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Irrigation return flows and phosphorus transport in the Middle Ebro River Valley (Spain)

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Abstract

Currently, there is an increased interest in the study of phosphorus (P) loss from soils aimed to understand and mitigate water eutrophication problems. The main objective of this study is to describe P losses in five irrigated agricultural watersheds considered as representative in terms of agricultural water management. Weekly water samples were collected during the 2007 hydrologic year (HY) at the watershed outlets and three P forms (total P, TP; total dissolved P, TDP; and particulate P, PP) were analyzed during irrigation (IS) and non-irrigation season (NIS). The P load per hectare was used to compare the study areas with other non-irrigated agricultural watersheds in Spain and Europe. Results indicate that most of the study areas showed increases in TP at higher flows. Annual TP concentrations were higher than the critical eutrophication threshold (0.02 mg L^{-1}), with TDP being the dominant fraction. The TP was higher during the IS than during the NIS, except for the Arba River where seasonal TP concentration showed the highest values (0.237 and 0.275 mg L^{-1}, respectively). Results also show that average TP yield (0.73 kg P ha^{-1} $year^{-1}$) was higher than others reported on non-irrigated agricultural lands in Spain and Europe. This work is of great relevance and indispensable for guiding future research on P transfer aimed at establishing corrective measures to sustain irrigated agricultural productivity and surface water quality.

Additional key words: agriculture; contamination; eutrophication; fertilization; water quality.

Resumen

Flujos de retorno de riego y transporte de fósforo en el valle medio del río Ebro (España)

Actualmente, hay un creciente interés por el control de la contaminación de las aguas superficiales por fósforo (P) para comprender y mitigar los problemas de eutrofización del agua. El objetivo de este trabajo es establecer un diagnóstico de la contaminación por P en cinco cuencas agrícolas de regadío consideradas representativas en términos de gestión del agua de riego. Durante el año hidrológico 2007 se tomaron muestras de agua semanalmente en los puntos de drenaje y se analizaron P total (PT), P disuelto total (PDT), y P particulado (PP) durante la estación de no riego (ENR) y la estación de riego (ER). La masa de P exportada por unidad de superficie se empleó para comparar entre las zonas de estudio con otras cuencas agrícolas de España y Europa. La mayoría de los puntos mostraron un aumento de la concentración de TP con el caudal de drenaje. Las concentraciones anuales de TP fueron altas y superiores al umbral de eutrofización (0,02 mg L^{-1}), siendo el TDP la fracción dominante. Las concentraciones medias de TP fueron superiores durante la ER que durante la ENR, con la excepción del río Arba. La masa unitaria media de TP exportada (0,73 kg P ha^{-1} $año^{-1}$) fue mayor que las de otras cuencas agrícolas de España y Europa. Este trabajo es de gran relevancia e indispensable para orientar futuras investigaciones sobre la transferencia de fósforo al objeto de definir medidas correctivas para mantener la productividad de las tierras agrícolas de regadío y la calidad de agua superficial.

Palabras clave adicionales: agricultura; calidad del agua; contaminación; eutrofización; fertilización.

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Abbreviations used: C_i (phosphorus concentration of day *i*); DF (drainage fraction); ET (crop evapotranspiration); HY (hydrologic year); ID (irrigated dose); IEG (irrigation efficiency global); IRF (irrigation return flows); IS (irrigation season); NIS (non-irrigation season); OCED (Organization for Economic Co-operation and Development); P (phosphorus); PP (particulate phosphorus); Q_i (flow rate of day *i*); SDQ (surface drainage flow); TDP (total dissolved phosphorus); TP_L (total phosphorus load); TP_Y

Introduction

In many areas, organic manure and inorganic fertilizers applied on agricultural lands in high quantities create a nutrient surplus [mainly nitrogen and phosphorus (P)] on soil and, therefore, an increase in their accumulation and/or transfers toward water bodies via hydrological transport process. In irrigated agriculture systems, the irrigation return flows (IRF) are considered as a major non-point contributor to the pollution of surface and groundwater bodies (Aragüés and Tanji, 2003). In Spain, irrigated agriculture uses 68% of total water consumption (FAO, 2009) for 3.2% of the total arable land (MARM, 2009). The potential to generate return flows from this area to receiving water bodies in terms of quantity and quality is considered significant (Aragüés and Tanji, 2003).

Recent research revealed that there is a threshold P level in soil above which P losses tend to increase exponentially (Sande-Fouz, 2005). It is acknowledged that the transport of P is more severe in areas where soil P levels are highest and where the risk of erosion and water movement from soil to surface water is greatest (Van Bochove *et al.*, 2006). The accumulation of bioavailable P in surface water leads to algae proliferation, an increase in oxygen demand, and a deterioration in water quality by eutrophication (Lemunyon and Gilbert, 1993; Sharpley *et al.*, 1993, 1996; Indiati and Sharpley, 1995). This phenomenon starts at P concentrations above 0.02 mg L^{-1} (Champ, 1998). Uunk (1990) considers that eutrophication can begin when P concentrations are between 0.05 and 0.10 mg L^{-1}. Phosphorus non-point sources cannot be submitted to treatment, as is the case with urban waste discharges, so P loaded from agricultural lands to surface aquatic systems can have serious consequences for the environmental water quality of rivers, streams and lakes. For this reason, the eutrophication of surface water induced by non-point P has been a worldwide environmental concern for more than 30 years (Sharpley, 1980; Sims *et al.*, 1998; Sharpley *et al.*, 2003).

Since 1980, P concentrations have diminished in the main European rivers thanks to initiatives such as progress in residual water treatment and use of phosphate-free detergents. However, in the Ebro basin (north-east of Spain), irrigated agriculture is a major component of the hydrologic balance and, therefore, may have a significant impact on the quality of the rivers in this basin. In fact, a reduction in phosphate concentration has been observed since 1989 in the majority of the Ebro's effluents, but this concentration remained high until 2006 (Isidoro and Aragüés, 2007). This shows the need to monitor IRF to evaluate the P losses resulting from such agricultural practices.

In Europe, several directives have established regulations on water quality, such as the Water Framework Directive (EC, 2000), which requires the widespread control of P inputs to rivers to sustain and improve riverine ecology. Levels of P concentrations of 0.07 mg L^{-1} and 0.13 mg L^{-1} are given as indicative in preventing the quality of fresh water from being suitable for fish life of the Salmonic and Cyprinid species, respectively (EC, 2006). In Spain, Directive 75/440/EEC (EC, 1975) imposed a total phosphorus (TP) threshold according to the type and use of water in order to meet ecological requirements for certain water resources. For water type A1 and demanding uses (protection of Salmonic species, bathroom and irrigation), maximum TP concentrations should be about 0.06 mg L^{-1}. Nevertheless, for other uses of water type A1, the limit of TP concentrations is about 0.17 mg L^{-1}. For water type A2 and A3 and all kinds of uses, the limit of TP is 0.30 mg L^{-1}. However, Quebec (Canada) and some states in the USA consider a TP value of 0.03 mg L^{-1} as threshold surface water quality criteria (MENV, 2001). This value is closer to the eutrophication threshold value (0.02 mg L^{-1}) and therefore, surface water quality is more protected. Dechmi *et al.* (2008), cited values above the guide level of 0.17 mg L^{-1} (EC, 1980) in 74% of the controlled drainage network located within the Alto Aragon Irrigation Scheme, Spain. Nevertheless, these studies do not provide firm conclusions regarding P contamination levels. The majority of research carried out in the Middle Ebro River Valley has been conducted to study the volume and quality (mainly salt and nitrates) of IRF for establishing non-point pollution control of irrigated agriculture proposals (Causapé *et al.*, 2004a,b, 2006; Isidoro *et al.*, 2004, 2006; García-Garizábal *et al.*, 2009).

The main objective of this study is to describe P losses in different irrigated areas of the Middle Ebro River Valley (Spain) during the 2007 hydrologic year (HY). The results of this description will provide valuable information on the impact of irrigation practices on P losses and thus to study the P contamination potential related to these practices in the area. A comparison between the non-irrigation season (NIS: October-March) and the irrigation season (IS: April-September) was performed and P loaded from each area considered was calculated. The monitoring of water quality in various production systems is not only important for sustaining agricultural productivity, but also offers opportunities for the timely implementation of corrective measures.

Material and methods

Study area description

The study areas are included within two important irrigation schemes located on the left bank of the Ebro River (between 41° 55' N, 1°15' W and 46° 12' N, 0°13' W) Northeast Spain (Fig. 1). Three areas are included in the Bardenas Irrigation Scheme (D-XIX-6, Lerma Creek and Arba River watersheds) and two in the Alto Aragon Irrigation Scheme (Alcanadre River and La Violada Creek watersheds). Each of the irrigated basins has a gauging station located at its outlet where continuous water flow measurements were performed during the study period. The main characteristics of each basin are presented in Table 1. Lerma (using a sprinkler irrigation system) and D-XIX-6 (using a surface irrigation system) are totally agricultural watersheds. The study areas are characterized by low levels of precipitation, ranging from 305 mm (Alcanadre River watershed) to 423 mm (Lerma irrigated basin). The main wet seasons are spring and fall, whereas the main dry seasons are summer and winter. Crop evapotranspiration values ranged from 545 mm (Lerma irrigated basin) to 834 mm (Arba River watershed). Peaks of evapotranspiration were mainly recorded during the summer months (June-September). The main crops are alfalfa (*Medicago sativa* L.), corn (*Zea mays* L.), winter cereals and vegetables (mainly potato, tomato and pepper). The Middle Ebro River Basin Valley is heterogeneous in terms of geology and topography. The uppermost altitudes are characterized by the presence

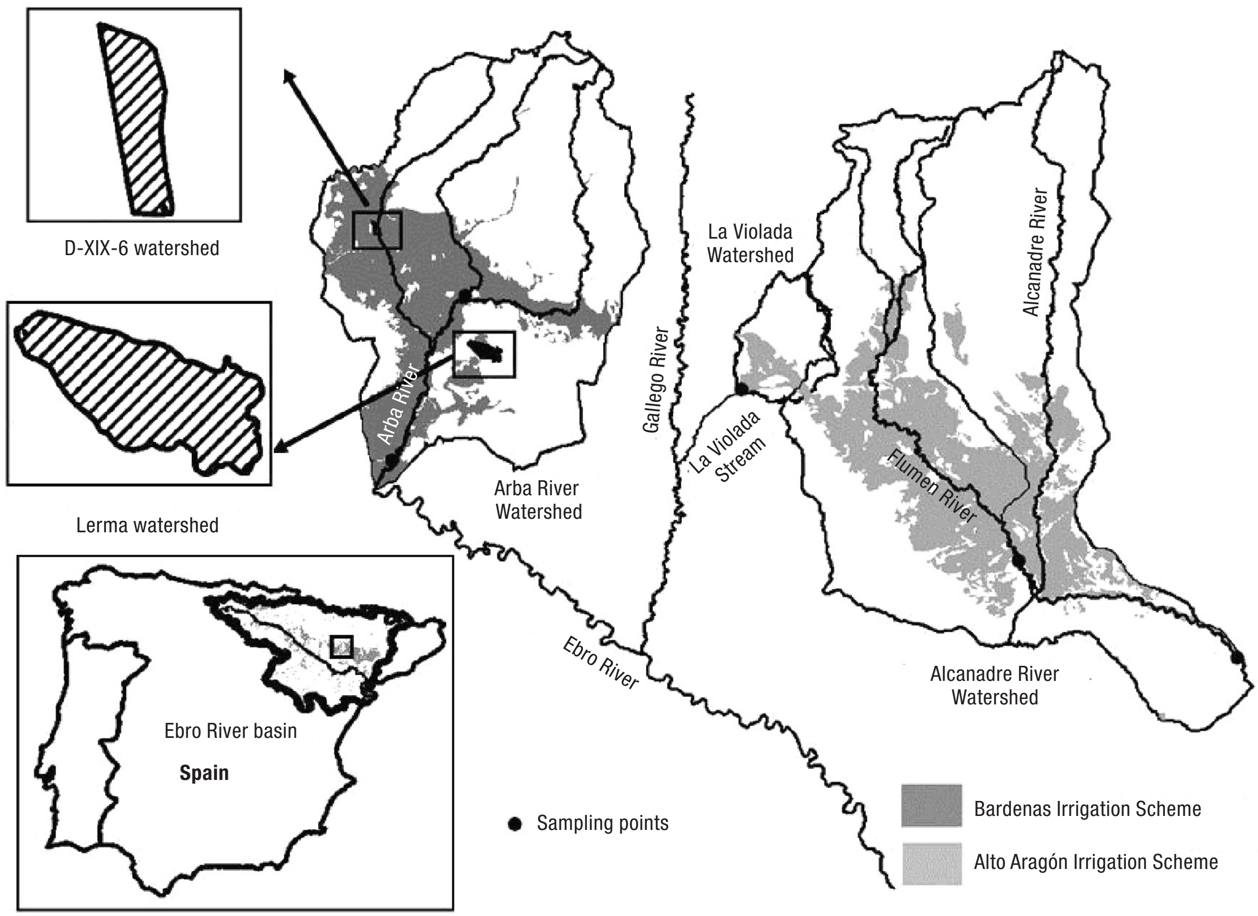

Figure 1. Distribution of the irrigable land in the Ebro River Basin and location of the five watersheds study areas in the middle valley of the Ebro River. The main rivers and gauging stations are also shown.

Table 1. Main characteristics of the study areas grouped by irrigation schemes

Irrigation scheme	**Bardenas I**			**Alto Aragón**	
Study area	**D-XIX-6**	**Lerma**	**Arba**	**La Violada**	**Alcanadre**
Main crops[1]	WC, AL	CO, WC	WC, AL	WC, AL	CO, AL
Total area (ha)	95	752	217,677	5,282	339,061
Total irrigated area (ha)	90	331	57,700	4,013	84,929
P fertilization (kg ha^{-1})	81.2 (AL) 74.4 (WC)	58.7 (CO)	No data	No data	113.0 (CO) 55.3 (AL)
P uptake (kg ha^{-1})	35.3 (AL) 18.6 (WC)	41.7 (CO)	No data	No data	39.0 (CO) 42.1 (AL)
ID (mm)[2]	512	214	534	543	569
Precipitation (mm)	372	423	401	369	305
ET (mm)[3]	733	545	834	614	No data
IEG (%)[4]	80	84	96	76	77-80
SDQ (mm)[5]	469	57	470	527	No data
DF (%)[6]	24	8	6	62	No data

[1] WC: winter cereal; AL: alfalfa; CO: corn. [2] ID: irrigated dose. [3] ET: crop's evapotranspiration. [4] IEG: irrigation efficiency global. [5] SDQ: surface drainage flow. [6] DF: drainage fraction.

of silicic materials, whereas calcareous materials are found at the lowest elevations. The central part of the Ebro River Basin is an evaporitic Tertiary depression of marine origin with a thick layer of gypsum, halite and other salts.

Sampling process and analysis

Water samples were collected weekly in glass bottles (filled completely to minimize changes in pH values due to gas exchange), transported to the laboratory in insulated coolers, and stored at 4°C in the dark until the laboratory analysis. Sampling was conducted at the watershed outlets during the period October 2006-September 2007, except in the case of the Alcanadre River watershed, where the sampling was conducted only during the irrigation season (IS) (April-September 2007). Because the Alcanadre and Arba watersheds cover a very large area, two additional sampling points were considered (Fig. 1). The first one was located at the Arba River in Ejea de los Caballeros (below referred as the Ejea sampling point). The second was located at the Alcanadre watershed in Albalatillo (below referred as the Albalatillo sampling point).

Total dissolved P (TDP), that include both soluble reactive P (thought to be the most bioavailable P fraction) and soluble organic P, was determined on samples filtered through a 0.45 µm membrane filter followed by persulphate digestion in acid media method (Muel, 2007). Total P (TP), include both total dissolved and particulate phosphorus (PP) fractions, was measured on unfiltered, persulphate-digested samples. TDP and TP were determined using a Bran + Luebbe automated analysis AA3 colorimeter. The colorimetric limit detection is 0.0005 mg L^{-1} for both TP and TDP. The PP fraction was calculated as the difference between TP and TDP. For each watershed and water sampling of the day *i*, the P flux was calculated as the product between the flow rate (Q_i) and P concentration (C_i). The resulted phosphorus flux was multiplied by the number of days between two measurements and cumulated to obtain total P losses. All concentrations were expressed in mg L^{-1} of P. For each study area, usual statistic parameters were calculated by month, irrigation season, NIS and hydrological year. The P load per hectare (kg ha^{-1}), was considered as an indicator to compare the P loads between the study areas. The relationships between P concentration and flows and between P fractions were determined. In addition, the percentage of water samples that exceed the concentration thresholds of 0.02, 0.03, 0.06, 0.17 and 0.30 mg L^{-1} in the drainage water of the five sampling points was calculated. Respectively, these values correspond to threshold values for triggering eutrophication effects (Champ, 1998), Quebec surface water quality criteria, and the Directive 75/440/EEC (EC, 1975) threshold requirements on water quality for different uses of water.

Results and discussion

Phosphorus dynamics in water flow

Plots of TP concentration versus flow indicated that, generally, most of the study areas showed increases in TP concentration at higher flows (Fig. 2). La Violada and D-XIX-6 sampling points, showed the best relationship between TP concentrations and flows with R^2 of 0.19 and 0.26 ($p < 0.05$), respectively. Such features have already been observed in rivers draining seven wide-ranging lowland United Kingdom watersheds (Jarvie *et al.*, 2006). In the case of La Violada sampling point, some difference in the temporal relationship between TP and flow compared to the other study areas was showed. First, results indicate less flow variability than may be induced mainly by irrigation canal seepage (CV = 28%). In addition and for four water-sampling dates, dilution features with increasing flow could be explained by substantial irrigation canal discharges operated by La Violada irrigation district. No correlation between TP concentration and flow was found for Tauste and Lerma sampling points (Fig. 2). Nevertheless, for Alcanadre, in which only IS data were available, TP was positively correlated with flow ($R^2 = 0.49$, $p < 0.05$).

In addition, and as shown in previous research performed (Causapé *et al.*, 2006; Isidoro and Aragües, 2007), the considered areas presented irrigation season (IS) average water flow higher than non-irrigation season (NIS), except for the case of Lerma, where irrigation return flows (IRF) were not significant due to the low irrigation dose applied (Table 1). In terms of average seasonal TP value, diffuse sources generate increased concentrations with flow (TP concentration during IS > TP concentration during NIS), except for

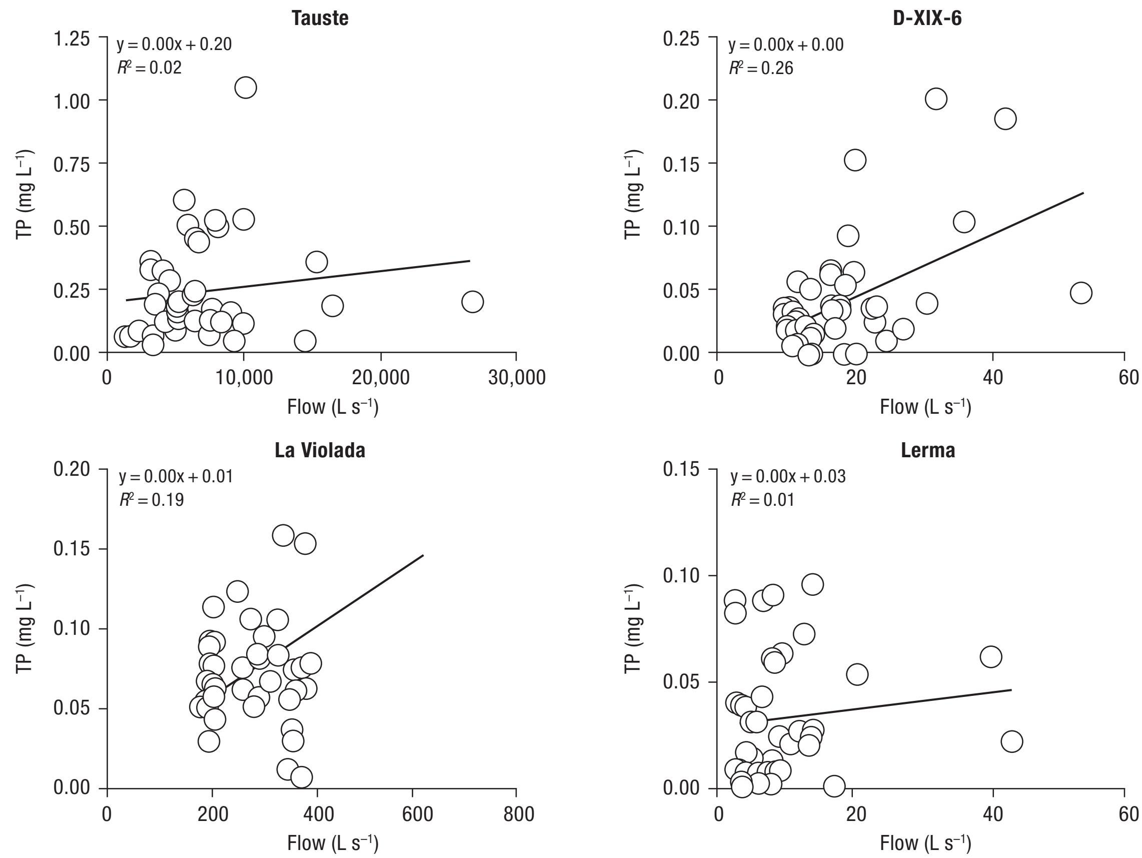

Figure 2. Scatter plots showing relationship between total phosphorus concentration (TP, mg L^{-1}) and river flow (L s^{-1}) measured in Tauste, D-XIX-6, La Violada and Lerma.

Table 2. Average (Ave.), range (maximum ± minimum) and standard deviation (SD) of total phosphorus (TP, µg L^{-1}), total dissolved phosphorus (TDP, µg L^{-1}) and particulate phosphorus (PP, µg L^{-1}) recorded in the study area during the 2007 hydrological year (HY), irrigation season (IS) and non-irrigation season (NIS)

		TP			TDP			PP		
		Ave	Range	SD	Ave	Range	SD	Ave	Range	SD
Arba Tause	IS	237	675 ± 44	151	139	388 ± 18	88	98	567 ± 0	127
	NIS	275	1,067 ± 39	268	157	967 ± 19	144	118	504 ± 2	143
	HY	255	1,067 ± 39	211	147	967 ± 18	111	107	567 ± 0	133
Arba Ejea	IS	75	706 ± 0	138	28	102 ± 0	26	47	655 ± 0	129
	NIS	87	556 ± 0	137	15	92 ± 0	22	73	464 ± 0	121
	HY	80	706 ± 0	136	22	102 ± 0	25	58	655 ± 0	215
La Violada	IS	79	283 ± 8	55	41	111 ± 0	24	39	240 ± 0	46
	NIS	71	122 ± 28	24	54	108 ± 8	24	18	50 ± 0	15
	HY	76	283 ± 8	43	46	111 ± 0	25	29	240 ± 0	37
Lerma	IS	48	97 ± 0	29	29	77 ± 0	22	19	54 ± 0	18
	NIS	13	53 ± 0	14	6	32 ± 0	8	7	39 ± 0	10
	HY	32	97 ± 0	29	18	77 ± 0	21	13	54 ± 0	16
D-XIX-6	IS	62	203 ± 0	54	49	191 ± 0	48	13	121 ± 0	25
	NIS	21	68 ± 0	17	17	62 ± 0	15	4	17 ± 0	5
	HY	43	203 ± 0	46	35	191 ± 0	40	9	121 ± 0	19
Alcanadre Ballobar	IS	98	146 ± 46	36	71	111 ± 40	31	28	80 ± 2	28
Alcanadre Albalatillo	IS	112	133 ± 76	18	89	122 ± 67	23	23	63 ± 0	26

Tauste, where the TP concentration was slightly diluted during the IS (Table 2). In this watershed and during the NIS, a significant positive relationship between PP concentrations and flows was showed ($R^2 = 0.20$, $p < 0.05$).

Phosphorus concentrations

Table 2 shows that P concentrations varied widely among and within watersheds. The average TP concentration ranged from 0.03 mg L^{-1} to 0.25 mg L^{-1} and total dissolved phosphorus (TDP) being the dominant form, except for Arba River watershed at the Ejea sampling point. Those values exceeded the critical values for triggering eutrophication effects (0.02 mg L^{-1}). However, those average TDP values were lower than at the Tajeria and Latxaga watersheds (Navarre, North Spain) in which values of 0.24 and 0.16 mg L^{-1}were recorded, respectively (Casali *et al.*, 2008, 2010). The TP recorded and the resulting TDP/PP ratio reveal the diversity of soil P patterns and P transport processes in the study areas. The lowest TDP/PP ratio (0.4) was recorded in the Arba River at the Ejea sampling point, while the highest one (3.9) was recorded at the D-XIX-6 watershed. This difference indicates the specificity of P transport process in those areas. The Tauste, La Violada and Lerma sampling points showed similar annual TDP/PP ratios (1.4, 1.6 and 1.4, respectively) and different ones during the NIS (1.3, 3.0 and 0.9, respectively).

Both Arba and Alcanadre watersheds were not similar with regard to land use and the amount of annual precipitation (Table 1). This may explain part of the difference in P concentrations recorded. The Lerma irrigated area was 3.7 greater than the D-XIX-6 area, but its TP average concentration was 1.3 less. In this case, the effects of irrigation systems can mainly explain TP concentration trends. Sprinkler irrigation systems generate less IRF (9.8 L s^{-1} at the Lerma sampling point) than surface irrigation systems (18.3 L s^{-1} at D-XIX-6 sampling point) because of better sprinkler irrigation efficiency. In addition, a low irrigation dose was applied in Lerma during the study period (Table 1).

Furthermore, the water trophic state was determined using the Organisation for Economic Co-operation and Development classification (OECD, 1982). With regard to annual average TP, water was classified as hypereutrophic (TP > 0.1 mg L^{-1}) only for Arba at Tauste. Lerma water was mesotrophic (0.010 > TP < 0.035 mg L^{-1}) and the rest of the sampling points were classified as eutrophic ($0.035 > TP < 0.100$ mg L^{-1}). In terms of average seasonal TP concentrations, Arba at both Tauste and Ejea sampling points and La Violada showed the same trophic state, during both IS and NIS, as the annual values. Therefore, a change in annual trophic class was observed during IS for Lerma (Eutrophic) and NIS for D-XIX-6 (Mesotrophic). For the Alcanadre IRF at the Albalatillo sampling point water was Hypereutrophic, although at Ballobar water was Eutrophic.

Arba River

At the Ejea sampling point, the highest total phosphorus (TP) concentration, which reached a value of 0.706 mg L$^{-1,}$ was recorded in April following two days of rainfall (total precipitation = 68 mm). In this case, particulate phosphorus (PP) represented 93% of TP measured (TDP = 0.051 mg L^{-1} *vs.* PP = 0.655 mg L^{-1}) indicating that soil P saturation was high and overland flow was the main transport factor. Moreover, if Champ (1998) restrictive criterion was considered, which acknowledges that eutrophication can begin with a concentration of 0.02 mg L^{-1} P, 73% of the analyzed water samples surpass this potential risk threshold (Table 3). In addition, it was found that more than 30% of water samples did not meet Directive 75/440/EEC (EC, 1975) ecological requirements for water type A1 (Table 3).

During the NIS, 79% of water samples presented PP as the dominant P form, while during the IS presented only 40%. Results also indicate that the average TP concentration during the NIS was higher than the IS (0.087 mg L^{-1} *vs.* 0.075 mg L^{-1}). Considering the whole year, results indicate that 57% of TP water concentration was recorded in the particulate fraction. This may be explained by the fact that over 85% of the total area drained at the Ejea measurement point was uncultivated and, thus, soil was exposed to water erosion induced by rainfall-runoff events (total annual precipitation = 401 mm, Table 1). As shown in Figure 3a, the monthly average P released in water flow does not present a clear temporal trend. During NIS, dominant values were in particulate form, except for December. The lowest monthly TP average concentration took place in January (0.014 mg L^{-1}) and July (0.015 mg L^{-1}). The highest average monthly TP concentration occurred in October (0.244 mg L^{-1}) and April (0.209 mg L^{-1}) for NIS and IS periods, respectively. Both values corresponded to water with a significant eutrophication risk (TP concentration > 0.02 mg L^{-1}) in which particulate form represents the dominant P form.

At the Tauste sampling point, the drainage water becomes more enriched by P (Fig. 3b). The maximum monthly average value was reached during the month of March (0.471 mg L^{-1}) and a clear decrease was observed during the IS, due probably to the decrease of irrigation return flows (IRF). The lowest TP concentrations were obtained during January and correspond to the lowest water flow measured at this point (2.29 m^3 s^{-1}). The annual average TP concentration was 3.2 times higher than the upstream sampling point of Ejea (Table 2). Moreover, TDP was the dominant P form (TDP=0.147 mg L^{-1} and PP = 0.107 mg L^{-1}) (Table 2). As far as the effect of irrigation is concerned, the surplus of irrigation water during the IS provokes the drainage water dilution process, reducing its TP content. In spite of this dilution, IRF still have a high TP concentration, with an average monthly concentration of 0.237 mg L^{-1} during the IS, a value that is very close to the annual

Table 3. Percentage of water samples that exceed the total phosphorus concentration (TP) threshold of 0.02, 0.03, 0.06, 0.017 and 0.30 mg L^{-1} in the study areas

	TP threshold (mg L^{-1})				
	0.02	**0.03**	**0.06**	**0.17**	**0.30**
Arba in Tauste[1]	100	100	91	52	30
Arba in Ejea[1]	73	64	32	7	7
La Violada[1]	96	91	67	2	0
Lerma[1]	52	39	23	0	0
D-XIX-6[1]	67	52	19	5	0
Alcanadre in Ballobar[2]	100	100	89	0	0
Alcanadre in Albalatillo[2]	100	100	100	0	0

[1] Hydrological year. [2] Irrigation season.

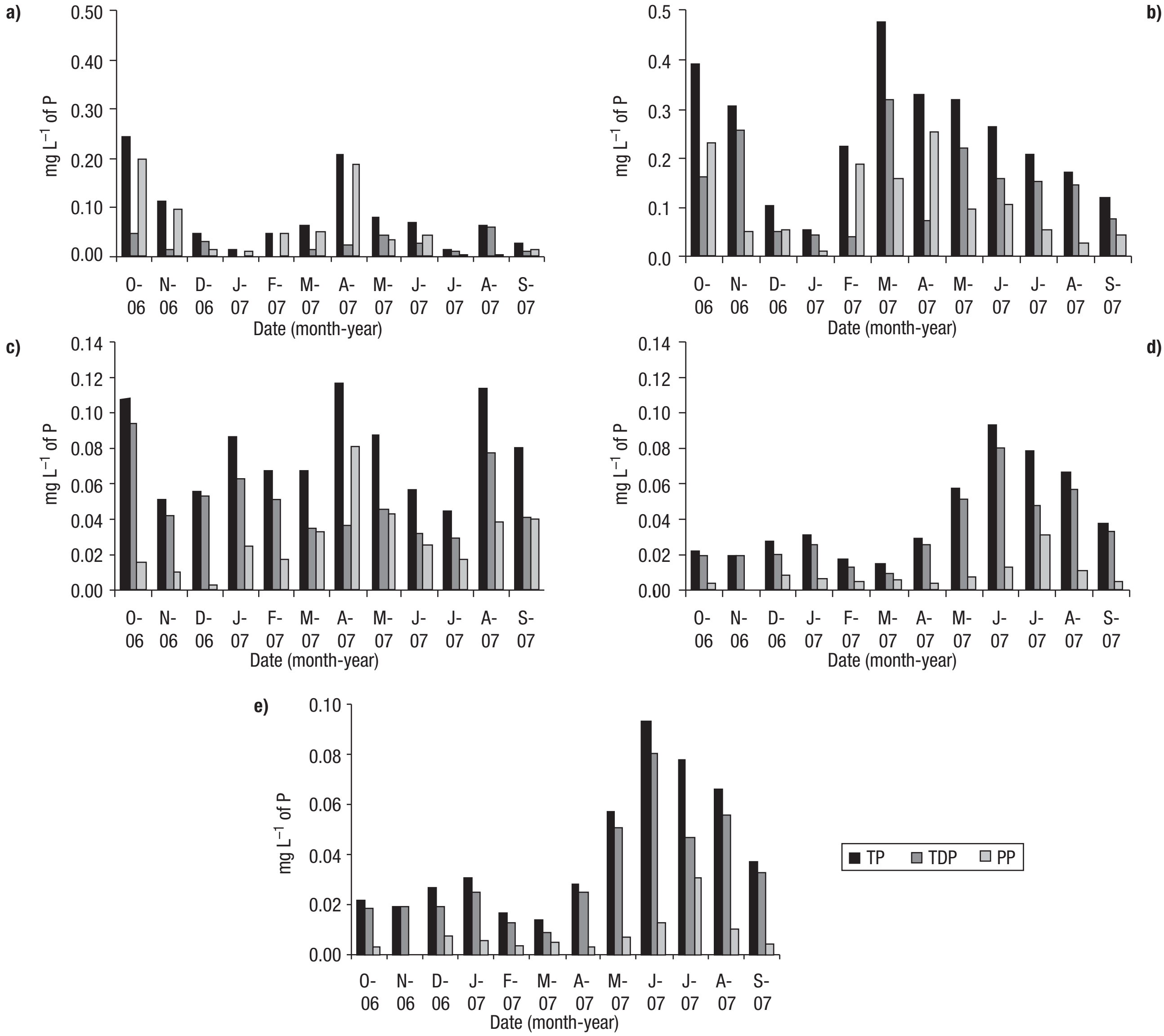

Figure 3. Evolution of average monthly concentration of total phosphorus (TP), total dissolved phosphorus (TDP) and particulate phosphorus (PP) in (a) Ejea, (b)Tauste, (c) La Violada, (d) Lerma and (e) DXIX-6 sampling points during the 2007 hydrological year.

mean concentration. However, the surplus of irrigation water does not reduce enough TP concentrations in the watershed outlet at both sampling points (the difference between averages IS and NIS TP was not significant).

Approximately 68% of TP measured in sampled water was recorded in dissolved form, whereas at the Ejea sampling point, 57% of water sampled presented PP as its dominant form. This may be explained by the fact that the Tauste sampling point drains the major cultivated part of the Arba River Watershed (73.4% of total cropped area). Thus, covered soils may reduce the particulate form of P but increase the dissolved form if soil water percolation occurs. In addition, more than 90% of water samples do not meet Directive 75/440/EEC (EC, 1975) ecological requirements for water type A1, and 100% of them exceeded the eutrophication threshold of 0.02 mg L^{-1} (Table 3).

La Violada

The annual average TP concentration was about 0.08 mg L^{-1} (Table 2), surpassing the critical level of eutrophication (0.02 mg L^{-1}). With regard to average monthly

TP distribution, concentrations were also higher, with a significant eutrophication risk especially during October, April and August (TP > 0.1 mg L^{-1}). For the remaining months, average TP concentrations were superior to 0.04 mg L^{-1}. Additionally, TP concentrations did not show a clear seasonal pattern (Fig. 3c) and similar average TP concentrations were recorded during both IS and NIS (Table 2). This indicates high soil P saturation that was continuously transported into the La Violada stream with peaks more accentuated when applications of fertilizers and manures were recent. Moreover, more than 66% of water samples did not meet Directive 75/440/EEC (EC, 1975) ecological requirements for water type A1, and 96% of them exceeded the eutrophication threshold of 0.02 mg L^{-1} (Table 3). It was observed that the TDP represented the dominant P form (74% of TP). However, PP concentration was markedly higher than TDP in April, indicating that P transport occurred mainly with sediments because of intensive rainfall events. In spite of TDP being the dominant P fraction, PP showed a stronger positive correlation with TP ($R^2 = 0.67$, $p < 0.001$) than TDP ($R^2 = 0.29$, $p < 0.001$).

Lerma

The P concentration values showed great variability (CV = 92%), with an average annual concentration of 0.032 mg L^{-1} (Table 2). Both dissolved and particulate phosphorus fractions were significantly correlated with TP ($R^2 = 0.73$ and $R^2 = 0.54$, respectively). However, TDP was the dominant form. It was also found that more than 50%, of analyzed samples showed TP concentrations over the eutrophication threshold of 0.02 mg L^{-1} (Table 3) and mainly recorded during the IS. Figure 3d shows seasonal trends in P concentrations where the highest values of TP were recorded during the IS, with an average concentration of 0.048 mg L^{-1}. However, during the remaining months, except for October when the average TP concentration was about 0.03 mg L^{-1}, TP concentration was very low (< 0.02 mg L^{-1}). The field survey performed in the Lerma irrigated basin indicated that the most fertilized crop during the study period was corn (occupying 65% of the total cultivated area) with an average phosphate application of 58.7 kg P ha^{-1}. In this case, P fertilization was higher than P uptake inducing an average P excess of about 17.0 kg P ha^{-1}. As corn P fertilization inputs in Lerma irrigated basin were mainly concentrated in April (presowing) and in June (side-dress applications), this indicates that the highest P loading was directly related to irrigation management and the timing of fertilizer application.

D-XIX-6

Results indicate that PP concentration was very low, with average annual concentration not exceeding 0.009 mg L^{-1} (Table 2). More than 86% of TP concentrations were recorded in dissolved form. This result was expected because the study zone is a very small basin (95 ha), parcelled in 30 plots, with an average slope of 1% (García-Garizábal *et al.*, 2009) and irrigated with a flood irrigation system. This makes it possible to reduce the soil erosion process. In addition, if Champ (1998) restrictive criterion is considered, 67% of the analyzed water samples surpass this potential threshold of eutrophication risk (Table 3). It was also found that more than 19% of water samples did not meet Directive 75/440/EEC (EC, 1975) ecological requirements for water type A1 (Table 3). Nevertheless, the monthly evolution of the TP concentration was similar to the Lerma irrigated basin (Fig. 3e). This seasonal variability might be coupled with the timing of P inputs as observed in the Lerma irrigated basin. Also, P application efficiency was low for main crops (41% and 25% for alfalfa and winter cereal, respectively).

Alcanadre

At the Albalatillo sampling point, results indicate slight TP concentration variability (CV = 16%). Moreover, the TDP formed the dominant P form. The average seasonal concentration of TP obtained at this point was about 0.112 mg L^{-1}, a very high concentration with a significant eutrophication risk. It was found that 100, 100, 100, 0 and 0% of analyzed samples surpass the 0.02, 0.03, 0.06, 0.17 and 0.30 mg L^{-1} threshold values considered (Table 3). At the Ballobar sampling point, the P concentration evolution did not feature the same profile as we found at Albalatillo (data not shown). Results indicated that the TP concentrations were very high, with an average concentration of 0.098 mg L^{-1}. This value was inferior to that recorded at the Albalatillo sampling point, with a difference of 0.014 mg L^{-1}. This means that the Flumen sub-watershed contributes more to the P than the rest of the Alcanadre river watershed, although the sampling point at Ballobar drains more area (180,581 ha) than at the Albalatillo point (158,481 ha). More than 89% of TP concentration is obtained in the dissolved fraction. This indicates that the erosion process was not very intense in this area during the irrigation season because surface irrigation, which favours P transfer through the subsurface water fluxes, is the dominant irrigation system in the area. It was found that 89% of analyzed samples surpass the Directive 75/440/EEC (EC, 1975) ecological threshold requirements for water type A1 (Table 3). High TP values were mainly affected by the excess of fertilization application and high P soil status. The estimated phosphorus losses represent on average 55% of the total amount applied with fertilization.

Phosphorus exports

Results indicate that both total phosphorus load (TP_L, mass of TP loaded in drainage waters from the whole watershed) and total phosphorus yield (TP_Y, mass of TP yielded per unit surface) at Tauste were the highest values recorded (Table 4). During the IS, the TP_L at Tauste was double that recorded at Ballobar, with important variability in both cases. Moreover, greater variability in the daily TP_L was observed during the IS than the NIS in all the study areas (data not shown). At Tauste 55% of the TP_L exported by the drainage water occurred during the IS (46,249 kg P). The maximum TP_L was recorded in April (29,216 kg P) and the minimum in January (373 kg P). The annual TP_Y in terms of TP was 1,463 g P ha^{-1} and was higher during the IS than the NIS (802 and 661 g P ha^{-1}, respectively). This result was expected since the mean flow recorded during the IS was much higher than the mean flow recorded during the NIS (11,005 and 6,197 L s^{-1}, respectively).

In the case of La Violada watershed, the annual TP_L was 1,722 kg P. Seventy two percent of TP_L exported by the drainage water occurred during the IS (1,235 kg P). The TP_Y from the irrigated land was 429 g P ha^{-1}, exported mainly during the IS (308 g P ha^{-1}). The D-XIX-6 watershed presents a profile of TP_L similar to that of La Violada watershed. The annual amount of TP_L in this watershed was 26 kg P, with 83% of the annual TP_L exported during the IS (22 kg P). The annual TP_Y from the whole D-XIX-6 watershed was 293 g P ha^{-1}, mainly yielded during the IS (244 g P ha^{-1}), whereas during the NIS the TP yielded was 50 g P ha^{-1}. These results support the idea that irrigation contributes to the increase of P loads on irrigated lands.

The amount of TP_L from the Lerma watershed was quite close to the TP_L during the NIS, with values of 9 kg and 7 kg, respectively. The annual TP_Y in this watershed was 49 g P ha^{-1}; this value being the lowest one among all sampled points. The TP_Y during the IS was quite similar to that obtained during the NIS, 28 and 21 g P ha^{-1}, respectively. In the case of the Alcanadre River watershed, the TP_L during the study period was 23,539 kg. Due to the large area of this watershed, the TP_Y was very low (130 g ha^{-1}) compared with the other sampling points (Lerma not included).

The TP_Y is proposed as an indicator to compare the P loads among different geographic boundaries and management. Considering only the Tauste, La Violada and D-XIX-6 data, the annual average P export value was about 0.73 kg P ha^{-1} yr^{-1}. Results indicate that TP_Y values were higher than others reported on non-irrigated agricultural lands and when the watershed is dominated by pasture in central Navarre, Spain (Casali

Table 4. Total phosphorus load (TP_L) and total phosphorus yield (TP_Y) from the Tauste, La Violada, D-XIX-6, Lerma and Alcanadre sampling points

	Tauste	La Violada	D-XIX-6	Lerma	Ballobar
TP_L (kg)					
HY[1]	84,394	1,722	26	16	—
IS[2]	46,249	1,235	22	9	23,539
NIS[3]	38,145	4,867	4	7	—
TP_Y (g h^{-1})					
HY[1]	1,463	429	293	49	—
IS[2]	802	308	244	28	130
NIS[3]	661	121	50	21	—

[1] HY: hydrological year. [2] IS: irrigation season. [3] NIS: non-irrigation season.

et al., 2008, 2010). With regard to agricultural P yield exported in other parts of Europe, Behrendt (2004) reported values varying between 0.19 and 0.36 kg P ha^{-1} in larger watersheds. Also, Kronvang *et al.* (1996) indicated that annual TP loading from diffuse sources was on average 3.5 times greater in Danish agricultural catchments (0.29 kg P ha^{-1}) than in the natural catchments (0.07 kg P ha^{-1}). In this case, the authors reported that the P load increased with the increase of agricultural land. Such a feature was not found in the irrigated agriculture of the Middle Ebro River Valley (Table 1).

Conclusions

This work showed that irrigation return flows induced mainly by low irrigation efficiency pose a great risk of surface water eutrophication. Significant interseasonal and inter-watershed phosphorus concentration variability was observed. Some difference in TP, TDP and yield may account, to some extent, for differences in morphology, land use, management practices (irrigation and fertilization), soil type and P status, irrigation system and erosion potential. All irrigated study areas showed average annual TP concentrations over the 0.02 mg L^{-1} eutrophication limit and TDP was the dominant phosphorus form in almost all drainage waters. Moreover, average TP concentrations obtained during the irrigation season were higher than average TP concentrations obtained during the non-irrigation season, except for the Arba River watershed. The P yield in these basins was higher than in some non-irrigated agricultural watersheds in Spain and other watersheds in Europe.

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