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Impact of sprinkler irrigation management on the Del Reguero river (Spain) II: Phosphorus mass balance

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ABSTRACT

In an earlier study, irrigation water use in the Del Reguero watershed (DRW) was assessed using various water management indices. In this study, the phosphorus (P) transport dynamics in the irrigation return flows were analyzed. Phosphorus fertilization practices were determined through interviewing farmers, and P loads were monitored from October 2007 to September 2009. In surface drainage waters, the average annual total phosphorus concentration (TP) was 0.112 mg L^{-1}. Total dissolved P (TDP) represented the dominant P form (93% of the TP concentrations) indicating that subsurface flow was the dominant pathway for P transfer. Drainage water was classified as hypertrophic during 2008 and eutrophic during 2009. Fertilizer contributed the most to the final result of P mass balance by contributing 98% of the total P inputs. P crop needs were exceeded by 16% leading to an excess of 43.8 kg P ha^{-1} $year^{-1}$. The exported mass of P was 240 kg in 2008 and 228 kg in 2009, and the TP loss was 205 g P ha^{-1} for 2008 and 195 g P ha^{-1} for 2009. The amount of TP load in the Del Reguero stream was considered small with regard to total phosphorus input (0.23%). However, the amount of TP load in the Del Reguero stream was considered significant in regard to surface water eutrophication. Because the majority of the TP load existed in the dissolved form (TDP = 93% of TP), a large portion of the P losses from the system was available for algae growth, thereby, enhancing eutrophication.

1. Introduction

Phosphorus (P), an essential nutrient for crops and animal production, can accelerate freshwater eutrophication (Carpenter et al., 1998). When the P applied to the agricultural land by means of fertilizers and manure exceeds the removal by harvested crops, repeated applications can lead to an accumulation of P in surface soils (Elrashidi et al., 2005). Soil P accumulation increases the potential transfer of P from agricultural soils through runoff and leaching to surface water and groundwater.

Phosphorus can be transported to surface waters in many forms including orthophosphate, polyphosphates (dissolved form), and P bound to particulate matter (particulate form) (Sharpley and Moyer, 2000). These compounds impact surface water quality by various degrees depending on their bioavailability or the potential for microbial or algae P uptake (Smith et al., 2005). P bound to particulate matter includes P associated to mineral and organic matter. Dissolved P forms constitute 10–40% of the P transported from most cultivated soils to water bodies through runoff (Sharpley et al., 1992).

Generally, most P exported from agricultural watersheds comes from only a small part of the landscape, where hydrological active areas are characterized by high soil P levels (Gburek and Sharpley, 1998; Pionke et al., 1997). Irrigation induces the leaching of P through soil profiles in coarse-textured and stony soils (Condron et al., 2006, 2007). Sharpley et al. (2001) mentioned that an improper irrigation management can induce surface runoff and transport of P adsorbed to eroded particles.

Recently, attention has been focused on the control of agricultural non-point diffuse contamination by phosphorus to minimize surface water degradation. The European Union Water Framework Directive requires achievement of “good ecological status” for all waters of the European Union by 2015 (WFD, 2000). This control should be carried out at a watershed scale to establish a comprehensive overview of water status within the watershed. Further, measures applied to reduce non-point contamination should correlate with the physical characteristics and management practices, including irrigation and fertilization.

In the Ebro River basin (Spain), numerous studies have been carried out to determine the type and levels of non-point pollutants. However, the majority of these studies has focused on agricultural contamination by salts and nitrate (Causapé et al., 2004; Isidoro et al., 2006a,b; Causapé, 2009; García et al., 2009). Few studies have been carried out focusing on diffuse phosphorus contamination. Dechmi et al. (2008), reported values above

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the guide level ($0.17\,\mathrm{mg\,L^{-1}}$) (EU, 1980) in 74% of the controlled drainage network located within the Alto Aragon Irrigation District. Nevertheless, these studies have not reached firm conclusions regarding phosphorus contamination levels. Therefore, it is necessary to conduct more detailed studies with daily control frequency to draw adequate conclusions regarding agricultural contamination by phosphorus.

The objectives of the paper were: 1) to determine the phosphorus concentrations and loads in the Del Reguero stream drainage water; 2) to characterize the P fertilization practices in the Del Reguero watershed; and 3) to quantify the phosphorus mass balance to identify the factors that had the biggest influence on the phosphorus exported mass. A map of the Del Reguero watershed (DRW) location has been presented in the companion paper of this series (Skhiri and Dechmi, 2012).

2. Material and methods

2.1. Phosphorus soil test

In the fall of 2008, a soil survey was performed to determine the plant available phosphorus in soil. Soil samples were taken from 0.3 to 1.2 m when possible. A total of 92 samples were collected from 28 representative plots, and the Olsen P concentration was determined in the laboratory (Olsen et al., 1954). Two other soil sampling surveys were performed in 2009 in the same plots to determine soil Olsen P evolution before and after the irrigation season. In this case, only a depth of 0.3 m was considered. For each plot, the potential risk of phosphorus loss in runoff was determined using the empirical curve number method (USDA-NRCS, 1989). This method depends on soil drainage class, hydrological conditions, land use, and management of the land use. The drainage class of each plot was determined based on the texture and rate of infiltration. In all cases, the hydrologic condition was considered to be good because the area is cultivated under irrigation. The curve number (CN) value of each plot was overlapped with the slope value of the same plot, and the potential risk of P loss in runoff was determined following the matrix as previously proposed by Beaudet et al. (1998).

2.2. Water sampling process and analysis

Irrigation return flows were measured at a gauging station (41°54′N, 0°06′W), located at the outlet of the watershed near the village of Peralta de Alcofea, as part of the combined return and normal runoff. The streamflow was measured once a day at the same hour (12 clocks). Water samples were automatically collected once a day using an automatic water sampler (ISCO 3700C). Three P forms were analyzed as follows: total P (TP), total dissolved P (TDP), and particulate P (P_P). Additional water sampling was manually performed once every three weeks to determine the suspended solids (SS). The sampling period was from October 2007 to September 2009 (two hydrological years). The TDP (on filtered samples using a 0.45-μm filter) and TP (on unfiltered samples) were colorimetrically analyzed following an acid persulfate digestion. The TDP concentrations included both soluble reactive P, which is thought to be the most bioavailable P fraction (Reynolds and Davies, 2001), and soluble organic P. The TP concentrations included the TDP and P_P fractions. The particulate P fraction was determined as the difference between the TP and TDP in water samples. The colorimetric limit detection was $0.001\,\mathrm{mg\,L^{-1}}$ for both TP and TDP. All concentrations were expressed as $\mathrm{mg\,L^{-1}}$ of P. Usual statistical parameters were calculated on a daily basis for the irrigation season (IS), non-irrigation season (NIS), and hydrological year (HY). The relationships between TP concentrations and streamflows and between TP concentrations and P fractions were determined. Moreover, the percentage of water samples with TP concentrations exceeding $0.02\,\mathrm{mg\,L^{-1}}$, $0.03\,\mathrm{mg\,L^{-1}}$, $0.06\,\mathrm{mg\,L^{-1}}$, $0.17\,\mathrm{mg\,L^{-1}}$, and $0.30\,\mathrm{mg\,L^{-1}}$ was calculated. These values corresponded to the beginning of the eutrophication phenomena (Sande, 2005), Quebec surface water criteria (MENV, 2001), and the Directive 75/440/EEC (EU, 1975) threshold requirements on water quality for different uses of water. Moreover, the relationships between TP concentrations and streamflows during storm events were also analyzed. The storm events considered in this case represent precipitation events which result in a total measured precipitation accumulation equal or greater than 14 mm of rainfall.

2.3. Phosphorus mass balance

The P mass balance was performed for the 2008 and 2009 hydrological years considering the most important inputs and outputs of P in the watershed. The P mass balance was calculated assigning P concentrations to each of the water balance components carried out in the first part of this study (Skhiri and Dechmi, 2012). Evapotranspiration and losses due to evaporation and wind drift in the sprinkler irrigation system were considered P-free. Therefore, these losses were not considered in P mass balance calculation. A phosphorus mass for each water balance component was calculated by multiplying the P concentration by the corresponding water volumes. In addition, P mass balance included fertilizers (mineral and organic) as an input into the system and the amount of P extracted by crops as P output from the system (Eq. (1)). The phosphorus mass balance was calculated with the following formula:

$$\Delta P = (P_{\mathrm{I}} + P_{\mathrm{P}} + P_{\mathrm{MW}} + P_{\mathrm{FC}} + P_{\mathrm{OF}} + P_{\mathrm{MF}}) - (P_{\mathrm{SO}} + P_{\mathrm{H}}) \tag{1}$$

where P_I is the P mass in irrigation water; P_P is the P mass in precipitation; P_{MW} is the P mass in municipal wastewaters; P_{FC} is the P mass in filter cleaning waters; P_{OF} is the P mass in organic fertilizers; P_{MF} is the P mass in mineral fertilizers; P_{SO} is the P mass from the surface drainage outflows; and P_H is the P mass from harvested biomass.

The phosphorus concentrations in irrigation and filter cleaning waters were determined in water samples taken from the Pertusa canal during the study period ($P_I = P_{FC} = 0.001\,\mathrm{mg\,L^{-1}}$, 10 samples). The phosphorus concentration in precipitation waters was obtained in water samples collected by a pluviometer located in the study area ($P_P = 0.148\,\mathrm{mg\,L^{-1}}$, 5 samples). This value is high but lower than those found in some States of America (Root et al., 2004). Concentrations of P in municipal wastewater were determined in water samples taken from the discharging tube ($P_{MW} = 2.320\,\mathrm{mg\,L^{-1}}$, 3 samples).

The amounts of P contained in organic (P_{OF}) and inorganic (P_{FM}) fertilizers were determined by interviewing farmers during the 2008 and 2009 agricultural season. For each application of P fertilizer to each crop, the mean amount of P and mean application dates were determined (Table 1). Multiplying the quantity of total P fertilizer applied per hectare to a given crop by the area of the crop gave the total quantity of P applied for that crop (Table 1). This calculation was repeated for all crops to obtain the total P applied in the entire watershed. The P use efficiency was also calculated as the ratio between P in harvested plants and P inputs (Chen et al., 2008).

The daily P loads in the drainage waters (P_{SO}) were calculated from the TP concentrations and daily mean streamflows measured at the monitoring station. Total dissolved P loads are commonly coupled to subsurface outflows. The crop P uptakes (P_H) were estimated from mean annual yields gathered from field surveys, surface area of different crops, and P content of the crops (CFI, 1998; Fixen and Garcia, 2006; MAPA, 2007).

Table 1
Average date of application and average amount of P fertilizer applied (PA, kg ha^{-1}) in each application for each crop in the Del Reguero watershed during the 2008 and 2009 hydrological years. Total amount of P fertilizer applied (total, kg ha^{-1}) was also calculated. The percentage of P fertilizer amount consumed by each crop is also presented.

Crop (ha)	Manure		Pre-plant		Side-dress				Total
	Date	PA	Date	PA	First		Second		
					Date	PA	Date	PA	
2008									
Alfalfa (212)	–	–	–	–	05/15	24	07/15	8	32 (9%)
Corn (405)	03/15	46	04/22	54	–	–	–	–	100 (72%)
Barley (620)	–	–	12/01	41	–	–	–	–	41 (14%)
Sunflower (32)	06/15	25	–	–	–	–	–	–	25 (5%)
2009									
Alfalfa (198)	–	–	–	–	02/20	38	06/07	30	68 (16%)
Corn (480)	02/17	41	04/14	54	–	–	–	–	95 (64%)
Barley (634)	–	–	10/30	59	–	–	–	–	59 (18%)
Sunflower (52)	04/29	20	–	–	–	–	–	–	20 (2%)

3. Results and discussion

3.1. Soil phosphorus test

Results indicate that in general, soil P-Olsen concentrations were very heterogeneous ranging from 5 to 137 mg kg^{-1} in the surface layer (0–30 cm) with an average of 28.0 mg kg^{-1} and standard deviation of 19.3 mg kg^{-1} (Fig. 1). Similar findings about P-Olsen heterogeneity were also reported by Stambouli (2008) and Sharpley et al. (1999a,b) in agricultural watersheds. This heterogeneity was due to a combination of different factors including soil type (texture, stoniness, and depth), crop type, irrigation system and mineral and organic fertilization (Stambouli, 2008). The average P-Olsen concentration in the soil decreased with increasing soil depth (Fig. 1). The highest average P-Olsen concentrations for each type of soil were obtained in the surface layer (0–30 cm). This was due to the low mobility of P in the soil (Haygarth and Jarvis, 1999) and/or the P fertilizer application method (Stambouli, 2008). The combination of those factors results in P surpluses on farms and buildup of P to excessive levels in surface soil layers.

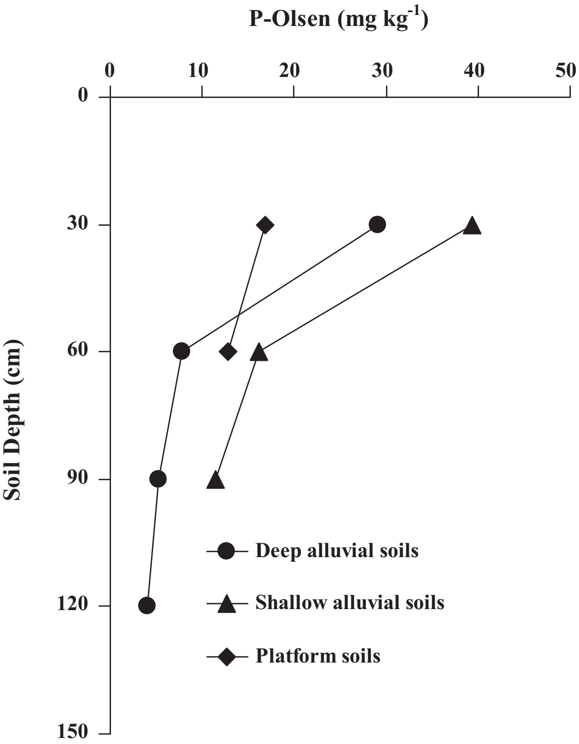

Fig. 1. Variation of average P-Olsen concentration with soil depth for each type of soil in Del Reguero watershed.

Platform soils presented the lowest average P-Olsen content in the layer 0–30 cm (ranging from 5.0 to 27.0 mg kg^{-1}, with an average of 16.9 mg kg^{-1}). In addition, no significant difference ($P < 0.05$) was found between average P-Olsen concentration in layers 0–30 and 30–60 cm (16.9 mg kg^{-1} vs. 12.9 mg kg^{-1}). This indicates that there is a transfer of P from the soil profile to the subsoil, mainly due to presence of stones (20% on volume in average) that induce macropore and preferential transfer pathways.

The highest average P-Olsen content (39.3 mg kg^{-1}) was measured in shallow alluvial soils at layer 0–30 cm (Table 2). For this soil type, no significant difference ($P < 0.05$) was found between average P-Olsen content in the different layers. This indicates that there is a transport from upper layers towards bottom layers via subsurface flow. Sharpley et al. (2001) cited that the closer the field to the stream, the greater the chance to reach it. This means that shallow alluvial soils could be responsible for a major part of P reaching Del Reguero stream.

Deep alluvial soils presented an average P-Olsen content of 29.1 mg kg^{-1} in the layer 0–30 cm (Table 2). A significant difference ($P < 0.001$) was found between the average P-Olsen concentrations in the layer 0–30 cm and the P-Olsen concentrations in deeper layers. This means that P transport via subsurface flow is not functional, since average P-Olsen concentrations in the deeper layers are the lowest ranging from 4.0 mg kg^{-1} (0.9–1.2 m layer) to 7.8 mg kg^{-1} (0.3–0.6 m layer). Sharpley et al. (1981) and Sharpley (1985) showed that the Effective Depth of Interaction (Zhang and Zhang, 2009) increased with an increase in soil slope. As an example, the effective depth of interaction between surface soil and runoff increased from 2.21 to 6.02 mm when soil slope was increased from 4 to 8% (Sharpley et al., 1981). In our study zone, 48 and 25% of deep alluvial soils surface have slopes ranging from 2 to 4% and from 4 to 8%, respectively. This characteristic induces the transport of P via surface runoff and erosion following an intense rainfall or irrigation events.

Fig. 2 shows the evolution of Olsen P concentrations in alfalfa, corn, sunflower, and barley plots between March 19, 2009 (a few days before the beginning the IS) and November 16, 2009 (more than one month after the end of the IS). The alfalfa, corn, and sunflower plots showed a decrease in the average Olsen P concentrations by 1 mg kg^{-1}, 4 mg kg^{-1}, and 5 mg kg^{-1}, respectively. However, the barley fields had an increase in soil Olsen P concentration by 4 mg kg^{-1}. With regard to the barley fields, the increase of the Olsen P concentration was expected because the same surveyed fields were fertilized and sown with the same crop several days before performing the soil sampling on November 16, 2009.

Table 2
P-Olsen concentrations mean (mg kg^{-1}), minimum (Min, mg kg^{-1}), maximum (Max, mg kg^{-1}), median (mg kg^{-1}), and coefficient of variation (CV, %) of each soil type (platform, shallow alluvial and deep alluvial soils) by 0.3 m layers.

	Soil type								
	Platform		Shallow alluvial			Deep alluvial			
	0–0.3	0.3–0.6	0–0.3	0.3–0.6	0.6–0.9	0–0.3	0.3–0.6	0.6–0.9	0.9–1.2
Mean	16.9	12.9	39.3	16.2	11.5	29.1	7.8	5.2	4.0
Min.	5.0	2.0	6.0	3.0	3.0	8.0	3.0	3.0	2.0
Max.	27.0	24.0	137.0	45.0	32.0	93.0	20.0	12.0	8.0
Median	18.0	12.0	18.0	5.0	4.0	22.0	7.0	5.0	3.0
CV	28	34	37	42	39	24	24	21	22

The decreases in soil Olsen P content in alfalfa, corn, and sunflower plots were attributed: crop P uptake; P loss through the processes of dissolution, incidental transfers, or physical transfers (Haygarth and Sharpley, 2000); and P fixation or retention processes (White, 1981; Barrow, 1987, 1987).

Using the agronomic interpretation of soil Olsen P concentrations as previously proposed by López Ritas (1978), all sampled fields presented high Olsen P concentrations in the 0–30 cm soil layer (25 mg kg^{-1} < Olsen P < 34 mg kg^{-1}). For these fields with an excessive Olsen P concentration (exceeding 20 mg kg^{-1}), extra P input by fertilizer will increase P runoff and leaching instead of crop production (Sharpley et al., 1999a,b). Soils with high Olsen P concentrations are more likely to transfer P to surface waters. However, a soil test alone is a poor indicator of the risk of P transfer (Beauchemin et al., 1997; Hooda et al., 2000). The combination of the curve number (USDA-NRCS, 1989) with the field slope values allowed the potential risk of P loss in runoff in each field to be calculated (Beaudet et al., 1998). Most plots occupied by corn presented a moderate or a high risk of P loss in runoff, and all alfalfa plots showed a low risk of P loss in runoff.

3.2. Phosphorus fertilization management

Table 1 shows the average date (d) of application and mean amount of phosphorus applied (PA) in each fertilizer application for the main crops during the 2008 and 2009 hydrological years. The P fertilization dates were variable among crops and years. The majority of farmers in the DRW applied solid and liquid P fertilizers on the soil surface. Moreover, the dates of P applications were mainly concentrated in the spring and summer months during ecologically sensitive periods (Withers and Hodgkinson, 2009). During these periods, the biological activity of some species, such as salmon, is at its highest activity.

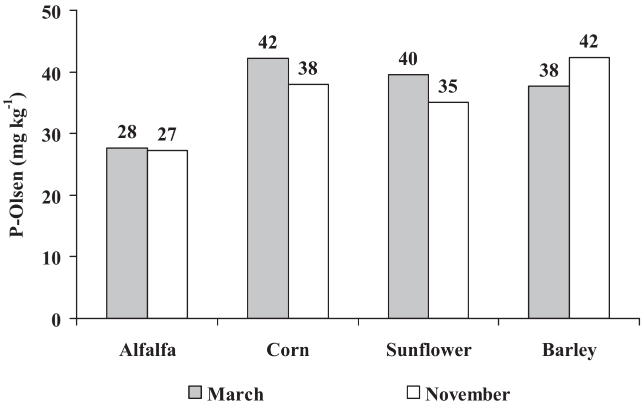

Fig. 2. Average P-Olsen concentration in alfalfa, corn, sunflower and barley plots in March/19/2009 and November/16/2009.

In all surveyed plots, alfalfa has more than one year stand. Therefore, the results shown in Table 1 do not show manure and preplant P fertilizer applications. Two P fertilizer applications were applied during the alfalfa growing season: one in spring and the other in summer. For corn, the common practice was to apply P organic fertilizers in late February or early March and to apply preplant P mineral fertilizers several days before sowing during the month of April. With regard to the fertilizer regime for corn fields, there was a high risk of P loss because P was applied to the soil surface before sowing (Beaudet et al., 1998). For barley, the dates of fertilizer applications depended on the type of fertilizers applied. If the fertilizer applied was organic (manure or slurry), farmers started fertilizing in the month of October. If the fertilizer applied was mineral, farmers started to fertilize several days before sowing. In both cases, the farmers fertilized early before the beginning of the fall season precipitations. For the sunflower crops, there was only one P fertilization application several days before sowing in the month of April, which presented a high risk of P loss (Beaudet et al., 1998).

The total amount of P fertilizers applied during 2009 was 15.3% higher than the total amount of P fertilizers applied during 2008. This increase was due to the increased amount of P fertilizers applied to alfalfa and barley crops because the areas occupied by these crops were similar during the two study years. As expected, corn was the most fertilized crop (72% and 64% of total P applied in the study area during 2008 and 2009, respectively) followed by barley (14% and 18%) and alfalfa (9% and 16%) (Table 1). Due to the small coverage of sunflower crops, only 5% and 2% of total P applied was applied to sunflower crops in 2008 and 2009, respectively (Table 1).

The crop harvested P (P_{H}) was lower than the P applied with fertilizers (P_{F}) in both years for the main crops, except for alfalfa crops in 2008 and sunflower crops in 2009 (Table 3). Corn and barley phosphorus fertilization more than doubled the calculated crop phosphorus extraction (Mean $P_{\mathrm{H}}/P_{\mathrm{F}} = 0.4$). For corn crop, the farmers applied more P than crop requirements trying to protect the high economic yield of the corn crop. In the case of alfalfa, the P_{F} was lower than the P_{H} in 2008, and the opposite occurred in 2009 even though the crop yields were similar for the two study years. For 2008, the result of P_{F} being lower than the P_{H} was logical because farmers fertilized the alfalfa taking into account the symbiotic fixation of N by the crop. Therefore, the alfalfa fields were not fertilized enough to replace P extractions leading to a $P_{\mathrm{H}}/P_{\mathrm{F}}$ ratio of 1.3. On the contrary, in 2009 alfalfa was over fertilized with a $P_{\mathrm{H}}/P_{\mathrm{F}}$ ratio of 0.5. This was due to the type of fertilizer used to satisfy nitrogen crop needs. In 2008, the type of fertilizer used was 06-09-19, with an average applied dose of 600 kg ha^{-1}. While in 2009, the type of fertilizer used was 08-15-15 with an average applied dose of 800 kg ha^{-1}. The kind of fertilizer and the applied dose have led to an excess in P fertilizer application in 2009. Sunflower crops were well fertilized in 2008 with a $P_{\mathrm{H}}/P_{\mathrm{F}}$ ratio of 0.9 and under fertilized in 2009 with a $P_{\mathrm{H}}/P_{\mathrm{F}}$ ratio of 1.2.

The mean annual P fertilizer application rate in the DRW was approximately 61 kg ha^{-1} year^{-1}. This rate was significantly higher than the rates previously reported in the Pister Hill watershed in

Table 3
Crop phosphorus content (PC) (kg P Mg^{-1}), crop yield (Mg ha^{-1}), P harvested (P_H) (kg ha^{-1}) and P harvested to P fertilization (P_F) ratio (P_H/P_F) of the main irrigated crops in Del Reguero watershed during 2008 and 2009 hydrological years.

Crop	PC	2008			2009		
		Yield	P_H	P_H/P_F	Yield	P_H	P_H/P_F
Alfalfa	2.90	14.0	41	1.3	12.4	36	0.5
Corn	2.98	11.9	35	0.4	13.5	40	0.4
Barley	3.35	6.2	21	0.5	5.3	18	0.3
Sunflower	7.74	3.0	23	0.9	3.0	23	1.2

the UK (26.0 kg ha^{-1} year^{-1}), which is mostly covered by grassland (Heathwaite and Dils, 2000), and in the North Wyke watershed in the UK (16.0 kg ha^{-1} year^{-1}) (Haygarth and Jarvis, 1999). An environmentally significant fraction of the annual fertilizer input is lost as incidental P in areas where rainfall closely follows fertilizer application (two days on average). Heathwaite and Dils (2000) reported high TP loss (maximum 2.2 mg L^{-1}) in storm generated runoff that occurred 2 days after the application of dirty water (derived from cattle slurry).

3.3. Phosphorus concentration pattern

Table 4 summarizes the main statistical parameters including the TP, TDP, and P_P concentrations measured in the Del Reguero stream in the IS (October to March) and NIS (April to September) during the 2008 and 2009 hydrological years. The annual average TP, TDP, and P_P concentrations were 0.112 mg L^{-1}, 0.102 mg L^{-1}, and 0.011 mg L^{-1}, respectively. Daily evolution of the TP, TDP, and P_P concentrations (Fig. 3) showed high variability (CV = 106%, 105%, and 416% for TP, TDP, and P_P, respectively), which may reflect the effect of rainfall duration and intensity on the magnitude of surface runoff and, therefore, P dynamics (Heathwaite and Dils, 2000). Moreover, 71% of the study area was irrigated by sprinkler irrigation systems, which applied water as rainfall and, thus, may induce the transport of P towards the Del Reguero stream.

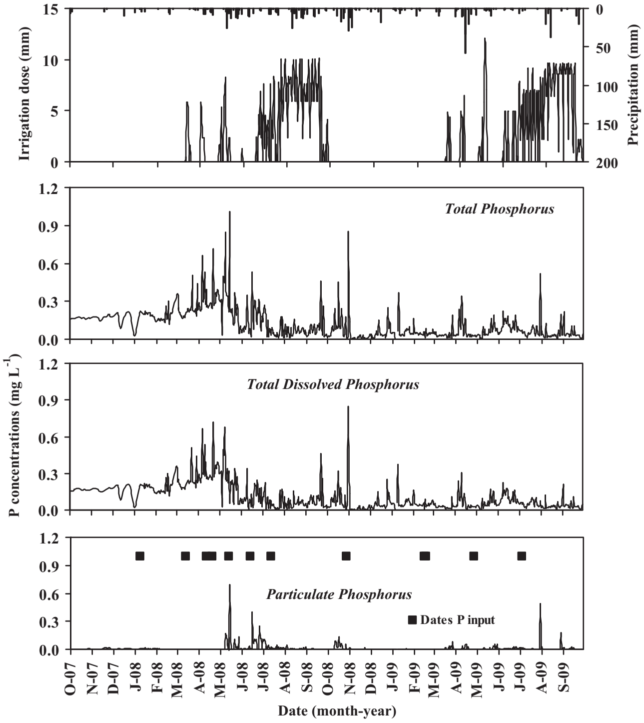

Fig. 3. Temporal pattern of (a) total phosphorus (TP), (b) total dissolved phosphorus (TDP) and (c) particulate phosphorus (P_P) concentrations in the Del Reguero stream during the period of October 2007 to September 2009. Precipitation (a), irrigation dose (b) and dates of P inputs are also presented (d).

TDP represented the dominant P form and occupied 93% of TP concentrations. A good correlation was observed between TP and TDP ($r = 0.93$ and $n = 643$; $P < 0.01$). Moreover, TDP concentrations were significantly ($P < 0.001$) higher than P_P concentrations for both years. The relatively low correlation found between TP and P_P ($r = 0.45$) was an expected result because a majority of the collected water samples were not turbid (with low suspended solids, SS). The relationship found between P_P and SS was relatively low ($r = 0.46$), which was mainly due to the low sampling frequency of SS (41 samples).

The peaks of TP concentrations not only depended on the rainfall duration and intensity but also on agronomic factors, such as irrigation and fertilization. Total phosphorus peaks were more frequent during spring and autumn (Fig. 3) when compared to the other seasons. In 2008, the maximum TP concentration (TP = 1.01 mg L^{-1}) was observed during the spring, and it matched the beginning of the IS and fertilization applications, reflecting the importance of irrigation (as a transport factor) and fertilization (as a source factor). In this case, P_P represented 69% of the TP measured (TDP = 0.315 mg L^{-1} compared to P_P = 0.695 mg L^{-1}), indicating that soil P saturation was high and overland flow was the main transport factor. During 2009, however, the maximum TP concentration (0.850 mg L^{-1}) was found during the fall following three days of rainfall (total precipitation = 46 mm). In this case, TDP represented 100% of the TP measured; indicating that the soil P saturation was low and that the subsurface flow was probably the only transport factor.

Total phosphorus concentrations recorded during 2008 were significantly ($P < 0.001$) higher than those recorded during 2009. This is mainly due to the effect of rainfall on Del Reguero stream water dilution. In fact, during the 2008 HY the amount of rainfall was 6.92 h m^3, while in 2009 it was 9.47 h m^3. This difference may have caused water dilution resulting in lower values of TP. The average TP concentration in 2008 was approximately three times higher than the average TP concentration registered during 2009 (0.179 mg L^{-1} compared to 0.061 mg L^{-1}, respectively). The difference between the TP concentrations in the IS and NIS was not statistically significant ($P < 0.001$) even though the average TP concentration in the IS (0.118 mg L^{-1}) was higher than the NIS average (0.105 mg L^{-1}). However, the difference between IS and NIS TP averages in each year 2008 and 2009 were statistically significant ($P < 0.001$).

Considering the restrictive criterion that eutrophication can start from the P threshold of 0.02 mg L^{-1} (Sharpley et al., 2001), almost all the water samples analyzed during 2008 and 2009 (97% and 83% of samples, respectively) surpassed this potential risk threshold (Table 5). Similar conclusions were obtained when the water quality criterion from the Environment Ministry of Canada (MENV, 2001) was considered (Table 5). Considering the criterion of the 75/440/EEC Directive (EU, 1975) implemented in Spain by the Ebro Water Plan, which considers that water type A1 used for baths and irrigation should have a P content less than 0.06 mg L^{-1}, 80% of the water samples analyzed during 2008 were unsuited for these

Table 4
Maximum, minimum and average concentration values of total phosphorus (TP, mg L^{-1}), total dissolved phosphorus (TDP, mg L^{-1}) and particulate phosphorus (P_P, mg L^{-1}) for the irrigation seasons (IS), the non-irrigation seasons (NIS), 2008 and 2009 hydrological years (HY). Mean values for the whole study period (2008 + 2009) and coefficient of variation (CV) are also presented.

	2008			2009			2008 + 2009		
	NIS	IS	HY	NIS	IS	HY	NIS	IS	HY
Total phosphorus (TP)									
Max.	0.507	1.010	1.010	0.850	0.520	0.850	0.850	1.010	1.010
Min.	0.023	0.011	0.011	0.000	0.002	0.000	0.000	0.002	0.000
Aver.	0.194	0.171	0.179	0.057	0.065	0.061	0.105	0.118	0.112
Median	0.183	0.110	0.172	0.038	0.042	0.040	0.062	0.070	0.066
CV (%)	30	93	74	150	97	123	96	112	106
Total dissolved phosphorus (TDP)									
Max.	0.507	0.717	0.717	0.850	0.307	0.850	0.850	0.717	0.850
Min.	0.023	0.007	0.007	0.000	0.002	0.000	0.000	0.002	0.000
Aver.	0.192	0.148	0.163	0.052	0.057	0.054	0.101	0.103	0.102
Median	0.182	0.087	0.162	0.037	0.040	0.038	0.058	0.054	0.056
CV (%)	31	94	73	152	86	120	98	111	105
Particulate phosphorus (P_P)									
Max.	0.020	0.695	0.695	0.133	0.485	0.485	0.133	0.695	0.695
Min.	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Aver.	0.002	0.023	0.016	0.005	0.008	0.006	0.004	0.016	0.011
Median	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
CV (%)	188	302	360	345	473	453	346	364	416

uses. In 2009, only 31% of the water samples would have been prohibited for bath and irrigation use. When considering other uses of water type A1, only 51% (2008) and 5% (2009) of the samples were inadequate. Considering a P threshold of 0.30 mg L^{-1}, which restricts the use of water types A2 and A3 for resistant fish species production (EU, 1975), only 12% (2008) and 1% (2009) of the analyzed samples were above of the indicated threshold. In general, waters that flowed through the Del Reguero stream during 2009 were less contaminated.

According to the Organization for Economic Co-operation and Development (OECD), waters that circulated in the stream during 2008 were classified as hypertrophic because they had a mean annual TP concentration higher than 0.100 mg L^{-1} (Olmos García, 2000). During 2009, however, waters were classified as eutrophic because they had a mean annual TP concentration higher than 0.035 mg L^{-1} and lower than 0.100 mg L^{-1} (Olmos García, 2000).

3.4. Phosphorus concentrations and streamflow relationships

Daily and monthly TP and TDP concentrations compared to streamflow are shown in Figs. 4 and 5, respectively. On a daily basis, there was a weak and negative relationship between TP concentrations and streamflow ($r = -0.30$; $P < 0.01$) (Fig. 4A) and between TDP concentrations and streamflow ($r = -0.36$; $P < 0.01$) (Fig. 5A). These relationships were also weak when considering the IS data. The correlation coefficient was −0.31 ($P < 0.01$) between the TP concentrations and streamflow (Fig. 4C) and −0.38 ($P < 0.01$) between TDP concentrations and streamflow (Fig. 5C). The correlation coefficient was −0.72 ($P < 0.01$) between monthly average TP concentrations and monthly average streamflow (Fig. 4D) and −0.72 ($P < 0.01$) between monthly average TDP concentrations and monthly average streamflow (Fig. 5D). In all cases and mainly during the irrigation season, there was an inverse relationship between phosphorus concentration (TP and TDP) and flow, indicating that P concentrations were diluted in higher streamflows. Skhiri and Dechmi (2012) did not find a significant correlation between TP concentrations and flows for several irrigated watersheds except for the Alcanadre watershed where they reported the TP in the IS to be positively and significantly correlated with flow ($r^2 = 0.5$; $P < 0.05$).

However, the dilution effect was not observed when only data of storm events were considered. The TP and flow temporal trends of the storm events studied were similar (Fig. 6A–C). Scatter plots showing the relationships between TP concentrations and streamflow during the three storm events showed strong relationships between the variables (Fig. 6A′, B′, and C′). For storm 1 (45 mm of precipitation in four days), TP concentrations reached a maximum value of 0.358 mg L^{-1} one day before the flow reached its maximum value (Fig. 6A). During storm events 2 and 3, however, TP concentrations reached 0.342 mg L^{-1} and 0.122 mg L^{-1}, respectively, matching the peak streamflow (Fig. 6B and C). Moreover, peak TDP concentrations always took place along with peak streamflow or with peak TP concentrations.

The maximum TP concentrations reached during storm events 1 and 2 were similar even though the peak streamflow was more than four times higher during storm 2 (915 L s^{-1} compared to 226 L s^{-1}), what may have been related to the intensity of rainfall of storm events 1 and 2.

Table 5
Number (N) and percentage (in parentheses, %) of water samples surpassing the thresholds of 0.02, 0.03, 0.06, 0.17 and 0.3 mg L^{-1} of total phosphorus (TP) during 2008 and 2009 hydrological years (HY), irrigation seasons (IS) and non-irrigation seasons (NIS).

Threshold (mg L^{-1})	2008			2009		
	HY	IS	NIS	HY	IS	NIS
N	280	183	97	363	183	180
$N > 0.02$ (Sharpley et al., 2001)	272 (97)	175 (96)	97 (100)	302 (83)	164 (90)	138 (77)
$N > 0.03$ (MENV, 2001)	257 (92)	161 (88)	96 (99)	243 (67)	126 (69)	117 (65)
$N > 0.06$ (EU, 1975)	224 (80)	128 (70)	96 (99)	111 (31)	67 (37)	44 (24)
$N > 0.17$ (EU, 1975)	142 (51)	76 (42)	66 (68)	19 (5)	10 (5)	9 (5)
$N > 0.30$ (EU, 1975)	33 (12)	29 (16)	4 (4)	5 (1)	2 (1)	3 (2)

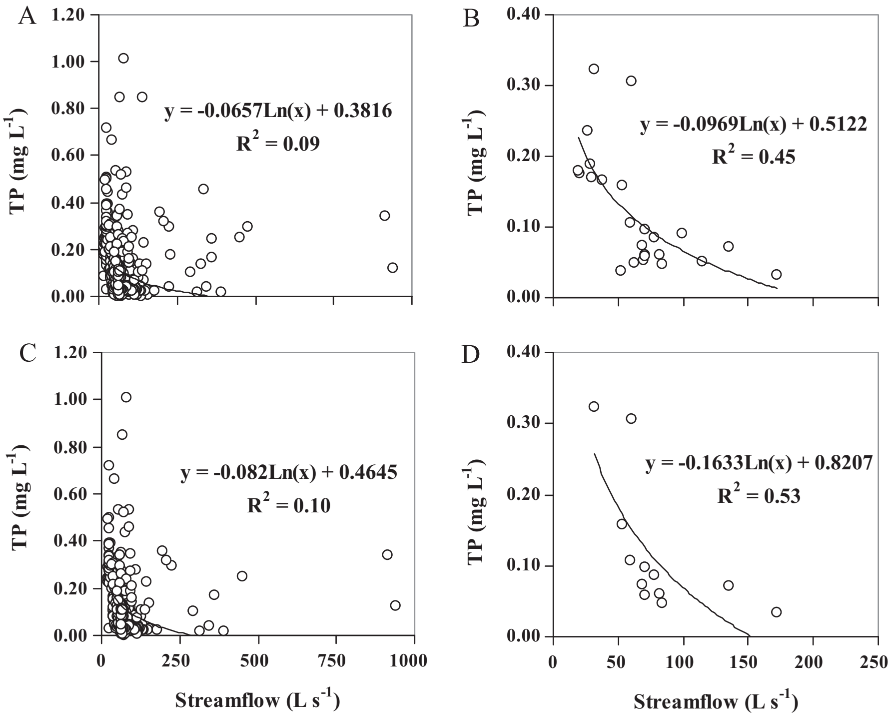

Fig. 4. Scatter plots showing the relationships between daily (A and C) and monthly (B and D) total phosphorus concentrations (TP) and streamflow during the study period. A and B correspond to all recorded period data and C and D correspond to irrigation season data.

3.5. Phosphorus mass balance

Table 6 presents the phosphorus mass balance components for the 2008 and 2009 hydrological years. The largest sources of P inputs in the study area were mineral (P_{MF}) and organic (P_{OF}) fertilizers, which represented 91% and 7%, respectively, of P inputs in 2008 and 92% and 6%, respectively, of P inputs in 2009.

The difference between the inputs and outputs (ΔP) represented the unaccounted terms of the phosphorus balance, such as initial soil P, P fixation processes, or P retention processes (White, 1981; Barrow, 1987). The ΔP value was 57.5 Mg in 2008 and

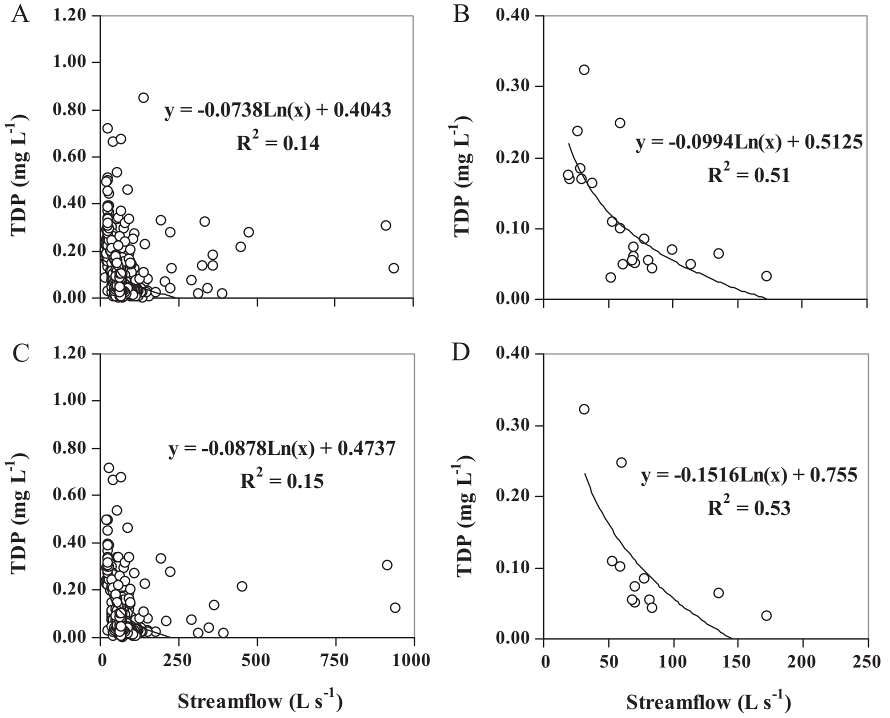

Fig. 5. Scatter plots showing the relationships between daily (A and C) and monthly (B and D) total dissolved phosphorus concentrations (TDP) and stream flow during the study period. A and B correspond to all recorded period data and C and D correspond to irrigation season data.

Table 6
Components of P mass balance: mass of P in irrigation water (P_I), precipitation (P_P), municipal wastewater (P_{MW}), filter cleaning (P_{FC}), organic fertilization (P_{OF}), mineral fertilization (P_{MF}), surface drainage (P_{SO}) and harvest (P_H). Difference between inputs and outputs (ΔP) and mean values are also presented.

HY	Inputs (Mg)						Outputs (Mg)		ΔP (Mg)
	P_I	P_P	P_{MW}	P_{FC}	P_{MF}	P_{OF}	P_{SO}	P_H	
2008	0.01	1.09	0.19	0.01	95.15	7.59	0.24	46.31	57.48
2009	0.01	1.54	0.15	0.01	111.43	7.59	0.23	43.79	76.70
Mean	0.01	1.32	0.17	0.01	103.29	7.59	0.23	45.05	67.09

76.7 Mg in 2009 representing approximately 42% of the average inputs and outputs in both study years. Higher ΔP values have been found in other studies, such as the 49% ΔP value reported in arable watersheds in China (Chen et al., 2008).

The P use efficiency (PUE) (plant harvest P/P input) in the study area was low with a value of 40.6%, which led to a P surplus of 43.8 kg ha^{-1} year^{-1}. Compared to other European countries and non-irrigated agriculture, the PUE in the study area was lower than the PUE in the UK (55.9%) (Withers et al., 2001) and Finland (45.9%) (Antikainen et al., 2005). In these countries and for their different climate characteristics, the main total annual P load occurred in the 2 or 3 months of the year with very high rainfall. Moreover, the annual P surplus for these countries was much lower (15.9 kg ha^{-1} year^{-1} and 12.7 kg ha^{-1} year^{-1} for the UK and Finland, respectively).

3.6. Phosphorus export

Table 7 presents the annual and seasonal TP load (TP_L) and the mass of TP yielded per hectare (TP_Y) calculated for the 2008 and 2009 hydrological years. The daily TP_L ranged between 0.1 kg d^{-1} and 7.2 kg d^{-1} for 2008 (TP_L = 0.66 kg d^{-1} on average) and between 0.0 kg d^{-1} and 27.0 kg d^{-1} for 2009 (TP_L = 0.62 kg d^{-1} on average). The comparison between daily TP loads during the IS and NIS resulted in no significant differences ($P < 0.05$). The annual stream TP loads were 240 kg and 228 kg for 2008 and 2009, respectively. The TP_L values in the DRW were higher than others reported for irrigated agricultural systems of the middle Ebro River Basin, such as the Lerma (16 kg) and D-XIX-6 (26 kg) watersheds, during the 2007 hydrological year (Skhiri and Dechmi, 2011). On the other hand, the TP_L values obtained in the DRW were lower than those calculated

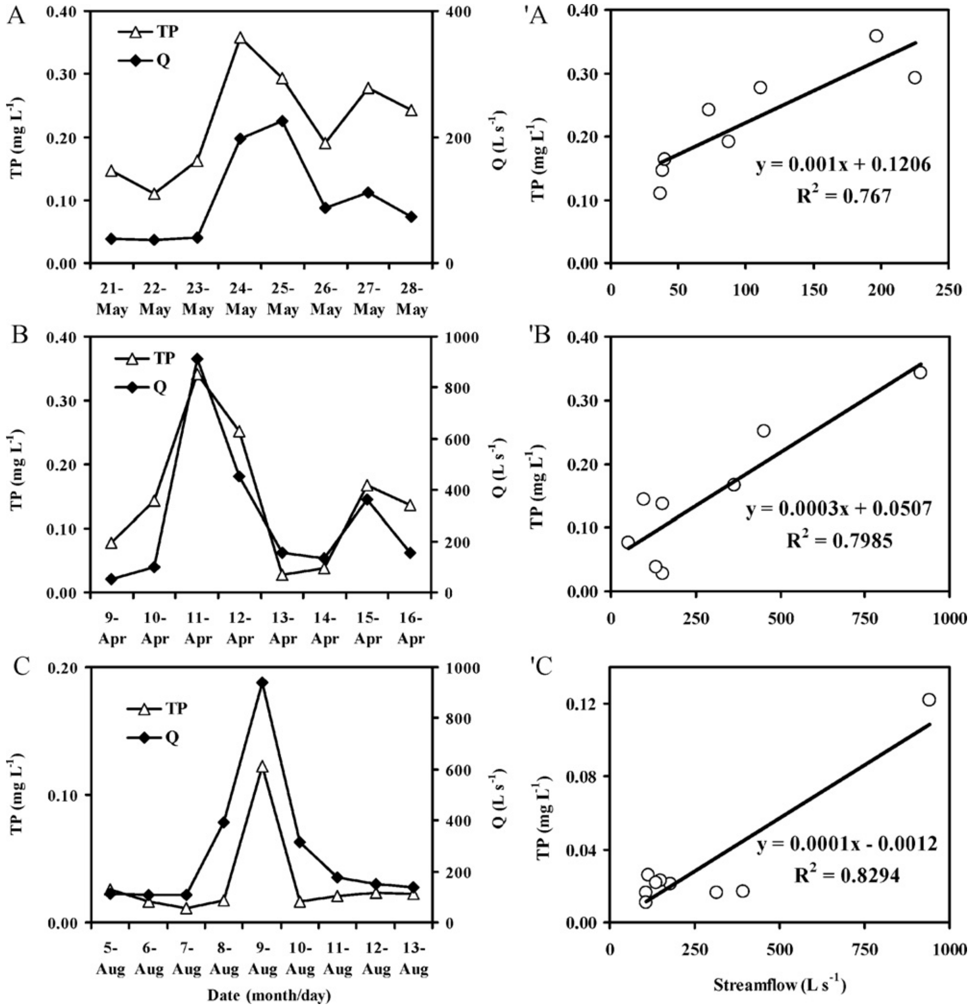

Fig. 6. Evolution of total phosphorus (TP) concentrations and streamflow (Q) during storm events in May 2008 (A), April 2009 (B), and August 2009 (C). Scatter plots between TP and streamflows during storm events in May 2008 (A′), April 2009 (B′) and August 2009 (C′).

Table 7
Total phosphorus load and yield form Del Reguero watershed during 2008 and 2009 hydrological years (HY), the non-irrigation season (NIS) and the irrigation season (IS). Mean values for both years are also presented.

HY	Phosphorus load (kg)			Phosphorus yield (g ha^{-1})		
	IS	NIS	HY	IS	NIS	HY
2008	158	82	240	135	70	205
2009	128	100	228	109	86	195
Mean	143	91	234	122	78	200

for the Tauste river watershed (84,394 kg) and La Violada (1722 kg) watershed during the 2007 hydrological year (Skhiri and Dechmi, 2011). Those watersheds cited as examples have the same soils, crops and climate as DRW. Phosphorus fertilizers are often applied on the soil surface in liquid and solid forms and mainly during the spring and summer months. Second side-dress P fertilizers applications are frequently concentrated during the months of June and July.

The mean TP_L was higher during the IS than the NIS (143 kg and 91 kg, respectively), which was expected because the streamflows recorded during the IS were significantly ($P < 0.01$) higher than those recorded during the NIS for both study years. Moderately strong relationships ($P < 0.01$) between TP_L values and streamflows were observed during 2008 and 2009 (r values of 0.50 and 0.80, respectively). Similar findings were reported by Haggard et al. (2003) in drainage waters of the Ozark Plateau catchment in the US.

Monthly TP_L values were variable with an average of 20 kg. As it has been found in our study and widely reported elsewhere (Kronvang, 1992; Grant et al., 1996; Sharpley et al., 1999a,b; Bechmann et al., 2005; Withers and Hodgkinson, 2009), the majority of TP was exported in a relatively short period (Fig. 7). In fact, 22% and 23% of yearly TP loads were exported during the months of May (2008) and April (2009), respectively. Withers and Hodgkinson (2009) mentioned that P export variation is strongly related to the annual flow variation and that between 60% and 80% of the P loads are typically exported in the two or three months of the year with highest rainfall (e.g., January and April).

The annual TP yields (TP_Y) of the irrigated area were 205 g ha^{-1} and 195 g ha^{-1} for 2008 and 2009, respectively (200 g ha^{-1} on average), and these values were lower than reported for other agricultural watersheds (Kronvang et al., 1995; Grant et al., 1996; Sharpley et al., 1999a,b). A TP_Y of 1,463 g ha^{-1} was found in the Tauste river watershed (Spain) during the 2007 hydrological year (Skhiri and Dechmi, 2011). Drainage TP losses of this order were considered small when compared to the annual net input of P in arable land in most European countries (Sibbesen and Runge-Metzger, 1995). However, these losses were significant with regard to eutrophication of surface water (Grant et al., 1996). Most of the TP yield was in the dissolved form (TDP = 90% of TP), indicating that the TP was available for algal growth in the water receiving bodies and, therefore, enhancing eutrophication (Graneli, 1999; Schernewski, 2003).

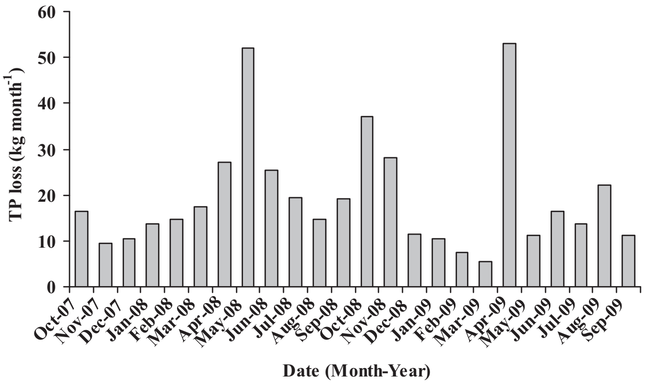

Fig. 7. Monthly total phosphorus loads in drainage water from the Del Reguero watershed during the period from October 2007 to September 2009.

4. Conclusions

Soil phosphorus levels observed in the study area remained above critical values, especially for shallow and deep alluvial soils. In addition, P fertilization management analysis showed that the majority of crops (especially corn) were over-fertilized. This was highlighted by the low P use efficiency. These results pointed to a great risk of increasing P concentrations in drainage waters and, therefore, in receiving water bodies. During the study period, 90% of the total analyzed water samples had TP concentrations over the threshold of eutrophication (0.02 mg L^{-1}) and, therefore, presented a high threat to water quality. Moreover, TDP was the dominant P form (90% of TP), which indicated that the majority of the P losses from the system was available for algae growth, and thereby, enhancing eutrophication. Furthermore, the irrigation return flows were classified as hypertrophic in 2008 and eutrophic in 2009.

TP decreased with increasing streamflow due to water dilution. However, this dilution effect was not observed during storm events (total phosphorus concentrations increased with increasing streamflow). This is due to the fact that during storm events surface flow processes and erosion were dominant and enriched streamflow with phosphorus in dissolved and particulate forms. The phosphorus mass balance showed a residual P in the system (67.09 Mg). The majority of P (61%) was exported during the IS when the flow was dominated by drainage waters. The exported amount of P was considered significant with regard to the eutrophication of surface water.

The sprinkler irrigation system is identified to release significant amounts of phosphorus to receiving water bodies. Fertilizers and irrigation management were identified and should be changed to improve the quality of the irrigation return flows. Many practices can be proposed including rate and method of nutrient application, depth of till, amount of irrigation water applied, time and dose of irrigation. However, their effectiveness in improving water quality at watershed scale should be tested.

Acknowledgments

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