) were compared and related to observed changes during the decade in cropping patterns and N fertilization and irrigation management. N fertilization exceeded crop N uptake due to over-fertilization of corn (426 kg N/ha in 1995-98 and 332 kg N/ha in 2006-08) and alfalfa (62 kg N/ha). Between the two periods, N fertilization decreased by 56%, primarily due to a change from corn to alfalfa and barley. Accordingly, N losses in the irrigation return flows (IRF) diminished from 31% of the applied fertilizer in 1995-98 to 20% in 2006-08. NO_3^- concentrations and $\text{NO}_3\text{-N}$ loads in the IRF decreased from 40 mg/L and 106 kg N/ha in 1995-98 to 21 mg/L and 22 kg N/ha in 2006-08, due to lower N fertilization, lower corn area and improved irrigation efficiency. N contamination in the IRF will be minimized by increasing the irrigation efficiency and decreasing the corn area and its N fertilization rates, particularly when supplemental organic N is applied at pre-sowing.

Keywords: Nitrogen use efficiency, non-point pollution, fertilization, nitrate, nitrogen balance, irrigation efficiency, La Violada irrigation district.

1. Introduction

Nitrogen contamination induced by irrigated agriculture has been recognized as an important environmental problem that affects the aquatic and terrestrial ecosystems. High nitrate concentrations may cause eutrophication, hypoxia, methemoglobinemia and certain cancers (Ongley, 1996; Tanji and Kielen, 2002; Addiscott and Benjamin, 2004). Thus, the European Nitrate Directive (EU, 1991) has set at 50 mg/L the maximum allowable nitrate concentrations in public water supplies. However, the off-site effect of irrigated agriculture on the resulting nitrate concentrations in the receiving water bodies should be evaluated in terms of loads rather than concentrations in its irrigation return flows (IRF), as it is the mass of pollutant in the IRF that increases the pollutant concentration in the receiving water bodies, rather than its concentration (EPA 1991; Goswami et al, 2009; Lecina et al., 2010; Peña-Haro et al., 2010).

Nitrate leaching from irrigated land has been widely studied from the agronomic (Lowrance 1992; Ramos et al., 2002; Salmerón et al., 2010) and modelling (Chowdary et al, 2005; Gowda et al., 2008; Nangia et al, 2008) points of view. The achievement of N balances in irrigation districts is a sensible approach to identify their main N sources and sinks, quantify N loads in IRF (Baron and Campbell, 1997; David et al., 1997; Jha et al., 2005; McMahon and Woodside, 1997; Meisinger and Delgado, 2002) and assess the influence of agricultural practices on N loads in the receiving water bodies (Donner et al., 2004; Snook and Whithead, 2004). Nitrate leaching from irrigated land depends on soil and climate characteristics, crop patterns, and irrigation and N fertilization management. Several studies have related these variables with nitrate leaching losses in IRF (Casalí et al., 2008; Randall and Mulla 2001; Silva et al., 2005) that may vary by one order of magnitude, from below 20 kg NO₃-N/ha-year to above 200 kg NO₃-N/ha-year (Aragüés and Tanji, 2003).

According to the European Environmental Agency (EEA, 1999), agricultural activities contribute 50% of total nitrate loads in waters. Hence, in compliance with the objectives set by the European Water Framework Directive for the attainment of a good ecological status of water bodies in Europe in year 2015, a reduction of N loads in IRF is needed (EU, 2000; EU, 2002). To reach this aim, a detailed knowledge of the contribution of agricultural practices (especially irrigation and N fertilization) to the N pollution loads in water courses is needed to establish effective control policies.

N pollution has been found to be of concern in the Ebro River Basin, especially in the IRF of poorly-managed irrigated areas, particularly with traditional surface irrigation systems (Causapé et al., 2006). Cavero et al. (2003) found that the nitrate loads exported per unit area in the IRF of two sprinkler irrigation districts predominantly grown to corn (*Zea Mays*, L.), a crop with high N requirements, vary, depending on irrigation and N fertilization management, between 18 and 49 kg NO₃-N ha⁻¹ year⁻¹, whereas García-Garizábal et al. (2009) found values of 21 to 72 kg NO₃- N ha⁻¹ year⁻¹ in a traditional flood irrigated district grown with winter cereals and alfalfa. Similar nitrate loads per unit area (16 to 37 kg NO₃- N ha⁻¹ year⁻¹) were found in a non-irrigated agricultural watershed high in precipitation (691 mm average) grown with winter cereals (Casalí et al., 2008), analogous to those found in other non-irrigated, high rainfall environments by Goswami et al. (2009) (7 to 43 kg NO₃- N ha⁻¹ year⁻¹).

However, the results obtained in the different areas depend both on their different physical and hydrological properties and their irrigation and management practices. The study of long data series in a given location (irrigation district or basin) allows assessing the evolution of IRF (volumes, concentrations and loads) and its relationships with changes in irrigation and management practices, eliminating the effect of the differences between areas. The IRF of La Violada irrigation district (VID, located in the Ebro River basin, NE Spain) have been monitored for several periods since 1982 (in the 80s: 1982-84 and the 90s: 1995-98) with studies focusing on irrigation hydrology (Isidoro et al., 2004; Barros et al., 2011a, 2011b) and management (Faci et al., 2000; Playán et al., 2000), salinity and salt mass balances (Faci et al., 1985; Bellot et al., 1989; Isidoro et al., 2006a; Barros et al. 2012), and nitrogen exports and imports (Bellot and Golley, 1989; Isidoro et al., 2006b). Surface irrigation was dominant in VID along these decades, and these studies provided relevant information about irrigation and its environmental off-site impact under traditional irrigation practices.

In 2006, the monitoring of the IRF from VID was resumed providing additional data for comparing the salt and N exports under the hydrological and irrigation conditions in the 00s (2006-08) that were rather different from those in the 80s and 90s, and just prior to the transformation of irrigation from surface to sprinkler systems during 2008-09. The main changes in VID between the 90s and 00s were (i) the construction of the elevated La Violada Canal (that substituted the old and deteriorated La Violada Canal with significant seepage losses) right

before the 2003 irrigation season, (ii) the construction of six internal reservoirs (allowing for more timely irrigation), (iii) the strengthened control of tail-waters from irrigation ditches (reducing direct irrigation water losses to La Violada gully) enforced by the Ebro River Basin Authority (Confederación Hidrográfica del Ebro, CHE); and (iv) the severe drought forcing the reuse of drainage waters for irrigation in 2005 (especially) and 2006 (Barros et al., 2011a; Barros et al., 2012).

Cropping patterns also changed from the 90s to the 00s (Tables 1 to 3), significantly affecting some of the main N inputs and outputs in VID. In the 90s the main crops were corn (51% of the total irrigated area), alfalfa (23%) and winter grains (15%). In the 00s, winter grains (41%) and alfalfa (44%) replaced corn (7%), due to the water-scarce 2005 and 2006 years and to the beginning of the irrigation transformation works in 2008, when farmers sowed winter grains and maintained alfalfa in the fields instead of sowing the more resource-intensive corn as they expected that the growing season would be interrupted by these works. Also, the irrigated area was 12% lower in the 90s than in the 00s due to these reasons.

The data gathered in VID along the 80s, 90s and 00s were used to establish the long-term water balances (Barros et al., 2011a), the evolution of the performance indicators of the irrigation system (Barros et al., 2011b), and the effects of these changes on the salt loads and concentrations in the IRF (Barros et al., 2012). Also, based on the N fluxes in La Violada gully, Cavero et al. (2011) applied APEX and identified that the improvement in irrigation was the most effective strategy to reduce N loads in the IRF.

Similarly, the differences in cropping patterns, irrigation management and N fertilization in VID along the 90s and 00s provided an opportunity to address their effects on the N exports (concentrations and loads) in the IRF. The aim of this work was to relate these N exports with the indicated changes and to identify best management practices for off-site N pollution control.

2. Materials and Methods

2.1. Summary description of La Violada Irrigation District (VID)

The 4000 ha VID is located in the upper reaches of La Violada gully watershed (north-east Spain; latitude: 41°02' N; longitude: 0°36' W; Fig. 1) and is underlain by a Tertiary impervious

clay layer that prevents deep percolation, so that all or most of the return flows are intercepted by the gully which is the single drainage outlet for the district. VID is mostly surrounded by dry land and is delimited by three lined irrigation canals forming a closed hydrological system well suited to perform mass balances (Faci et al., 1985; Aragüés et al., 1990; Isidoro et al., 2006; Barros et al., 2011a). La Violada gully collects the IRF from VID and its flow is measured at the gauging station n° 230 of CHE (D-14 in Fig. 1). A detailed description of VID, its Mediterranean climate, its surface irrigation system (prior to 2009), the main soil hydraulic properties, and the changes in the irrigation system from the 90s to the 00s is given in Barros et al. (2011a; 2011b; 2012).

2.2. Nitrogen mass balances

The 1995 and 1996 N fertilization practices and crop yields in VID, and the 1995 to 1998 daily nitrate concentrations and nitrate-N loads measured at La Violada gully D-14 monitoring station were taken from Isidoro (1999) and Isidoro et al. (2006b), respectively. The methodology given in this section refers to the 2006-2008 hydrological years and is basically similar to that of the 90s.

The N mass balances were performed in the 2006-2008 hydrological years by assigning the NO₃-N concentrations measured in each water input and output to the corresponding measured volumes (except ET that was not included in the balance because it is N-free), and by measuring or estimating the mass of other direct N inputs and outputs. The N mineralization and immobilization were not included in the balance because they do not change the total N content in the system, but rather transform one type of N into another. Therefore the nitrogen balance is given by:

$$\Delta N = N_F + N_{SF} + N_I + N_P + N_{OI} + N_{CS} - N_U - N_Q - N_V - N_{DN} \quad (1)$$

where N stands for mass of nitrogen. The inputs are nitrogen fertilization (N_F) (both organic and mineral), symbiotic fixation (N_{SF}), and nitrogen in irrigation water (N_I), precipitation (N_P), other inputs (N_{OI}) and canal seepages (N_{CS}). The outputs are crop nitrogen uptake (N_U), nitrogen exported by the flow of water (Q) at the exit of VID (La Violada gully D-14 monitoring station) (N_Q), volatilization from applied manure and ammonia fertilizers (N_V), and denitrification (N_{DN}). The differences between the N inputs and outputs (ΔN) represent the increase in the organic

and mineral N stocks in the system. In this study, only the N fluxes in the components of the water balance (N_I , N_P , N_{OI} , N_{CS} , and N_Q) along with N fertilization and crop N uptake (N_F and N_U) were actually determined from measured data (the former through sampling and analysis of the different water flows and the latter through field surveys). The components N_{SF} , N_V and N_{DN} were estimated from literature sources and are presented mainly to show their magnitude relative to the measured components. As some of the estimated terms (particularly N_{SF}) were so high, the ΔN calculated through eq. 1 cannot be regarded as a true estimate of N accumulation or removal.

2.3. N inputs

2.3.1. N fertilization practices

The N fertilization practices (manure and mineral fertilizers) for the main irrigated crops grown in the 2006-2008 period were obtained through a total of 142 interviews. Around 27% of total farmers belonging to the Almodévar Water User Association (Comunidad de Regantes de Almodévar; CRA) were interviewed each year. The farmers were asked for manure applications, types of fertilizers applied, doses per unit area, dates of application, crop yields and management of crop residues. Only the irrigated crops were included in the surveys because 91% of the total fertilization was applied to them (Isidoro et al. 2006b). The main crops surveyed were corn, alfalfa, barley and ryegrass. Since the number of answers for rice, wheat, and sunflower were low in each year, only the 2006-2008 average was calculated for those crops. Due to the lack of answers for fruit trees and orchards during 2006-2008, the information for these crops was taken from Isidoro et al. (2006b). In the 90s, N fertilization was only established in years 1995 and 1996 through a similar interviewing process (Isidoro et al., 2006b).

The amount of N (kg/irrigated ha) and the different forms of N (nitrate, ammonia, urea) present in each fertilizer were obtained from its composition and application doses. The organic and ammonia N contents in manure and pig slurry were taken from Andreu et al. (2007).

The mean mass of N (\bar{N}) applied in each fertilizer or manure application to each crop and its standard deviation [$S(N)$] were calculated by means of the equation for the propagation of the error (Deming, 1966):

$$\bar{N} = p \cdot \bar{C}_N \quad (2)$$

$$S(N) = p \cdot S(C_N) + S(p) \cdot \bar{C}_N \quad (3)$$

where p is the percentage of farmers that performed the application, $S(p)$ is the standard deviation of the percentage calculated as $S(p) = \sqrt{\frac{p \cdot (1-p)}{n}}$ (where n is the number of answers for that crop), and \bar{C}_N and $S(C_N)$ are the average and standard deviation of the N applied by the farmers who actually performed that application (C_N). The average dates of each application and their standard deviations were also calculated for each crop.

The total N rate applied to a crop (in kg N/ha) was obtained as the sum of the N applied in all fertilizer applications to the given crop. The series of total N applied to each crop in 1995-1996 (Table 1) and 2006-2008 (Table 2) were compared statistically at $P=0.05$. If the data were normally distributed following the Shapiro-Wilk test, a Duncan's multiple-range test was performed to determine if there were significant differences in the fertilization practices between these two periods. If the data did not follow a normal distribution, the non-parametric Kruskal-Wallis test was applied to compare the medians.

The annual mass of N applied in VID with fertilization (N_F) was calculated as the sum of the N applied to each crop per hectare multiplied by its land area in each year provided by CRA. The total N applied in VID was divided by the annual irrigated area to obtain the unitary amount of N applied ($\text{kg N ha}^{-1} \text{ year}^{-1}$).

2.3.2. Other N inputs

Nitrogen symbiotic fixation is an important N input especially in agricultural areas devoted to leguminous crops. The alfalfa N symbiotic fixation (N_{SF}) was estimated using the equation $N_U = 0.66 \cdot (N_{SF} + N_F)$ (Isidoro et al. 2006) assuming that up to 66% of the N in alfalfa can be present in its aerial biomass (Rauschkolb and Hornsby, 1994).

The frequency of sampling and analysis to determine the mass of nitrogen in irrigation (I), precipitation (P), other inflows (OI) and canal seepages (CS) was low due to the small variability of NO_3^- in these flows. Thus, the N loads in I, P, OI and CS were calculated as the product of their average NO_3^- and their volume for the study period. The estimations of the volumes of OI and CS were given in Barros et al. (2011a).

The 2006-2008 average NO_3^- in irrigation (1.9 mg/L) was calculated from 29 samples taken in the Monegros Canal (CMO) with a frequency of 40-48 days. Measurements along the hydrological year 2006 showed that other nitrogen forms different from NO_3^- were negligible. The average NO_3^- in precipitation (2.8 mg/L) was determined from 50 grab samples collected along the hydrological years 2007 and 2008 in the Almodévar meteorological station (Fig. 1). The average NO_3^- in canal seepages was considered to be the same as in irrigation. The average NO_3^- in other inflows [OI = canal operational releases (CR) + lateral surface runoff (SR) + municipal wastewaters (MW)] was calculated annually by weighing the NO_3^- of CR, SR and MW by their annual volumes. Nitrate in CR was that of irrigation water (1.9 mg/L), NO_3^- in SR (0.64 mg/L) was measured in two water samples taken in the three main gullies entering the irrigated area during high flow events (Barros et al., 2011a), and NO_3^- in MW (50 mg/L) was taken from Hernández (1992).

2.4. N outputs

2.4.1. Nitrogen exported in La Violada gully and in the VID irrigation return flows

Daily water samples were collected along 2006-2008 with an ISCO 6712C automatic sampler installed at La Violada gully D-14 monitoring station located at the exit of VID. NO_3^- was measured in all samples with an autoanalyzer (Bran+Luebbe AA3). Missing daily NO_3^- data were obtained by linear interpolation between the previous and following days.

The daily NO_3^- -N loads (N_{Qd}) were obtained from the product of the daily mean water flows (Q_{dm} provided by CHE) and the daily NO_3^- -N concentrations [with NO_3^- -N (mg/L) = 0.2259 NO_3^- (mg/L)]:

$$N_{Qd} \text{ (Mg/d)} = 0.0864 \cdot \text{NO}_3^- \text{-N (mg/L)} \cdot Q_{dm} \text{ (m}^3\text{/s)} \quad (4)$$

The daily N_{Qd} data for the 1995-1998 (Isidoro, 1999) and the 2006-2008 periods were tested for significant differences by means of the Duncan's multiple-range test. The daily values were aggregated to calculate the total N loads exported by La Violada gully at D-14 (N_Q) along the hydrological year (HY), the irrigation season (IS: April to September) and the non irrigation season (NIS: October to March). The average NO_3^- was also calculated for each period.

Outflows in La Violada gully arise from several sources such as drainage waters originated in the irrigated land of VID, CS, and OI (Barros et al, 2011a). In order to determine the N loads solely arising from the VID irrigation return flows (N_{Q^*}) (i.e., N loads in outflows minus N loads in OI), the N loads in OI (N_{OI}) were discounted from the total N loads exported through La Violada gully at D-14 (N_Q):

$$N_{Q^*} = N_Q - N_{OI} \quad (5)$$

The nitrate concentrations in the IRF ($NO_{3Q^*}^-$) were then obtained from:

$$NO_{3Q^*}^- = \frac{NO_{3Q}^- \cdot Q - NO_{3OI}^- \cdot OI}{Q - OI} \quad (6)$$

The yearly N loads per irrigated hectare ($kg\ N\ ha^{-1}\ year^{-1}$) in La Violada gully total outflows and in the IRF were calculated for comparison purposes between years and with other irrigation districts. This approach assumes that the non irrigated area within VID has a negligible contribution to the N loads in the IRF.

2.4.2. Other N outputs

The total annual N uptake (N_U) by crops was calculated as the sum of N_U for each crop in each hydrological year. For a given crop, N_U was calculated as the N content in the harvested product (taken from literature sources) times crop's yield. The total N_U was divided by the annual irrigated area to obtain the unitary N_U ($kg\ N\ ha^{-1}\ year^{-1}$). The N content in the crop residues was not considered as an output because according to the surveys performed, crop residues were generally incorporated into the soil. Volatilization losses from applied urea and ammonia fertilizers (N_V) were taken as 10% of the N applied in urea and ammonia fertilizers and 35% of the N applied as manure (Puckett et al. 1999). A value of 15 kg N/ha was chosen from several bibliographic sources as the mean denitrification losses (N_{DN}) (Isidoro et al. 2006). These N_V and N_{DN} estimates are rough approximations, and they were included only to compare their magnitudes relative to other N inputs and outputs in VID.

2.5. Regression analysis

A functional relationship yielding the seasonal N_{Q^*} from the cropping pattern (S_{corn}), fertilization (N_F), and irrigation management (ICUC and DRF) was obtained by means of linear regressions. The simple regression of N_{Q^*} on S_{corn} was tested alone, along with the multiple and single regressions of N_{Q^*} on N_F , ICUC and DRF. Only the significant regression models ($P < 0.05$) with all their coefficients significantly different from 0 ($P < 0.05$) were accepted. The level of significance of the regression equations is shown as an indication of the strength of the relationship.

2.6. Nitrogen Use Indices

Three indicators were used to compare N fertilization and N losses in the IRF of VID and to establish the relative use of the N applied by the different crops in the district:

- (1) The N_{Q^*}/N_F ratio that determines the fraction of the applied fertilizer N that is exported by the IRF of VID. This ratio depends on fertilization practices (amount of N applied in relation to crop needs and type of fertilizers applied), irrigation practices (efficiency, uniformity and frequency of irrigations) and timing of fertilization in relation to irrigation that affects the actual leaching of the applied N.
- (2) The bulk Nitrogen Fertilizer Use Efficiency (NFUE), calculated as the ratio of crop's N uptake (N_U) minus the fraction of the N uptake originating from symbiotic fixation by leguminous crops ($0.66 \cdot N_{SF}$) to the total N fertilizer inputs (thus representing a measure of the recovery fraction of the N fertilizer applied; Pierce and Rice, 1988):

$$NFUE = (N_U - 0.66 \cdot N_{SF}) / N_F \quad (7)$$

- (3) The N_F/N_U ratio (for each crop and averaged for the irrigated area) that determines the use of N fertilizers above crop needs due to inefficiencies in N fertilization.

3. Results and Discussion

3.1. Nitrogen fertilization practices

Tables 1 (years 1995-1996) and 2 (years 2006-2008) summarize the manure N_F and the pre-plant and side-dress mineral N_F applied to the main irrigated crops grown in VID. The

information includes the mass of N_F (mean and, in parenthesis, standard deviation) applied in each date, the percentage of farmers that performed the applications over the total answers for each crop, and the average dates of each application. For each crop, the area, yield, mass of N_F applied (manure plus mineral fertilizers), N_U uptake, N_F/N_U ratio, and N content in the harvested product (NC) are given in Table 3 (average \pm standard deviation for the 90s and 00s periods).

3.1.1. Corn fertilization

Corn was the most heavily fertilized crop in all years (five-year average N_F applied = 370 kg N/ha; CV = 18 %). All farmers applied a mineral pre-plant fertilization (generally, a 10-26-26 N-P-K complex) in April (except in 2006 where the percentage of farmers performing this application was only 82 %), and a first side-dress application in June (urea-46 % N or 32 % N solution). A second side-dress was given by 71 % of farmers, and a third by 10 %, whereas only 1.5 % of farmers performed a fourth side-dress application (Tables 1 and 2). These side-dress applications were given as N32. Bovine manure was applied only by 20 % of farmers.

The average N_F applied to corn in 2006-2008 (332 kg N/ha, CV = 17%) was 22% lower than in 1995-1996 (426 kg N/ha, CV = 9%) showing significant differences between both periods. The higher N fertilization in the 90s did not result in higher corn yields that were similar in both periods, since N fertilization was always higher than N uptake (Table 3). The average corn yields of 10.4 Mg/ha (Table 3) is comparable to the yield measured by Cavero et al. (2003) (average of 11.0 Mg/ha) in two sprinkler irrigation systems of the Middle Ebro River Basin.

The lower N_F and higher variability in 2006-2008 was due to (i) a significant N_F decrease in 2008 (267 kg N/ha), the year when irrigation modernization works started, (ii) a lower N_F applied at pre-plant, and (iii) a lower percentage of farmers giving the second side-dress applications (Table 2). Even so, corn was overfertilized in both periods since the average N_F application rate per unit corn yield (41 kg N/Mg in the 90s and 32 kg N/Mg in the 00s) exceeded the recommended value of 28 kg N/Mg to 30 kg N/Mg in flood-irrigated systems with low irrigation efficiencies (Betrán and Pérez-Bergés, 1994). The excess fertilization ratio (N_F/N_U) decreased over the studied decade from 1.5 to 1.1 (Table 3).

Regarding the forms of N applied to corn, Figure 2 shows that, in both periods, the maximum total N applications generally corresponded to farmers that supplemented their crops with manure (organic N) without reducing significantly their mineral applications (extreme right in Figures 2a and 2b). This result was also found in the 00s for barley and wheat. The percentage of farmers that applied manure to corn in the 90s (about 33%) was significantly higher than in the 00s (about 16%) (Table 1). The average mineral N fertilization applied to corn, obtained by discounting the organic N from the total N, was also significantly higher in the 90s (369 kg N/ha) than in the 00s (313 kg N/ha).

3.1.2. Alfalfa fertilization

Although N fertilization in alfalfa is regarded as unnecessary due to its ability to fix the atmospheric N, it was fertilized with an amount of 62 kg N/ha (five-year average). The high variability of this average (CV = 41%) resulted from the absence of N applications by some farmers. Alfalfa yields were similar in the 90s and 00s (Table 3).

The mean N_F was higher in the 00s (67 kg N/ha) than in the 90s (54 kg N/ha) due to a higher N content of the applied fertilizers in the 00s (10-24-24, 13.5-34.5-15 and urea-46 % N) than in the 90s (8-24-8 and 8-15-15), and to the three side-dressings given in the 00s compared to only two in the 90s (Tables 1 and 2). As in the case of corn, N_F in 2008 was very low due to the on-going irrigation modernization works.

3.1.3. Barley fertilization

The five-year average barley N fertilization was 120 kg N/ha (CV = 16%), without significant differences between the 90s and 00s (Table 3). However, some fertilization practices were different: manure was applied in summer by 9% of farmers in the 00s against 0% in the 90s, and 40% of farmers gave a second side-dress in the 90s against only 10% in the 00s (Tables 1 and 2). N fertilization in both periods was close to crop N uptake, as shown by the N_F/N_U ratios close to 1 (Table 3).

Barley yield was 27% lower in the 00s than in the 90s (Table 3), mainly due to the low 2008 yield derived from the irrigation modernization works.

3.1.4. Fertilization of minor crops

The average N_F applied to ryegrass in the 00s (no data for the 90s) was 202 kg N/ha. The variability was high (CV = 51%) due to the low fertilization rate in 2008 (92 kg N/ha) obtained in a single answer, and the large differences between farmers applying only mineral N (92 kg N/ha) and those applying both organic and mineral N (355 kg N/ha).

For other minor crops (wheat, sunflower and rice) only the average values are given for the 00s due to the low number of answers gathered. The N_F applied to wheat was 169 kg N/ha in the 90s and increased to 237 kg N/ha in the 00s due to manure applications that accounted for 0% of the total N applied in the 90s against 21% in the 00s. Hence, the N_F/N_U ratio increased from 0.9 in the 90s to 1.2 in the 00s, although the yields were similar in both periods (Table 3).

The average N_F applied to sunflower was low (71 kg N/ha in the 90s and 32 kg N/ha in the 00s), because this crop benefits mainly from subsidies established by the European Agricultural Policy (EAP) and not from yields. Hence, very low yields and N_F/N_U ratios were obtained for sunflower (Table 3).

The N_F applied to rice in the 90s doubled that in the 00s, although the yields were similar. The N_F given to vegetables and fruit trees were taken as 189 kg N/ha and 49 kg N/ha, respectively, the average values obtained by Isidoro et al. (2006b).

3.1.5. Total N fertilization (N_F)

The average \pm standard deviation of the N_F rates (kg N/ha) given to the crops grown in the VID irrigated area in the 90s and 00s are summarized in Table 3. The average N_F decreased from 261 kg N/ha in the 90s to only 114 kg N/ha in the 00s (i.e, a 56% reduction) due to changes in cropping patterns (from corn heavily fertilized in the 90s to alfalfa and barley with much lower N fertilization needs in the 00s) and lower N fertilizer applications given in the 00s and, in particular, in 2008 (start of irrigation modernization works).

Figure 3a shows that in the 90s the monthly maximum amounts of applied N_F occurred in June and July, when side-dresses were given to corn that occupied 51% of the irrigated area, followed by March (corn manure applications) and April (corn pre-planting applications). In contrast, in the 00s the monthly maximum amounts of applied N_F occurred in February, when

the first side-dress was given to barley that occupied 37% of the irrigated area, followed by May-June, when side-dresses were given to alfalfa that occupied 44% of the irrigated area.

The irrigated area average N_F/N_U ratio was 0.9 in the 90s and 0.5 in the 00s (Table 3). However, if the alfalfa crop (with lower N_F requirements due to N symbiotic fixation) is excluded, the irrigated area N_F/N_U ratio varied between 1.1 and 1.5 depending on years, showing that N fertilization was 10 to 50% higher than crop N uptake.

Ammonia N and urea N were the most extensively used N forms (Figure 4). In the 90s, ammonia N amounted to 37-42 % and urea N to 23-31 % of the total applied N. In the 00s, the ammonia N percentage remained unchanged, whereas the urea N increased to about 50%. This is linked to the drastic reduction in the use of N32 (liquid solution with 25 % of its total N being $\text{NO}_3\text{-N}$) causing the nitrate N to diminish from about 21% in the 90s to about 4% in the 00s. The applied organic N was low in all years (average of 12% of total applied N in the 90s and 9% in the 00s). In the 90s only corn received cow manure (Table 1), whereas in the 00s also barley and alfalfa received cow manure and/or pig slurry (Table 2).

3.2. Nitrogen exported in La Violada gully and in the VID irrigation return flows

Monthly-average nitrate concentrations (NO_3^-) in waters collected at La Violada gully D-14 monitoring station showed different patterns in the 90s and 00s (Figures 3a and 3b, respectively). Consistent NO_3^- peaks were observed in February along 1995-1998, corresponding with the first side-dress N applications given to winter grains. Similar NO_3^- peaks were observed in June-July, corresponding with the side-dress N applications given to corn. In contrast, NO_3^- in 2006-2008 were much lower and quite uniform due to the lower corn land area and the much lower N_F in this period (Table 3).

The hydrological year daily mean NO_3^- significantly ($P < 0.05$) decreased from 40.4 mg/L in the 90s to 20.6 mg/L in the 00s (Table 4) due to the already indicated lower N_F in the 00s. Within each decade, the irrigation (IS) and non irrigation (NIS) season daily mean NO_3^- were similar (Table 4), due to the presence of NO_3^- peaks in both seasons in different years (Figure 3). The NO_3^- European threshold of 50 mg/L for drinking waters (EU, 1998) was exceeded in 21% of the samples collected in the 90s, but only in 1% of the samples collected in the 00s (Table 4).

The monthly N_Q loads in the 90s were systematically higher in summer (particularly in July), due to a combination of high drainage outflows (Q in Fig. 3a) and NO_3^- in these months. These high Q were due to high irrigation depths in summer (I in Fig. 3a), whereas the high NO_3^- was due, as previously discussed, to the side-dress N applications given to corn in June and July (Figure 3a). Relatively high monthly N_Q loads were also observed in April (average of 34.1 Mg NO_3^- -N/month) due to corn pre-sowing N applications leached by irrigations given in April to promote corn emergence (Barros et al., 2011b), and in February (average of 29.5 Mg NO_3^- -N/month) due to winter grain side-dressing N applications following significant precipitation events, especially in 1996 and 1997 (Figure 3a).

In contrast, the monthly N_Q loads in the 00s were more regular and much lower than in the 90s due to the more regular and lower Q and NO_3^- values in this period (Figure 4b). The lower Q in 2005-08 was the result of lower I , decreased canal seepages and tailwaters, intensification of drainage water reuse, and a higher proportion of non-cultivated land (Barros et al., 2011b).

To determine the N loads solely arising from the VID irrigated land (N_{Q^*}), the N loads in other inflows (N_{OI}) were discounted from the N loads measured at La Violada gully D-14 monitoring station (N_Q). It is pertinent to note that the contribution of N_{OI} to N_Q in VID was irrelevant since N_{Q^*} represented 98% of N_Q . The HY mean N_{Q^*} per unit irrigated area was about five times lower in the 00s (22 kg NO_3^- -N/ha) than in the 90s (106 kg NO_3^- -N/ha) (Table 4). In both periods, about 80% of the total HY N_{Q^*} loads were exported along the IS (Table 4), suggesting that the VID irrigation return flows were responsible for most of the off-site N pollution induced by this irrigation district. N loads in the 90s were among the highest found in the Ebro River Basin, whereas the low N loads in the 00s were close to the average N load of 18 kg NO_3^- -N/ha measured in two highly efficient sprinkler-irrigated Monegros II districts of the Ebro River Basin (Cavero et al., 2003). However, it should be noticed that the low Monegros II N load was the result of very low return flows (70 mm) coupled to high nitrate concentrations (123 mg NO_3^- /L), whereas the low N_{Q^*} load of VID in the 00s was the result of very low nitrate concentrations (21 mg/L) coupled to high return flows (519 mm) (Barros et al., 2011a).

3.3. Relationships between N exported in VID irrigation return flows (N_{Q^*}) and crop patterns, N fertilization and irrigation management

Since corn was the most heavily N fertilized crop in VID, we assessed if the irrigation season (IS) N_{Q^*} loads were related to the IS areas cropped to corn (S_{corn}). Figure 5a shows that the 1998 IS clearly deviated above the general tendency. This high N_{Q^*} could not be explained satisfactorily, but might be attributed to the accumulation of N in the irrigated soils derived from the excess N applications and high corn land areas in 1995-1997 that was leached in 1998, when corn land area decreased (Barros et al., 2011b). Excluding this year from the regression, N_{Q^*} and S_{corn} were linearly correlated ($P < 0.001$), so that each 100-ha increment in corn land area will increase N export loads by about 2.9 kg N/ha. Within its limitations, the regression in Figure 5a could predict the effect of corn land area on N export loads from irrigated areas with similar characteristics to those of VID and under the current fertilization and irrigation practices. This information is particularly relevant in areas declared vulnerable to N pollution where farmers are required to manage their farms in a way compatible with the protection of surface and groundwater bodies from nitrate contamination. Comparisons with the literature values is deferred to the discussion of the N_{Q^*}/N_F ratio in the next section.

A significant ($P < 0.05$) and positive linear relationship was also obtained between IS N_{Q^*} and IS N_F (Figure 5b). Based on the regression equation and the N_F variation interval shown, each 100 kg N/ha increment in the N applied will increase N export loads by about 22 kg N/ha. Hence, under the current irrigation management around 22% of the N applied will be wasted in the IRF, a significant economic loss to farmers. This N loss is within the already indicated 1.1 to 1.5 interval for the N_F/N_U ratio (excluding alfalfa).

Excluding again the anomalous 1998 year from the regression, a significant ($P < 0.01$) and negative linear relationship was obtained between IS N_{Q^*} and the seasonal irrigation consumptive use coefficient (ICUC), an index that reflects the efficiency of irrigation that is defined as $ICUC = 100 \cdot [(ET_a - P_e) / (I - \Delta W_s)]$, where ET_a is the actual evapotranspiration, P_e is the effective precipitation, I is irrigation and ΔW_s is the change in soil water content (Barros et al., 2011b). The lower ICUC values in the 90s than in the 00s were due to the already indicated changes in irrigation infrastructures and management. Hence, as found in other studies (Bonati and Borin, 2010; Cavero et al., 2011; Spalding et al., 2001), a key strategy to reduce N export

loads is the improvement of irrigation performance. In the case of VID, each 10% increase in ICUC, above 40% ICUC, will decrease N export loads by 31 kg N/ha (Figure 5c). Though N_{Q^*} seemingly increased with the seasonal drainage fraction ($DRF = 100 \cdot [Q^* / (I + P)]$); Barros et al., 2011b), this relationship was not significant (Figure 5d). Furthermore, this figure suggests a discontinuity in DRF and N_{Q^*} from the 90s to the 00s that was attributed to the higher CS (i.e., higher DRF) in the 90s, before the construction of the new elevated La Violada canal. In all the multiple regression models tested, the variable selection process led to the linear model N_{Q^*} - N_F .

Although the relationships shown in Figure 5 are conceptually consistent and relevant from a management point of view, Figures 5c and, especially, 5d reveal two different sets of observations (corresponding to the two study periods) rather than a continuous trend behaviour along the variables interval, pointing to differences between the two periods besides a direct dependency of N_{Q^*} on irrigation management (ICUC and DRF). Hence, these relationships should be further validated with more observations leading to a population distribution closer to normality. The need to exclude year 1998 from the N_{Q^*} - S_{corn} and N_{Q^*} -ICUC regressions was justified by a potential N logging effect in VID after years 1995 to 1997, with corn as the dominant crop. This shows that these equations might be only applicable under equilibrium conditions and not when the N dynamics of the system are varying rapidly (like the continued 90s applications of excess N).

3.4. N inputs and outputs and N use indices

Table 5 summarizes the annual average \pm standard deviation of the main inputs and outputs of N in the 90s and 00s, as well as (in brackets) the corresponding percentages over the total N inputs or outputs. N fertilization (N_F) and N symbiotic fixation (N_{SF}) were the most important inputs, accounting for more than 96% of total inputs in both study periods. However, N_F was the main input in the 90s (968 Mg or 67% of total inputs), whereas N_{SF} was the main input in the 00s (694 Mg or 63% of total inputs) due to the 56% decrease in N_F and the 65% increase in the alfalfa land area in the 00s. N uptake by crops (N_U) was the main output in both periods, accounting for 68% (90s) and 82% (00s) of total outputs. The second most important output in the 90s was N_Q (N in drainage outflow), that accounted for 21% of total outputs. However, N_Q in

the 00s only accounted for 8% of total outputs, due to lower S_{corn} and N_F and higher ICUC in this period (Figure 5).

The N_Q/N_F ratio shows that 31% (90s) and 20% (00s) of the applied fertilizer N was wasted in the IRF, and that this loss was 37% higher in the 90s than in the 00s due to the already indicated higher corn land area and lower ICUC in this decade. These N_Q/N_F values were lower than the 42% ratio found in a traditional flood-irrigated district (García-Garizábal et al., 2009) and higher than the 13% ratio found in a well managed sprinkler-irrigated district (Cavero et al., 2003) both of them located in the middle Ebro River Basin. Lower N loss ratios were found in a non-irrigated agricultural catchment in the same basin (Casalí et al. 2008). Previous studies have focused particularly in reducing N losses in irrigated areas where corn was the predominant crop. Gowda et al. (2008) predicted through the ADAPT model a 17% reduction in N losses by reducing the N fertilization rate by 20% in an irrigated area in Illinois. Using the same model, Nangia et al. (2010) predicted a 23% reduction in N losses by reducing the N fertilization rate by 38% in the Minnesota River Basin. These N losses are similar or lower, respectively, than the N losses estimated from the linear regression equation shown in Figure 5b.

The Nitrogen fertilizer use efficiency (NFUE) shows that the recovery fraction of the N fertilizer applied increased from 73% in the 90s to 84% in the 00s basically due to the sharp decrease in N_F in the last period. The higher NFUE during the 00s was similar to the 81% NFUE average found in two sprinkled irrigation systems in the Ebro River Basin with crop distributions similar to those in VID (Cavero et al., 2003).

4. Conclusions

Significant differences were found in La Violada irrigation district (VID) between the 90s and 00s in terms of (i) crop patterns (corn preponderant in the 90s versus alfalfa and barley in the 00s), (ii) N fertilization rates (261 kg N/ha in the 90s versus 114 kg N/ha in the 00s) and (iii) irrigation efficiencies (irrigation consumptive use coefficients (ICUC) below and above 50 % in the 90s and 00s, respectively).

The three most important N fertilization mismanagements found in VID were (i) excessive N applications given to corn (five-year average = 370 kg N/ha), particularly due to the

high side-dress rates given in June-July and the use of liquid N fertilizers leached by excess irrigation depths, (ii) high supplemental organic N (manure) pre-sowing applications given to corn without significantly reducing their mineral N applications, and (iii) unnecessary N applications given to alfalfa (62 kg N/ha). Thus, the overall N fertilization was, depending on years, 10 to 50 % higher than the crop N uptake needs.

The changes in cropping patterns, fertilization and irrigation performance between the 90s and 00s were responsible for the differences found in terms of (i) nitrate concentrations (NO_3^-) in the IRF (40 mg/L in the 90s and 21 mg/L in the 00s, and with 21 % of the samples above the 50 mg/L threshold in the 90s against 1% only in the 00s), (ii) N loads in the IRF (106 kg NO_3^- -N/ha in the 90s and 22 NO_3^- -N/ha in the 00s), and (iii) N losses in the IRF (31 % in the 90s and 20 % in the 00s of the applied fertilizer N).

Although more observations are needed for validation purposes, the preliminary results indicate that N loads were linearly and positively correlated ($P < 0.05$) with the area cropped to corn and the amount of applied N fertilizers, and negatively correlated ($P < 0.01$) with the efficiency of irrigation (ICUC). The same conclusion was obtained by model studies in the same area by Caverio et al. (2011). The substantial differences in cropping patterns between the two periods make it difficult to establish the effect of irrigation efficiency alone on N loads. These tentative relationships are of interest in terms of delineation of best management practices because N loads in the irrigation return flows determine the nitrate concentrations in the receiving water bodies, and could be strategically used in areas declared vulnerable to N contamination.

Acknowledgments

The authors thank the Almodévar Water User Association (Comunidad de Regantes de Almodévar, CRA) and the Ebro River Basin Authority (Confederación Hidrográfica del Ebro, CHE) for their support and cooperation. This work was sponsored by the Spanish Ministry of Science and Education project AGL2006-11860/AGR, the European Regional Development Fund (FEDER) and the European Union project INCO CT-2005-015031.

REFERENCES

- Addiscott, T.M., Benjamin, N., 2004. Nitrate and human health. *Soil Use and Manage.* 20: 98-104.
- Andreu, J., Betrán, J., Delgado, I., Espada, J.L., Gil, M., Gutiérrez, M., Iguácel, F., Isla, R., Muñoz, F., Orús, F., Pérez, M., Quílez, D., Sin, E., Yagüe, M.R., 2007. Fertilización nitrogenada. Guía de actualización. *Informaciones Técnicas.* Gobierno de Aragón, Zaragoza. 196 pp.
- Aragüés, R., Tanji, K.K., 2003. Water quality of irrigation return Flows. In: Stewart, B.A., Howell, T.A. (Eds.), *Encyclopaedia of Water Science.* Marcel Dekker, New York, USA. 502-506.
- Aragüés, R., Tanji, K.K., Quílez, D., Faci, J., 1990. Conceptual irrigation project hydrosalinity model, Chapter 24. In: *Agricultural salinity assessment and management.* Am. Soc. Civil Eng. New York, USA, 504-529.
- Baron, J.S., Campbell, D.H., 1997. Nitrogen fluxes in a high elevation Colorado Rocky Mountain Basin. *Hydrol. Process.* 10: 783-799.
- Barros, R., Isidoro D., Aragüés R., 2012. Three study decades on irrigation performance and salt concentrations and loads in the irrigation return flows of La Violada irrigation district (Spain). *Agric. Ecosyst. Environ.* 151: 44-52.
- Barros, R., Isidoro, D., Aragüés, R., 2011a. Long-term water balances in La Violada Irrigation District (Spain): I. Sequential assessment and minimization of closing errors. *Agric. Water Manage.* 102(1): 35-45.
- Barros, R., Isidoro, D., Aragüés, R., 2011b. Long-term water balances in La Violada Irrigation District (Spain): II. Analysis of irrigation performance. *Agric. Water Manage.* 98(10): 1569-1576.
- Bellot, J., Golley, F., 1989. nutrient inputs and outputs of an irrigated agroecosystem in an arid Mediterranean landscape. *Agric. Ecosyst. Environ.* 25: 175-186.
- Bellot, J., Golley, F., Aguinaco, M.T., 1989. Environmental consequences of Salts exports from an irrigated landscape in the Ebro River basin, Spain. *Agric. Ecosyst. Environ.* 27: 131-138.
- Betrán, J.A., Pérez-Bergés, M., 1994. Respuesta del maíz al abonado. *Info. Técnica 8/94.* Dep. Agricultura del Gobierno de Aragón.

- Bonati, G., Borin, M., 2010. Efficiency of controlled drainage and subirrigation in reducing nitrogen losses from agricultural fields. *Agric. Water Manage.* 98: 343-352.
- Casalí, J., Gastesi, R., Álvarez-Mozos, J., De Santisteban, L.M., Del Valle de Lersundi, J., Giménez, R., Larrañaga, A., Goñi, M., Agirre U., Campo, M.A., López, J.J., Donézar, M., 2008. Runoff, erosion, and water quality of agricultural watersheds in central Navarre (Spain). *Agric. Water Manage.* 95: 1111-1128.
- Causapé, J., Quílez, D., Aragüés, R., 2006. Irrigation efficiency and quality of irrigation return flows in the Ebro river basin: An overview. *Environ. Monit. Assess.* 117: 451-461.
- Cavero, J., Beltrán, A., Aragüés, R., 2003. Nitrate Exported in Drainage Waters of Two Sprinkler-Irrigated Watersheds. *J. Environ. Qual.* 32: 916-926.
- Cavero, J., Barros, R., Sellam, F., Topçu, S., Isidoro, D., Hartani, T., Lounis, A., Ibrikçi, H., Çetin, M., Williams, J.R., Aragüés, R., 2012. APEX simulation of best irrigation and N management strategies for off-site N pollution control in three Mediterranean irrigated watersheds, *Agricultural Water Management* 103: 88-99.
- Chowdary, V.M., Rao, N.H., Sarma, P.B.S., 2005. Decision support framework for assessment of non-point-source pollution of groundwater in large irrigation projects. *Agric. Water Manage.* 75: 194-225
- David, M.B., Gentry, L.E., Kovacic, D.A., Smith, K.M., 1997. Nitrogen Balance in and Export from an Agricultural Watershed. *Journal of Environmental Quality* 26(4): 1038-1048.
- Deming, W.E., 1966. *Some theory of sampling*. Dover Publication Inc., New York, USA, 595 pp.
- Donner, S.D., Kucharik, C.J., Foley J.A., 2004. Impact of changing land use practices on nitrate export by the Mississippi River. *Global Biogeochem. Cycles* 18(1): GB1028.
- EEA-European Environmental Agency, 1999. *Groundwater quality and quantity in Europe*. Environmental Assessment Report No 3. Copenhagen, Denmark, 123 pp.
- EPA-Environmental Protection Agency, 1991. *Guidance for Water Quality-Based Decisions: The TMDL Process*. United States Environmental Protection Agency Office of Water. Washington, USA, 59 pp.
- EU-European Union, 1991. Council Directive 91/676/CE of 12 December 1991 concerning the protection of waters against pollution caused by nitrates from agricultural sources. *Official Journal L 375 of 31/12/1991*: 1-8.

- EU-European Union, 1998. Council Directive 98/83/CE of 3 November 1998 imposed to the surface waters devoted to the production of water for human consumption. Official Journal L 330, 5/12/1998: 32-54.
- EU-European Union, 2000. Directive 2000/60/CE of the European Parliament and of the Council establishing a framework for community action in the field of water pollution. Official Journal L327, 22/12/2000: 1-72.
- EU-European Union, 2002. Towards a global partnership for sustainable development. Communication from the Commission to the European Parliament, the Council, the Economic and Social Committee and the Committee of the Regions. Disponible en: http://eur-lex.europa.eu/LexUriServ/site/en/com/2002/com2002_0082en01.pdf. Consultado el 1 de Mayo de 2011.
- Faci, J., Aragüés, R., Alberto, F., Quilez, D., Machin, J., Arrue, J.L., 1985. Water and salt balance in an irrigated area of the Ebro River Basin (Spain). *Irrig. Sci.* 6: 29-37.
- Faci, J.M., Bensaci, A., Slatni, A., Playán, E., 2000. A case study for irrigation modernisation. I. Characterisation of the district and analysis of water delivery records. *Agric. Water Manage.* 42, 313–334.
- García-Garizábal, I., Valenzuela, J.C., Abrahao, R., 2009. Evolution of the efficiency and agro-environmental impact of a traditional irrigation land in the middle Ebro Valley (2001-2007). *Span J. Agric. Res.* 7(2), 465-473.
- Goswami, D., Kalita, P.K., Cooke, R.A.C., Mclsaac, G.F., 2009. Nitrate-N loadings through subsurface environment to agricultural drainage ditches in two flat Midwestern (USA) watersheds. *Agric. Water Manage.* 96: 1021-1030.
- Gowda, P.H., Mulla, D.J., Jaynes, D.B., 2008. Simulated long-term nitrogen losses for a Midwestern agricultural watershed in the United States. *Agric. Water Manage.* 95: 616-624.
- Hernández, A., 1992. Depuración de aguas residuales. Segunda edición. Colección Senior nº 9. Colegio de Ingenieros de Caminos, Canales y Puertos. Madrid, 927 pp.
- Isidoro, D., 1999. Impacto del regadío sobre la calidad de las aguas superficiales del Barranco de La Violada (Huesca): salinidad y nitratos. Ph.D. Tesis. Universidad de Lleida, Lleida. 267 pp.

- Isidoro, D., Quílez, D., Aragüés, R., 2006a. Environmental impact of irrigation in La Violada district (Spain): I: Salt export patterns, *J. Environ. Qual.* 35 (3): 766-775.
- Isidoro, D., Quílez, D., Aragüés, R., 2006b. Environmental impact of irrigation in La Violada district (Spain): II: Nitrogen fertilization and nitrate export patterns in drainage waters, *J. Environ. Qual.* 35(3): 776-785.
- Jha, R., Ojha, C.S.P., Bhatia, K.K.S., 2005. Estimating nutrient outflow from agricultural watersheds to the River Kali in India. *J. Environ. Eng.* 131(12): 1706-1715.
- Lecina, S., Isidoro, D., Playán, E., Aragüés, R., 2010. Irrigation modernization in Spain: effects on water quantity and quality. A conceptual approach. *Int. J. Water Resour. D.* 26: 265-282.
- Lowrance, R., 1992. Nitrogen Outputs from a field-size agricultural shed. *J. Environ. Qual.* 21: 602-607.
- McMahon, G., Woodside, M.D., 1997. Nutrient mass balance for the Albemarle-Palmico drainage basin, North Carolina and Virginia, 1990. *J. Am. Water Resour. Assoc.* 33(3): 573-589.
- Meisinger, J.J., Delgado, J.A., 2002. Principles for managing nitrogen leaching. *J. Soil Water Conserv.* 57: 485-498.
- Nangia, V., Gowda, P.H., Mulla, D.J., 2010. Effects of changes in N-fertilizer management on water quality trends at the watershed scale. *Agric. Water Manage.* 97: 1855-1860.
- Nangia, V., Gowda, P.H., Mulla, D.J., Sands, G.R., 2008. Water Quality Modeling of Fertilizer Management Impacts on Nitrate Losses in Tile Drains at the Field Scale. *J. Environ. Qual.* 37: 296-307.
- Ongley, E.D., 1996. Control of water pollution from agriculture. *FAO Irrig. and Drain. Paper no 55*, Rome, Italy, 112 pp.
- Peña-Haro, S., Llopis-Albert, C., Pulido-Velázquez, M., Pulido-Velázquez, D., 2010. Fertilizer standards for controlling groundwater nitrate pollution from agriculture: El Salobral-Los Llanos case study, Spain. *J. Hydrol.* 392: 174–187.
- Pierce, F.J., Rice, C.W., 1988. Crop rotation and its impact on efficiency of water and nitrogen use, in: Hargrove (Ed.), *Cropping strategies for efficiency use of water and nitrogen*, ASA Special Publication Number 51, Madison, Wisconsin, pp. 21-34.

- Playán, E., Slatni, A., Castillo, R., Faci, J.M., 2000. A case study for irrigation modernisation. II. Scenario analysis. *Agric. Water Manage.* 42, 335–354.
- Puckett, L.J., Cowdery, T.K., Lorenz, D.L., Stoner, J.D., 1999. Estimation of nitrate contamination of an agro-ecosystem outwash aquifer using a nitrogen mass-balance budget. *J. Environ. Qual.* 28: 2015–2025.
- Ramos, C., Agut, A., Lidón, A.L., 2002. Nitrate leaching in important crops of the Valencian Community region (Spain). *Environ. Pollut.* 118(2): 215-223.
- Randall, G.W., Mulla, D.J., 2001. Nitrate Nitrogen in Surface Waters as Influenced by Climatic Conditions and Agricultural Practices. *J. Environ. Qual.* 30: 337-344.
- Rauschkolb, R.S., Hornsby, A.G., 1994. Nitrogen management in irrigated agriculture. Oxford Univ. Press, New York.
- Salmerón, M., Cavero, J., Quílez D., Isla, R., 2010. Winter Cover Crops Affect Monoculture Maize Yield and Nitrogen Leaching under Irrigated Mediterranean Conditions. *Agron. J.* 102(6): 1700-1709
- Silva, R.G., Holub, S.M., Jogensen, E.E., Ashanuzzaman, A.N.M., 2005. Indicators of nitrate leaching loss under different land use of clayey and sandy soils in southeastern Oklahoma. *Agric. Ecosyst. Environ.* 109: 346-359.
- Snook, D.L., Whitehead, P.G., 2004. Water quality and ecology of the River Lee: mass balance and a review of temporal and spatial data. *Hydrol. Earth Syst. Sci.* 8(4): 636-650.
- Spalding, R.F., Watts, D.G., Schepers, J.S., Burbach, M.E., Exner, M.E., Poreda, R.J., Martin, G.E., 2001. Controlling nitrate leaching in irrigated agriculture. *J. Environ. Qual.* 30(4): 1184-1194.
- Tanji, K.K., Kielen, N.C., 2002. Agricultural drainage water management in arid and semiarid areas. *FAO Irrig. and Drain. Paper no 61*, Rome, Italy, 188 pp.

Figure captions

Fig. 1. Map of La Violada Irrigation District (VID) and location within the Ebro River Basin.

Fig. 2 – Stacked area graph of the different N forms [nitrate N (N-NO_3), ammonia N (N-NH_4), urea N (N-NH_2), and organic N] applied to corn in each survey performed in years (a) 1995 and 1996, and (b) 2006, 2007 and 2008. Surveys ordered from minimum to maximum total N applied.

Fig. 3 – Monthly irrigation (I), precipitation (P), outflow (Q) and mass of fertilizer N (N_F) applied in VID, and monthly averages of NO_3 concentrations and $\text{NO}_3\text{-N}$ loads (N_Q) measured in La Violada gully D-14 monitoring station along the a) 1995-1998 (only 1995-1996 for N_F) and b) 2006-2008 hydrological years.

Fig. 4 – Total amounts of the different N forms [nitrate N (N-NO_3), ammonia N (N-NH_4), urea N (N-NH_2), and organic N] applied in VID along the 1995, 1996, 2006, 2007 and 2008 hydrological years.

Fig. 5 – Relationships between the irrigation season nitrogen loads (N_{Q^*}) in the VID irrigation return flows and a) the area cropped to corn in VID (S_{corn}), b) the nitrogen fertilization applied in VID (N_F), c) the irrigation consumptive use coefficient (ICUC), and d) the drainage fraction (DRF) in 1995-1997 (except for N_F with data available only in 1995 and 1996), and 2006-2008. The significant linear regression equations after eliminating year 1998 are also shown.

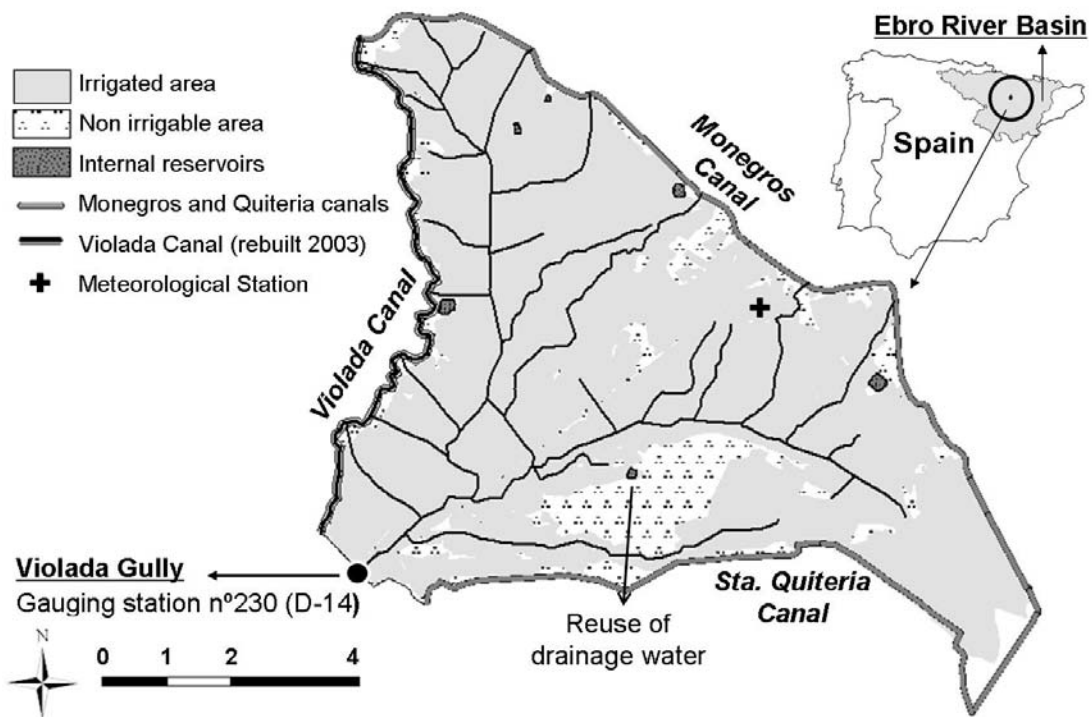


Fig. 1. Map of La Violada Irrigation District (VID) and location within the Ebro River Basin.

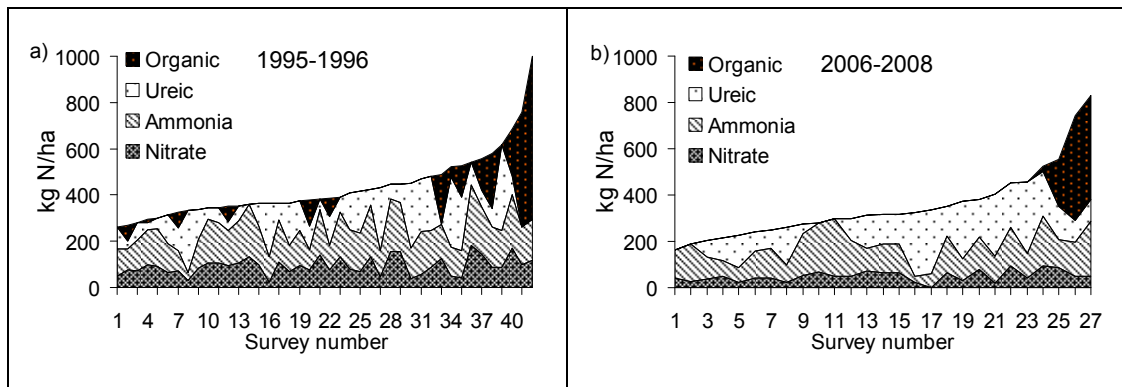


Fig. 2 – Stacked area graph of the different N forms [nitrate N ($N-NO_3$), ammonia N ($N-NH_4$), ureic N ($N-NH_2$), and organic N] applied to corn in each survey performed in years (a) 1995 and 1996, and (b) 2006, 2007 and 2008. Surveys ordered from minimum to maximum total N applied.

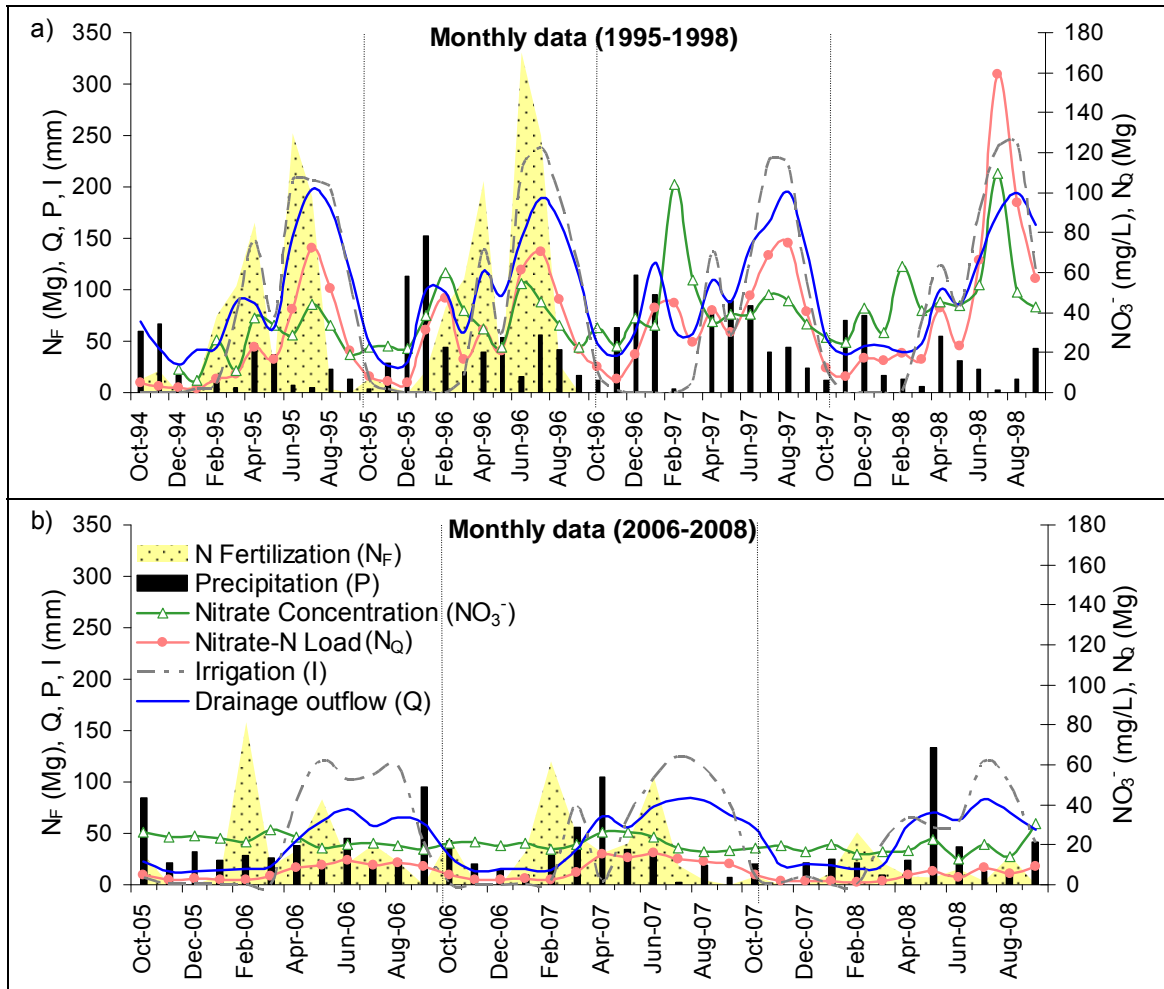


Fig. 3 – Monthly irrigation (I), precipitation (P), outflow (Q) and mass of fertilizer N (N_F) applied in VID, and monthly averages of NO_3^- concentrations and NO_3^- -N loads (N_Q) measured in La Violada gully D-14 monitoring station along the a) 1995-1998 and b) 2006-2008 hydrological years.

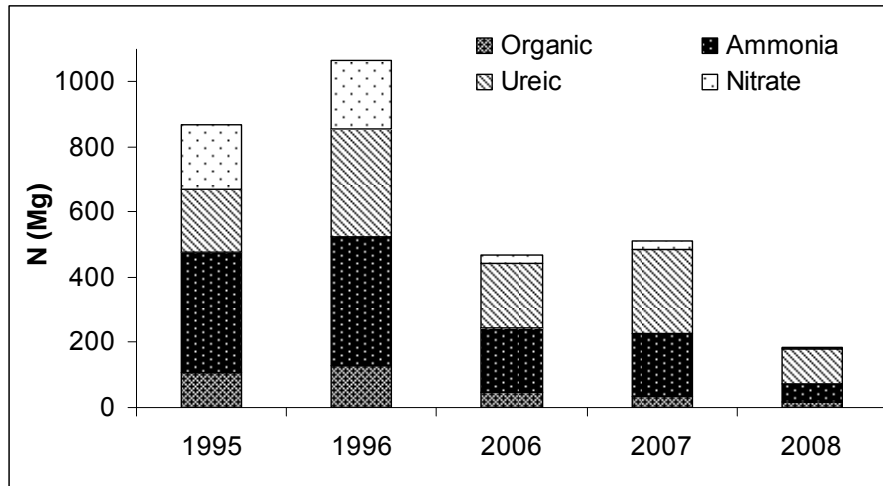


Fig. 4 – Total amounts of the different N forms [nitrate N (N-NO_3), ammonia N (N-NH_4), urea N (N-NH_2), and organic N] applied in VID along the 1995, 1996, 2006, 2007 and 2008 hydrological years.

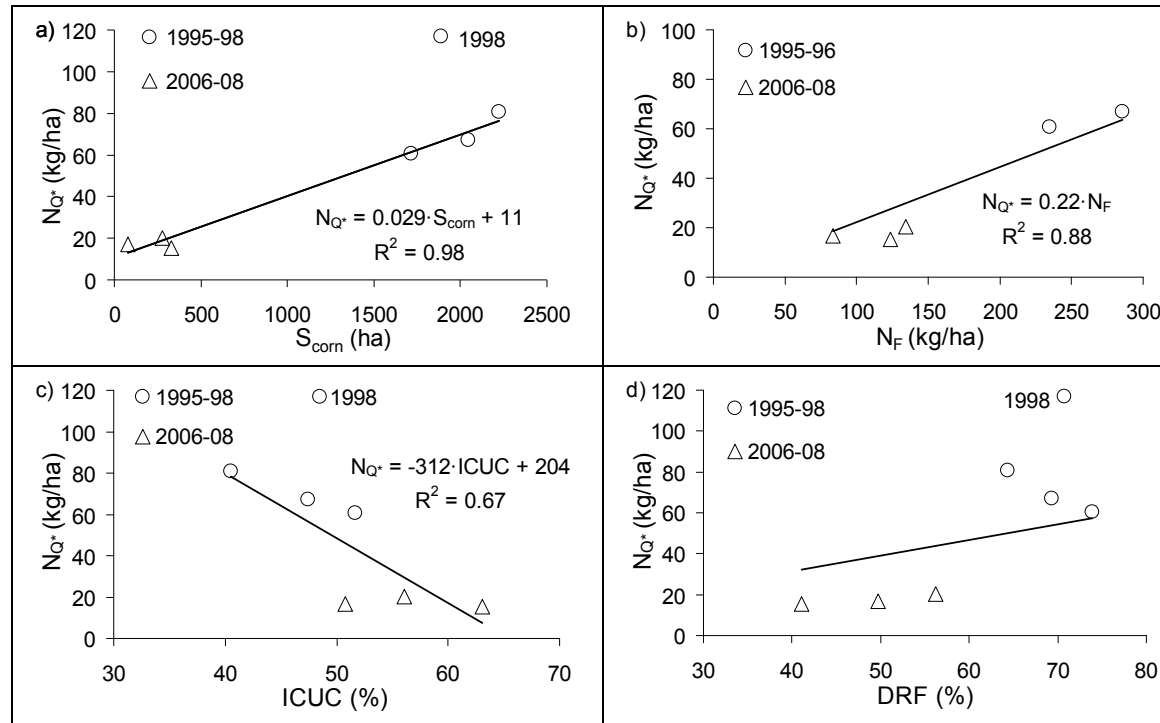


Fig. 5 – Relationships between the irrigation season nitrogen loads (N_{Q^*}) in the VID irrigation return flows and a) the area cropped to corn in VID (S_{corn}), b) the nitrogen fertilization applied in VID (N_F), c) the irrigation consumptive use coefficient (ICUC), and d) the drainage fraction (DRF) in 1995-1997 (except for N_F with data available only in 1995 and 1996), and 2006-2008. The significant linear regression equations with significant coefficients ($P < 0.05$) after eliminating year 1998 are also shown.

Table 1. Manure, pre-plant and side-dress average dates of application (Date, with standard deviation (days) in brackets) and mean amounts of N applied (N_F , with standard deviation in brackets and % of farmers that performed the application) to the main crops grown in La Violada Irrigation District in the 1995 and 1996 hydrological years. Source: Isidoro et al. (2006).

Crop	Manure		Pre-plant		Side-dress					
	Date (d)	N_F (kg/ha)	Date (d)	N_F (kg/ha)	First		Second		Third	
					Date (d)	N_F (kg/ha)	Date (d)	N_F (kg/ha)	Date (d)	N_F (kg/ha)
Year 1995										
Corn	8 Mar (28)	62 (80), 35%	5 Apr (13)	82 (33), 100%	18 Jun (24)	153 (43), 100%	18 July (19)	96 (36), 88%	18 July (-)	4 (-), 6%
Alfalfa	-	-	-	-	4 Apr (38)	33 (20), 100%	3 July (14)	19 (16), 89%	-	-
Barley	-	-	24 Oct (37)	46 (32), 100%	7 Feb (29)	92 (27), 100%	11 Apr (47)	21 (23), 29%	-	-
Wheat	-	-	9 Nov (30)	51 (25), 100%	15 Feb (35)	85 (40), 100%	29 Mar (37)	24 (18), 44%	-	-
Sunflower	-	-	31 Mar (41)	26 (14), 100%	15 May (-)	59 (-), 50%	-	-	-	-
Year 1996										
Corn	5 Mar (38)	61 (89), 32%	5 Apr (14)	99 (41), 100%	8 Jun (16)	162 (50), 100%	21 July (13)	114 (46), 92%	5 Aug (11)	17 (12), 20%
Alfalfa	-	-	-	-	31 Mar (27)	31 (15), 100%	1 July (31)	24 (16), 92%	-	-
Barley	-	-	21 Oct (25)	37 (10), 100%	10 Feb (28)	75 (37), 83%	21 Mar (22)	22 (14), 50%	-	-
Wheat	-	-	4 Nov (6)	43 (16), 100%	26 Jan (8)	115 (35), 100%	30 Mar (-)	24 (-), 50%	-	-
Sunflower	-	-	14 Apr (18)	29 (17), 88%	19 Jun (6)	20 (17), 25%	16 Aug (-)	8 (-), 13%	-	-
Mean of years 1995-1996										
Rice	-	-	18 Apr (7)	111 (8), 100%	8 July (0)	118 (66), 100%	-	-	-	-
Pepper	8 Apr (0)	34 (59), 100%	6 May (8)	73 (33), 67%	9 July (21)	106 (40), 100%	-	-	-	-
Fruit-trees	13 Jan (53)	39 (24), 64%	18 Feb (16)	53 (30), 45%	-	-	-	-	-	-

Table 2. Manure, pre-plant and side-dress average dates of application (Date, with standard deviation (days) in brackets) and mean amounts of N applied (N_F , with standard deviation in brackets and % of farmers that performed the application) to the main crops grown in La Violada Irrigation District in the 2006, 2007 and 2008 hydrological years.

Crop	Manure		Pre-plant		Side-dress					
	Date (d)	N_F (kg/ha)	Date (d)	N_F (kg/ha)	First		Second		Third	
					Date (d)	N_F (kg/ha)	Date (d)	N_F (kg/ha)	Date (d)	N_F (kg/ha)
Year 2006										
Corn	21 Feb (9)	63 (45), 18%	18 Apr (24)	48 (17), 82%	13 Jun (20)	140 (52), 100%	13 July (19)	95 (38), 82%	15 July (-)	9 (-), 9%
Alfalfa	-	-	-	-	23 Feb (22)	30 (23), 73%	16 May (86)	37 (28), 82%	6 Aug (15)	6 (5), 14%
Barley	15 Aug. (-)	18 (13), 10%	17 Oct (11)	25 (9), 81%	10 Feb (29)	80 (17), 100%	15 Mar (16)	4 (1), 14%	-	-
Raygrass	15 Jul (15)	19 (45), 63%	4 Nov (101)	53 (23), 100%	18 Feb (24)	46 (0), 100%	4 Jun (43)	37 (19), 67%	19 Jun (-)	15 (-), 33%
Year 2007										
Corn	15 Feb (-)	42 (52), 15%	18 Apr (16)	82 (28), 100%	12 Jun (13)	164 (56), 100%	8 July (23)	68 (35), 62%	4 Jul (28)	14 (10), 15%
Alfalfa	-	-	4 Mar (22)	41 (25), 82%	1 Jun (34)	45 (30), 73%	11 Jun (16)	12 (4), 14%	-	-
Barley	19 Aug (-)	3.2 (-), 6%	13 Oct (7)	27 (12), 88%	4 Feb (25)	79 (32), 94%	25 Mar (-)	2 (-), 6%	-	-
Raygrass	5 Aug (-)	96 (-), 50%			19 Apr (36)	92 (33), 100%	15 May (-)	58 (-), 50%		
Year 2008										
Corn	-	-	2 May (6)	58 (34), 100%	25 Jun (0)	177 (91), 100%	15 July (-)	32 (-), 33%	-	-
Alfalfa	15 Aug. (-)	3 (-), 10%	2 Mar (15)	21 (17), 30%	28 May (25)	7 (4), 20%	-	-	-	-
Barley	-	33 (-), 10%	16 Oct (16)	10 (8), 40%	8 Feb (30)	60 (24), 90%	15 Apr (-)	4 (-), 10%	-	-
Raygrass					5 Mar (-)	92 (-), 100%				
Mean of years 2006-2008										
Wheat	15 Aug (-)	138 (-), 50%	5 Nov (-)	10 (-), 50%	4 Feb (29)	69 (0), 100%	15 Apr (-)	20 (-), 50%	-	-
Sunflower	-	-	-	-	20 Jun (-)	32 (-), 50%	-	-	-	-
Rice	-	-	29 Apr (12)	44 (14), 100%	3 Jul (8)	59 (11), 100%	-	-	-	-

Table 3. Average \pm standard deviation of crop area, crop yield, N fertilization (N_F), crop N uptake (N_U), N fertilization to N uptake ratio (N_F/N_U), and crop N content (NC) for the main irrigated crops grown in La Violada Irrigation District (VID) in the 1990s (1995-1996) and 2000s (2006-2008) periods. The corresponding average \pm standard deviation values for the irrigated area are given in the last row.

Crop	Crop Area (ha)		Yield (Mg/ha)		N_F (kg/ha)		N_U (kg/ha)		N_F/N_U		NC (kg N/Mg)
	1990s	2000s	1990s	2000s	1990s	2000s	1990s	2000s	1990s	2000s	
Corn ^a	1879 \pm 234	228 \pm 133	10.4 \pm 0.2	10.4 \pm 0.2	426 \pm 39	332 \pm 57	290 \pm 6	292 \pm 7	1.5 \pm 0.2	1.1 \pm 0.2	28
Alfalfa ^b	865 \pm 1	1428 \pm 451	12.5 \pm 1.1	12.2 \pm 2.6	54 \pm 2	67 \pm 34	363 \pm 34	354 \pm 75	0.1 \pm 0	0.2 \pm 0.1	29
Barley	280 \pm 23	1193 \pm 348	6.2 \pm 0	4.5 \pm 0.9	147 \pm 17	116 \pm 9	149 \pm 0	108 \pm 21	1.0 \pm 0.1	1.1 \pm 0.2	24
Wheat	259 \pm 227	141 \pm 41	6.3 \pm 0	6.6 \pm 0	169 \pm 18	237 \pm 0	189 \pm 0	198 \pm 0	0.9 \pm 0.1	1.2 \pm 0	30
Sunflower	210 \pm 14	42 \pm 15	1.7 \pm 0	1.8 \pm 0	71 \pm 20	32 \pm 0	85 \pm 0	88 \pm 0	0.8 \pm 0.2	0.4 \pm 0	50
Raygrass	86 \pm 21	103 \pm 16	-	7.6 \pm 0.4	-	202 \pm 104	-	167 \pm 8	-	1.2 \pm 0.7	22
Rice	34 \pm 22	16 \pm 19	5.6 \pm 0.6	5.0 \pm 0	229 \pm 0	100 \pm 0	122 \pm 14	73 \pm 64	1.9 \pm 0.2	0.9 \pm 0.1	22
Fruit Tree	50 \pm 2	79 \pm 20	1.9 \pm 0	1.9 \pm 0	49 \pm 0	49 \pm 0	28 \pm 0	28 \pm 0	1.8 \pm 0	1.8 \pm 0	15
Orchard	49 \pm 3	27 \pm 22	35 \pm 0	35 \pm 0	189 \pm 0	189 \pm 0	161 \pm 0	161 \pm 0	1.2 \pm 0	1.2 \pm 0	5
Irrigated Area	3712 \pm 28	3257 \pm 918			261 \pm 36	114 \pm 27	306 \pm 8	232 \pm 48	0.9 \pm 0.1	0.5 \pm 0.1	

^a Corn grain at 14% moisture content

^b Alfalfa dry matter at 12% moisture content

Table 4. Nitrate concentrations measured at La Violada Gully D-14 monitoring station in the non irrigation season (NIS), irrigation season (IS), and hydrological year (HY) of the 1990s (1995-1998) and 2000s (2006-2008) periods: number of samples (n) analyzed in each period, average \pm standard deviation, maximum, minimum and percent of total samples higher than the European standard of 50 mg/l. N loads per unit irrigated area in VID irrigation return flows (N_{Q^*}) measured at La Violada Gully D-14 monitoring station in the non irrigation season (NIS), irrigation season (IS), and hydrological year (HY) of the 1990s (1995-1998) and 2000s (2006-2008) periods.

		NO ₃ (mg/L)					N _{Q*} (kg NO ₃ -N/ha)
		n	Average \pm std dev	Maximum	Minimum	>50 mg/L (% of total)	
1990s	NIS	309	40.8 \pm 24.3	123.5	5.8	22	24.9
	IS	517	40.1 \pm 17.8	132.0	12.3	21	81.4
	HY	826	40.4 \pm 20.4	132.0	5.8	21	106.3
2000s	NIS	505	20.9 \pm 5.5	52.3	7.4	0.4	4.6
	IS	504	20.3 \pm 9.3	74.3	1.1	3	17.5
	HY	1009	20.6 \pm 7.7	74.3	1.1	1	22.1

Table 5. Measured and estimated components of the nitrogen balances in La Violada Irrigation District in the 1990s (1995-1996) and 2000s (2006-2008): average \pm standard deviation and, in brackets, percentages of each N input or output over the total N inputs or outputs, respectively. Inputs: mass of N in irrigation water (N_i), precipitation (N_p), other inflows (N_{OI}), canal seepage (N_{CS}), fertilization (N_F) and symbiotic fixation (N_{SF}); Outputs: mass of N in drainage outflow (N_Q), volatilization (N_V), denitrification (N_{DN}) and uptake by crops (N_U). The ratio of the mass of N in the VID irrigation return flows (N_{Q^*}) to N_F and the Nitrogen Fertilizer Use Efficiency (NFUE = $(N_U - 0.66 \cdot N_{SF}) / N_F$) are also given.

		1990's	2000's
Inputs	N_F (Mg/yr)	968 \pm 139 (67%)	387 \pm 178 (35%)
	N_i (Mg/yr)	27 \pm 0 (2%)	8 \pm 2 (1%)
	N_p (Mg/yr)	8 \pm 4 (0.6%)	8 \pm 3 (1%)
	N_{OI} (Mg/yr)	4 \pm 1 (0.3%)	5 \pm 0 (0.5%)
	N_{CS} (Mg/yr)	8 \pm 0 (0.5%)	2 \pm 0 (0.1%)
	N_{SF} (Mg/yr)*	429 \pm 41 (30%)	694 \pm 308 (63%)
Outputs	N_Q (Mg/yr)	310 \pm 78 (21%)	77 \pm 25 (8%)
	N_U (Mg/yr)	979 \pm 8 (68%)	781 \pm 339 (82%)
	N_V (Mg/yr)*	104 \pm 16 (7%)	45 \pm 19 (5%)
	N_{DN} (Mg/yr)*	56 \pm 1 (4%)	49 \pm 14 (5%)
Nitrogen Use Indices			
	N_{Q^*}/N_F (%)	31	20
	NFUE (%)	73	84

* The terms N_{SF} , N_V and N_{DN} were not measured. These estimates were obtained from literature sources and are presented here only to allow for comparison with the actually measured components of the N balance.