

1 **Sediment and nutrient dynamics during storm events in the Enxoé**
2 **temporary river, southern Portugal**

3

4 Tiago B. Ramos¹ Maria C. Gonçalves^{2,*}, Maria A. Branco², David Brito³, Sara
5 Rodrigues², José-Miguel Sánchez-Pérez^{4,5}, Sabine Sauvage^{4,5}, Ângela Prazeres², José C.
6 Martins², Manuel L. Fernandes², Fernando P. Pires²

7

8 ¹ CEER, Institute of Agronomy, Technical University of Lisbon, Lisbon, Portugal.

9 ² INIAV, Instituto Nacional de Investigação Agrária e Veterinária, Oeiras, Portugal.

10 ³ IST, Instituto Superior Técnico, Technical University of Lisbon, Lisbon, Portugal.

11 ⁴ Université de Toulouse, INPT, UPS, Laboratoire Ecologie Fonctionnelle et
12 Environnement (ECOLAB), Ecole Nationale Supérieure Agronomique de Toulouse
13 (ENSAT), Castanet Tolosan, France.

14 ⁵ CNRS, Laboratoire Ecologie Fonctionnelle (ECOLAB), Castanet Tolosan, France.

15

* Correspondence to: Maria da Conceição Gonçalves, Instituto Nacional de Investigação Agrária e Veterinária, Quinta do Marquês, Av. República, 2784-505, Oeiras, Portugal. E-mail: maria.goncalves@iniav.pt

16 **ABSTRACT**

17 In temporary rivers the first flood event after a dry period are responsible for
18 transferring significant amounts of sediments and nutrients into water reservoirs,
19 thereby justifying close monitoring. The Enxoé river (southern Portugal) was monitored
20 for suspended sediment concentration (SSC), total phosphorous (TP), particulate
21 phosphorous (PP), soluble reactive phosphorous (SRP), and nitrate (NO_3^-) between
22 September, 2010 and August, 2013. Twenty-one flood events were observed. An
23 empirical model was used to describe changes in solute concentrations, and the
24 magnitude and rotational patterns of the hysteretic loops during flood events. SSC, TP,
25 PP, SRP, and NO_3^- varied between 1.6–1447.9, 0.05–5.15, 0–4.77, 0–0.67, and 0–27.84
26 mg L^{-1} , respectively. Sediment and phosphorous transport was influenced by the stream
27 transport capacity and particle availability, whereas nitrate loads were influenced by soil
28 hydraulic characteristics and land management. Annual sediment ($9.3\text{--}338.2 \text{ kg ha}^{-1} \text{ y}^{-1}$)
29 and nitrate ($3.24\text{--}33.70 \text{ kg ha}^{-1} \text{ y}^{-1}$) yields were low, while phosphorous losses (0.03--
30 $0.65 \text{ kg ha}^{-1} \text{ y}^{-1}$) were medium average. Flood events were responsible for the majority
31 of sediment and phosphorus transport ($>55.8\%$), while NO_3^- reached the river mostly
32 through subsurface flow ($>84.8\%$). The implementation of conservation practices, such
33 as no-tillage techniques and the preservation of the riparian vegetation should reduce
34 sediment and nutrient loads to the reservoir. This work highlights the main processes
35 involved in sediments and nutrients loads in a temporary river during flood events, with
36 a precise quantification of those elements.

37

38 **Keywords:** Flood events; Hysteresis; Nitrate; Phosphorous; Suspended sediments.

39

40

41 **1. INTRODUCTION**

42 Suspended sediment transport from agricultural catchments to stream networks is
43 responsible for aquatic habitat degradation, reservoir sedimentation and the transport of
44 sediment-bound pollutants (pesticides, particulate, nutrients, heavy metals and other
45 toxic substances). Flood events are a natural phenomenon responsible for driving those
46 sediments and nutrients into streams and lakes. Such events result in pollution peaks
47 that can last from a few minutes to a few days, leading to the eutrophication of water
48 bodies, and to the contamination of drinking water and ecosystems (Langlois *et al.*,
49 2005; Yevenes and Mannaerts, 2011). In the particular case of southern European
50 regions, flood events appear to contribute substantially to phosphorous and nitrogen
51 removal due to the characteristics of the Mediterranean climate and soils, as well as land
52 use (Torrent *et al.*, 2007). Phosphorous, which is usually considered the limiting
53 nutrient to primary production, is normally transferred from agricultural soils through
54 runoff and soil erosion, as inorganic P forms bind preferentially to soil sediments
55 through interactions with iron or aluminium (Skoulikidis and Amaxidis, 2009; Oeurng
56 *et al.*, 2010a; Zhu *et al.*, 2012). Nitrogen, which may also play an important role in
57 autotrophic production, namely in the nitrate form, is more often transported in drainage
58 water (Sánchez-Pérez *et al.*, 2003; Buda and DeWalle, 2009; Oeurng *et al.*, 2010b;
59 Cerro, 2013).

60 However, finding a direct relationship between flood events and water quality
61 deterioration is not straightforward as it depends on the catchment topography, hydro-
62 morphology, land use and management, and the remobilisation of sediments and
63 pollutants (Klein and Koelmans, 2011; Zhu *et al.*, 2012). These complex relationships
64 are even more undetermined in catchments with temporary rivers located in semi-arid
65 regions where those phenomena remain largely unassessed (Alexandrov *et al.*, 2003;

66 Rovira and Batalla, 2006; Torrent *et al.*, 2007; Butturini *et al.*, 2008). In these water
67 scarce regions studies with a high sampling density focusing on the hydrological and
68 biogeochemical regimes of temporary rivers are very rare, but are crucial for
69 implementing effective conservation measures and other good agricultural practices.

70 Over an annual cycle, temporary streams form small lentic shallow systems where
71 sediments and nutrients accumulate, and lotic systems where high flushing rates are
72 often registered (Lillebø *et al.*, 2007). During dry periods with flow cessation followed
73 by pool formation, the shallowness of the water column associated with the low
74 discharge and high temperatures may enhance important biochemical processes at the
75 sediment/water column interface leading to the accumulation of nutrients. During flood
76 events, surface or subsurface flow becomes more enriched with sediments and dissolved
77 nutrients accumulated in those pools with severe implications to the physical and
78 chemical environment of the water bodies. Hence, nutrient dynamics in these temporary
79 streams is mainly determined by sequences of dry periods and the following flood
80 events (Lillebø *et al.*, 2007), providing a significant challenge in developing sustainable
81 water management plans (Tzoraki and Nikolaidis, 2007).

82 Monitoring programs are thus essential for understanding the hydrological regime
83 of a temporary river, and the sediment and nutrient dynamics across the catchment.
84 Long-term nutrient concentrations datasets are important to understand nutrient trends,
85 loads, nutrient behaviour, the effectiveness of past nutrient migration and supporting
86 data for future management decisions regarding issues of eutrophication and nutrient
87 control (Burt, 2003; Oeurng *et al.*, 2010b). Nevertheless, while monitoring of nutrient
88 concentration is important in determining the nutrient status of a water body, it does not
89 necessarily provide information on the source of those sediments and nutrients. That
90 information is often obtained by analyzing the hysteresis in the concentration-discharge

91 relationship (House and Warwick, 1998; Bowes *et al.*, 2005; Eder *et al.*, 2010; Oeurng
92 *et al.*, 2010a).

93 This study analyses the temporal variability of suspended sediments concentration
94 (SSC), phosphorous (in both soluble and particulate forms), and nitrate (NO_3^-) in the
95 Enxoé river, southern Portugal. The Enxoé reservoir exhibits the highest eutrophic state
96 in Portugal, where many others are also classified as eutrophic (CCDR Alentejo, 2005;
97 Instituto da Água, 2008).

98 The objectives of this paper are: (i) to present the temporal variability in
99 suspended sediments, soluble and particulate phosphorous forms, and nitrate transport
100 in the Enxoé river (Alentejo region, southern Portugal) during three hydrological year
101 (September, 2010 to August, 2013); (ii) to determine sediment and nutrient loads to the
102 Enxoé reservoir at the outlet of the watershed during the monitored period; and (iii) to
103 identify sediment and nutrient source areas and processes associated based on the
104 interpretation of hysteresis in the concentration-discharge relationship. The results
105 permit to have data on sediment and nutrients loads during storm events in the case of
106 temporary rivers and pretend to help decision-makers to improve the management of
107 drinking water catchments areas by minimizing pollution risks during flood events and
108 reducing the trophic state of freshwater reservoirs.

109

110 **2. MATERIAL AND METHODS**

111 **2.1. Catchment description**

112 The Enxoé catchment is located in the Alentejo region, southern Portugal (Figure 1).
113 The river is a tributary of the Guadiana river, and has a bed length of 9 km, a catchment
114 area of 6080 ha, and an average altitude of 200 m.

115 The dominant soils are Luvisols (covering 47% of the area), Cambisols (31%),
116 and Calcisols (14%). The main land uses are olive groves (1830 ha), agro-forestry of
117 holm-oaks “Montado” (1760 ha), and annual winter crops (1700 ha). The main
118 agricultural practices are summarized in Table I. The main pressures are essentially
119 originated from non-point sources with loads arriving along the margins of the river
120 (associated to surface or subsurface flow). Average fertilization inputs are estimated to
121 amount 25.40 kg N ha⁻¹ and 11.68 kg P ha⁻¹ (Table I). Additionally, based on Livestock
122 Units (LSU) presented in Table I, animal excretions are estimated to reach 25.69 kg N
123 ha⁻¹ and 3.04 kg P ha⁻¹ (Portaria 259/2012). Therefore, nutrient inputs in Enxoé
124 catchment can be considered low since more intensive agricultural catchments are
125 normally characterized by much higher N and P inputs (e.g., Yevenes and Mannaerts,
126 2011).

127 The climate is dry sub-humid to semi-arid. The precipitation regime is
128 characterized by a highly irregular behaviour, varying between relatively abundant
129 rainfall episodes, concentrated in only a few minutes or hours, and frequent drought
130 episodes that can last from a few months to a couple of years. The annual average
131 precipitation is 500 mm, irregularly distributed along the year (80% of the annual
132 precipitation is concentrated between October and April). Thus, the hydrological regime
133 presents a strong inter and intra-annual variation of the discharges. From fall to spring,
134 the river frequently presents high flow discharges after storm events. During summer,
135 the river normally exhibits no flow. The annual average temperature is 16 °C, and the
136 annual reference evapotranspiration varies between 1200 and 1300 mm. Weather data
137 used in this study was collected from a weather station located in Serpa (37° 58' 06" N
138 and 07° 33' 03" W).

139 The catchment has a population of 1000 inhabitants, mainly concentrated in Vale
140 de Vargo (Figure 1), and is limited downstream by a dam (10.4 million m³) built in
141 2000, which supplies the villages of Mértola and Serpa (25000 inhabitants) located
142 outside the catchment area. Immediately after the reservoir was built cyanobacteria
143 blooms (up to 300 µg L⁻¹) occurred due to phosphorous overloads and the
144 eutrophication of the reservoir waters. Since then, management actions were
145 implemented in the area, namely, the building of small ditches to control flood events
146 and prevent materials to be carried out from upland to the water reservoir, and the
147 pumping of the waste waters of the treatment plant of Vale de Vargo to a water stream
148 located outside the Enxoé catchment area. Nonetheless, the reservoir continues to be
149 classified as eutrophic.

150

151 **2.2. River Enxoé water quality monitoring**

152 The river Enxoé water was monitored at the sampling station located at the outlet of the
153 watershed before the reservoir (Figure 1). Sampling waters was for suspended sediment
154 concentration (SSC), total phosphorous (TP), particulate phosphorous (PP) consisting of
155 phosphorous adsorbed to particulate (>0.45 µm) suspended material, soluble reactive
156 phosphorous (SRP), and nitrate (NO₃⁻). An YSI 6920 measuring probe (YSI
157 Incorporated, Ohio, USA) was used to monitor the water stream level and turbidity
158 (nephelometry). An automatic water sampler (EcoTech Umwelt-Meßsysteme GmbH.
159 Bonn, Germany) with 8 bottles, 2 L each, was used for monitoring water quality during
160 floods. The monitoring station was positioned near the bank of the river, where the
161 homogeneity of water movement was considered representative of all hydrological
162 conditions. The pump inlet of the automatic water sampler was placed next the
163 measuring probe pipe. The probe was programmed to activate the automatic water

164 sampler when the water level varied more than 10 cm on both rising and falling stages
165 of flood events. Manual sampling was also carried out at weekly intervals using 2 L
166 bottles collected near the probe location. The total number of water samples taken from
167 both automatic and manual sampling was 191. Flow was obtained from the measured
168 water level with the well established Gauckler-Manning formula.

169 Water samples (250–1000 ml) were filtered in the laboratory to determine SSC
170 using pre-weighted glass microfiber paper (GFF 0.75 μm). The sediments retained on
171 the filter paper were oven dried at 50° C during 24 h. The filters were again weighted
172 and SSC was calculated.

173 Aliquots of each sample were filtered using a cellulose acetate membrane (0.45
174 μm), and analyzed for total dissolved phosphorous (TDP), SRP, and NO_3^- . TP was
175 determined in the unfiltered samples. TP and TDP were quantified, after sulfuric acid
176 and nitric acid digestion, colorimetrically by reacting with ammonium molybdate. SRP
177 was also quantified colorimetrically, using the same reaction (APHA, 1995). PP was
178 determined from the difference between TP and TDP concentrations. NO_3^-
179 concentration was measured directly in the filtered solution with an automated
180 segmented flow analyser, using the cadmium reduction method (Hendriksen and Selmer-
181 Olsen, 1970).

182

183 **2.3. Water, sediment, and nutrient loads**

184 Water yield was determined by integrating river discharge over a time period, as
185 follows:

$$186 \quad W = \sum_i \frac{(Q_{(i)} + Q_{(i-1)})}{2} \times (t_{(i)} - t_{(i-1)}) \quad (1)$$

187 where W is the accumulated water yield (L^3), and Q_j is the instantaneous river discharge
188 ($L^3 T^{-1}$) at time i (T). Sediments and nutrient loads were obtained by integrating
189 sediment and solute concentrations over water yield, as follows:

$$190 \quad M_d = \sum_i \frac{(C_{d(i)} + C_{d(i-1)})}{2} \times W_i \quad (2)$$

191 where M_d is the solute mass lost in the catchment from diffuse (d) sources (M), and C_j is
192 the instantaneous solute concentration ($M L^{-3}$) at time i (T). As referred above there are
193 no point source emissions in Enxoé.

194 A linear interpolation procedure was applied between two neighboring
195 instantaneous sampling points to develop continuous sediments and nutrient series. This
196 was only possible due to the high frequency of data collection provided by the
197 automatic sampler. Turbidity measurements were taken every 3 min to 1 hour during
198 flood events and daily during non-flood events. This quasi-continuous turbidity
199 recording has been shown to reduce significantly uncertainty due to interpolation and
200 extrapolation of low-frequency measurements (Langlois *et al.*, 2005; Lefrançois *et al.*,
201 2007; López-Tarazón *et al.*, 2009; Eder *et al.*, 2010; Oeurng *et al.*, 2010a). This data
202 was used to determine suspended sediment (SSL) and phosphorous loads based on SSC-
203 turbidity and TP-turbidity relations found in Enxoé. Nitrate was measured directly in the
204 water samplers taken every 3 min to 15 hours during flood events and weakly during
205 non-flood events.

206

207 **2.4. Solute-discharge hysteresis analysis**

208 For each flood event, the analysis of the concentrations (C) of SSC, TP, PP, SRP, and
209 NO_3^- versus discharge (Q), was performed with the approach proposed by Butturini *et*
210 *al.* (2006). The shape, rotational patterns and trends of hysteretic loops of each

211 determinand are here described with two parameters: the changes in solute
212 concentrations (ΔC), and the overall dynamics of each hysteretic loop (ΔR).

213 ΔC (%) describes the relative changes in solute concentration and hysteresis trend,
214 as follows:

$$215 \quad \Delta C = (C_s - C_b) / C_{max} * 100 \quad (3)$$

216 where C_b and C_s are the solute concentrations at base flow and during peak storm flow,
217 respectively, and C_{max} is the highest concentration observed in the stream during a
218 storm. ΔC ranges from -100 to 100%, where positive values indicate solute flushing,
219 and negative values solute dilution. The ΔR (%) descriptor integrates information about
220 the magnitude (area) and direction (rotational pattern) of the C - Q hysteresis, as follows:

$$221 \quad \Delta R = R A_h 100 \quad (4)$$

222 where A_h is the area of the C - Q hysteresis, estimated after standardizing discharges and
223 concentrations to a unity scale, which means that A_h will be lower than the unity. If A_h is
224 closer to zero, the area of the hysteresis loop is smaller, more linear, and the
225 concentration in the rising limb is similar to the concentration in the recession limb. If
226 A_h is closer to the unit, the area of the hysteresis loop is larger, with more magnitude,
227 and the concentration of the rising limb is different from the concentration in the
228 recession limb. R summarizes the rotational pattern of the C - Q hysteresis. If the C - Q
229 hysteresis is clockwise, then $R=1$; if anticlockwise, then $R=-1$; for unclear (for example,
230 eight-shaped hysteresis loops) or non-existent hysteresis, $R=0$. ΔR thus ranges also from
231 -100 to 100%.

232 The variability of the C - Q hysteresis descriptors for the different determinands is
233 described in the unity plane ΔC vs. ΔR , where four regions can be identified, according
234 to flushing/dilution of the constituent and the hysteresis loop sense (clockwise or
235 anticlockwise). All this information allows clarifying the source of solutes and

236 particulate matter, and separating different kind of floods. Further details can be found
237 in Butturini *et al.* (2006, 2008).

238

239 **3. RESULTS**

240 **3.1. General description of monitored flood events**

241 Twenty-one flood events were registered between September, 2010 and August, 2013
242 (Figure 2). These events took place during autumn (10), winter (8), and spring (3), and
243 were defined as complete hydrological events with rising and recession limbs. During
244 summer there was no flow in the river.

245 Table II summarizes the main characteristics of all flood events monitored. Major
246 rainfall events generally occurred in autumn (October/December) and spring
247 (March/April). Flood events lasted between 1.8 and 210.5 h (mean=67.1 h; standard
248 deviation, $\sigma=45.1$ h). Eight events lasted longer than the average duration. Maximum
249 hourly discharge varied between 2.4 and 28.0 $\text{m}^3 \text{s}^{-1}$ (mean=7.7 $\text{m}^3 \text{s}^{-1}$; $\sigma=5.8 \text{ m}^3 \text{s}^{-1}$).
250 Several events produced multiple discharge peaks. The mean rising time to reach the
251 first discharge peak was 8.5 h ($\sigma=6.9$ h). The shortest time was only 1 h. Water yield
252 ranged from 10.0 to 2823.7 dam^3 (mean=560.2 dam^3 ; $\sigma=662.6 \text{ dam}^3$). Six events
253 produced higher water yields than average.

254 Precipitation amounted 695, 270, and 570 mm in 2010/2011, 2011/2012, and
255 2012/2013, respectively, thus classifying the corresponding monitored years as humid,
256 dry, and average. Annual water yield was 28737.9 (2010/2011), 1269.8 (2011/2012),
257 and 10138.8 dam^3 (2012/13) corresponding to 62.6, 6.5, and 26.5% of the water budget
258 outputs, respectively.

259

260 **3.2. Temporal variation of suspended sediments, phosphorous forms and nitrate**
261 **concentrations**

262 Figure 3 presents the evolution of SSC and turbidity between September, 2010 and
263 August, 2013. Generally, SSC was at a minimum ($2.0\text{--}215.0\text{ mg L}^{-1}$) during non-flood
264 events and at a maximum ($1.6\text{--}1447.9\text{ mg L}^{-1}$) during flood events. For all hydrological
265 periods, SSC averaged 187.4 mg L^{-1} ($\sigma=269.6\text{ mg L}^{-1}$). The maximum value was
266 reached in April, 2011 (event n° 9). Higher suspended sediment concentration generally
267 coincided with higher rainfall intensities as in Nadal-Romero *et al.* (2008). Turbidity
268 values followed the same tendencies observed for SSC. However, the maximum value
269 (1520.3 NTU) was observed in October, 2012 (event n° 13). During the monitored
270 period, turbidity averaged 22.8 NTU ($\sigma=55.0\text{ NTU}$).

271 Figure 4 presents TP, SRP, PP, and NO_3^- concentrations monitored during the
272 studied period. P concentrations varied between flood events and seasons, decreasing
273 from autumn to winter and increasing again during spring. Maximum values were again
274 observed during flood events. TP values ranged from 0.05 to 5.15 mg L^{-1} (mean= 0.94
275 mg L^{-1} ; $\sigma=0.83\text{ mg L}^{-1}$). PP varied from 0 to 4.74 mg L^{-1} (mean= 0.60 mg L^{-1} ; $\sigma=0.74$
276 mg L^{-1}). Both maximums were obtained in October, 2010 (event n° 2), when SSC also
277 reached a high value. SRP ranged from 0 to 0.67 mg L^{-1} (mean= 0.22 mg L^{-1} ; $\sigma=0.16\text{ mg}$
278 L^{-1}). The highest values were observed again during flood events. The maximum value
279 was reached again in October, 2010 (event n° 2). TDP varied between 0.01 and 1.34 mg
280 L^{-1} (mean= 0.34 mg L^{-1} ; $\sigma=0.26\text{ mg L}^{-1}$). SRP contribution to TDP varied between 49%
281 and 97%, while PP fraction constituted the major proportion of TP during most events,
282 averaging 56.3%. SRP constituted only a small fraction of TP, but reached values >35%
283 in 6 events. Since SRP is directly adsorbed by algae, these events may have had a more
284 negative contribution to the eutrophication of the Enxoé reservoir than all the remaining

285 events. Nitrate (NO_3^-) varied between 0 and 27.84 mg L^{-1} (mean=8.02 mg L^{-1} ; $\sigma=4.99$
286 mg L^{-1}). The maximum value observed was reached in November, 2010 (also during
287 event n° 2).

288 Figure 5 presents the relations found for SSC–turbidity ($R^2=0.861$), for SSC–TP
289 ($R^2=0.850$), and for SSC–PP ($R^2=0.822$). These relations suggested that turbidity could
290 also be used to indirectly estimate TP ($R^2=0.803$). These relations also confirmed that
291 the major portion of P was adsorbed onto suspended solids.

292

293 **3.3. Suspended sediments, total phosphorous and nitrate loads assessment**

294 Figure 6 presents the cumulative suspended sediment and nutrient loads to the Enxoé
295 reservoir from September, 2010 to August, 2013. Table III shows the same sediment
296 and nutrient yields by flood event. The results demonstrate the strong seasonal and
297 annual variability in suspended sediment, phosphorous, and nitrate transport in the
298 Enxoé catchment. Sediment transport during flood events ranged from 1.4 to 543.4 t
299 (mean=115.6 t; $\sigma=159.0$ t), and was higher during autumns and springs. Maximum load
300 was obtained in March, 2013 (event n° 18), which also corresponded to the event with
301 maximum water yield (2823.7 dam^3). Minimum load was observed in October, 2011
302 (event n° 10) during a drought period. Annual sediment yield accounted for 1146.9,
303 56.3, and 1277.5 t in 2010/2011, 2011/2012, and 2012/2013, respectively. Flood events
304 were thus responsible for 55.8, 5.7, and 76.8% of the annual sediment transport. On the
305 other hand, water yield during flood events only amounted 18.7, 18.0%, and 60.9% of
306 each year's annual flow.

307 The temporal dynamics in phosphorous transport was similar to suspended
308 sediment since both particulate elements were taken directly from turbidity
309 measurements. Phosphorous transport during flood events ranged from 4.2 to 1356.3 kg

310 (mean=301.5 kg; σ =382.5 kg). Flood events were responsible for 82.4, 5.24, and 80.4%
311 of the annual phosphorous transport in 2010/2011, 2011/2012, and 2012/2013,
312 respectively. Phosphorous transport also showed to be dependent on the intensity and
313 amplitude of the flood events as higher loads corresponded generically to larger water
314 yields.

315 Nitrate loads also demonstrated large seasonal and annual variability. Nitrate yield
316 was higher mainly during autumns, but also during springs. The nitrate load transported
317 during observed flood events varied from 0.04 to 10.2 t (mean=2.7 t; σ =3.2 t). The
318 highest nitrate load (10.2 t) was transported in October, 2010 (event n° 2). Nitrate
319 transport during flood events amounted 30.9 (2010/2011), 3.3 (2011/2012), and 12.7 t
320 (2012/2013) while the annual nitrate yield summed 204.8, 19.7, and 67.8 t, respectively.
321 Thus, flood events were directly responsible for only 15.2, 16.9, and 18.1% of each
322 year's annual load, i.e., the most significant loads reached the river during non-flood
323 events (with the exception of summer seasons).

324 From December 19th, 2010 to January 9th, 2011 it was not possible to measure
325 turbidity directly with the automatic probe due to equipment malfunctioning. Loads
326 were therefore estimated from the statistical relationship between SSL (or total
327 phosphorous) and discharge obtained during the remaining monitored period (Figure 7).
328 The relationship between SSL or phosphorous loads (or concentrations) and discharge is
329 generally represented by a power function (Langlois *et al.*, 2005; Lefrançois *et al.*,
330 2007). However, in this case, the SSL-discharge and TP-discharge was polynomial, i.e.,
331 only high discharges led to significant sediment and phosphorous transport since they
332 were normally a function of the transport capacity of a river (Asselman, 1999).
333 However, the relationships found do not include high sediment and phosphorous loads
334 measured in low discharges, i.e., it cannot represent hysteresis events. Therefore, the

335 polynomial relations described in Figure 7 can eventually lead to underestimations of
336 sediment and nutrient loads during the time period (22 days) when the equipment
337 malfunctioned.

338

339 **3.4. Hysteresis patterns**

340 The relationships between discharge and SSC, TP, PP, SRP, and NO_3^- were analyzed
341 for most events observed in the Enxoé catchment. Those that did not produce sufficient
342 detailed information, as a result of equipment malfunctioning or data limitation (soluble
343 elements) were not analyzed for their hysteresis patterns.

344 Figure 8 shows the unity plane ΔC vs. ΔR of Butturini *et al.* (2006), and
345 summarizes C - Q hysteresis loop types of the particulate determinands (SSC, TP, and
346 PP) during the monitored flood event. The components of the particulate matter were
347 located in regions A and D, indicating a flushing behavior (positive ΔC). Obviously,
348 SSC, TP, and PP presented similar or equal hysteresis loops during each discharge peak,
349 and were thus located very close to each other in the unity plane ΔC vs. ΔR . Most flood
350 events registered during autumn were located in region A, presenting a clockwise
351 hysteresis loop trajectory (positive ΔR). Events n° 15 and 16 were the exception,
352 registering anticlockwise loop trajectories in all discharge peaks (region D). Winter
353 flood events registered mixed (eight-shaped hysteresis loops; $\Delta R=0$) or anticlockwise
354 loop trajectories (negative ΔR). Spring flood events showed contrasting behaviors with
355 the event observed during the first hydrological year revealing an anticlockwise
356 trajectory and the events observed during the third hydrological year presenting
357 anticlockwise trajectories.

358 Generally, the first peaks of autumn flood events showed larger dispersion of the
359 C - Q hysteresis loops when compared with the remaining events. Those peaks presented

360 a large area ($\Delta R > 20\%$) while all other events had a smaller magnitude (-
361 $20\% < \Delta R < 20\%$). Thus, autumn floods were responsible for transferring more particulate
362 elements from the soil to the reservoir than the remaining events. Also, many events
363 (especially those that occurred during winter) presented a ΔC near 100% indicating that
364 the hysteresis patterns presented a coincidence between the maximum concentration
365 values and maximum discharge, i.e., the delay between concentration and discharge
366 peaks was small.

367 Figure 9 shows the unity plane ΔC vs. ΔR for the soluble elements (SRP, and
368 NO_3^-) monitored. SRP was located in all regions of the unity plane leading to some
369 uncertainty when analyzing its hysteresis patterns. Nevertheless, SRP seems to
370 generically have registered a dilution behavior (negative ΔC) during autumn and a
371 flushing behavior (positive ΔC) during winter and spring. Most autumn flood events
372 also showed contrasting hysteresis patterns, but during winter and spring most
373 hysteresis loops were clockwised ($\Delta R > 0$).

374 NO_3^- were located in regions B, C, and D in the unity plane ΔC vs. ΔR . Autumn
375 flood events autumn presented, in general, a flushing behavior (positive ΔC) and an
376 anticlockwise trajectory (negative ΔR). Those $C-Q$ hysteresis loops revealed a large
377 magnitude ($\Delta R < -20\%$) indicating large transfer of nitrate in the catchment area during
378 autumn which is in agreement with load estimates presented above. The remaining
379 flood events showed a dilution behavior (negative ΔC) and anticlockwise trajectories.

380

381 **4. DISCUSSION**

382 **4.1. Hydrological behavior**

383 The Enxoé river is a temporary river that normally exhibits no flow or ephemeral
384 conditions from June to October. In each monitored hydrological year, the first rain

385 events generated flow peaks that were quickly reduced as the soil was not saturated and
386 groundwater flow was greatly diminished. From October to December, with successive
387 heavy rains the soil became increasingly saturated and subsurface flow was enhanced,
388 resulting most times in flood events with multiple discharge peaks. From
389 December/January to April, the response to rain events still existed as the soil continued
390 to be saturated and groundwater flows were maintained for longer periods. However,
391 these subsurface flows still tended to fall quickly, especially during months in which
392 rain was less intense (January/February). Hence, flow in the river Enxoé was mostly
393 influenced by rainfall events, whereas the effect of groundwater table was not
394 significant.

395 Table IV presents the relationships between floods and rainfall events. Floods
396 duration (FD) were mainly correlated with water yield (W), the rainfall amount
397 registered between the rising and recession limbs of a flood event (TR), the size of the
398 first discharge peak (P_{max}), and the time to reach it after the start of the rainfall event
399 (T_{peak}). TR was further related to the amount of precipitation registered in the 24 h prior
400 to an event (RI). Thus, the stream transport capacity of the Enxoé river was indirectly
401 influenced by RI . Finally, W and the average discharge of a flood event (P_{aver}) were also
402 strongly related.

403

404 **4.2. Sediment and nutrient dynamics**

405 **4.2.1. Suspended sediments**

406 The strong seasonal and annual variability observed in SSC was mostly explained by
407 variations in stream transport capacity and particle availability. Sediment was stored at
408 low flow and transported under high discharge conditions. Heavy rains registered
409 during autumn and tillage operations carried out simultaneously in agricultural area

410 (Table I) enhanced soil erosion. Tillage operations were thus an important mechanism
411 associated to sediment transport. They ended up promoting the removal of the soil cover
412 surface provided by crop residues or growing plants which absorb the energy of
413 raindrops and reduce the cutting energy of runoff during rain events.

414 Another important mechanism associated to sediment transport during autumn
415 was related to bank destruction or trampling caused by cattle pasturing near the river
416 during drier seasons. Bull (1997) estimated that the contribution of bank eroded
417 materials to river sediment systems may vary between less than 5 to over 80%.
418 Pasturing near streams, or even in the river bed, leads to vegetation reductions, affecting
419 flow erosion, bank stability, bank accretion, and bank stabilization. Bull (1997) also
420 refers the mechanisms on how vegetation contributes to prevent bank erosion, namely,
421 by retarding the near-bank flow and damping turbulence, by resisting tension and
422 increasing cohesion, and by reducing the impact of moisture and loosening processes,
423 which are a precursor to removal of materials. Therefore, pasturing the river bed
424 promotes bank erosion, with the ruined bank materials adding to the deposited sediment
425 stock to increase the quantity of available particles that can be easily transported
426 (Lefrançois *et al.*, 2007). Thus, at the beginning of autumn, particle availability is at
427 maximum. The first flood events are then responsible for significant loads to the
428 reservoir. These conditions explain the dominant clockwise loop trajectories and the
429 flushing effect registered during the first peak discharge of autumn floods (Table V).
430 Multiple discharge peaks can then be responsible for carrying sediment from multiple
431 locations (arable lands located upstream) or from new deposited originated from a high
432 rate of bank collapse just after the passage of the first flood peaks (Asselman, 1999).

433 During winter, sediment loads remained generally low. Asselman (1999) observed
434 that in a situation where storm events occur in rapid succession (e.g.,

435 October/November, 2012), SSC loads become progressively reduced because of
436 insufficient time for exhausted sediments to accumulate between events. Sediment
437 transport is originated from more distant locations, namely soil erosion in agricultural
438 fields, as confirmed by the anticlockwise or mixed patterns registered in the *C-Q*
439 relation.

440 During March and April, sediment loads increased again, as a result of high
441 precipitation values and consequent soil erosion. During these periods, tillage
442 operations are again carried for sowing spring crops like sunflower, weed control, and
443 fire prevention in the agro-forestry of holm-oaks “Montado” system. These practices
444 again promoted particle availability to runoff (flushing). There was also a return of the
445 cattle to pasturing near the stream with consequent bank erosion. Clockwise and
446 anticlockwise trajectory loops were observed whenever sediments were transported
447 from the river deposits or from more distance locations upstream, respectively.

448 Similar patterns to those observed for SSC in Enxoé have been observed in
449 different regions of the Mediterranean (Rovira and Batalla, 2006; Lefrançois *et al.*,
450 2007; López-Tarazón *et al.*, 2009; Oeurng *et al.*, 2010a). Based on the hysteretic
451 patterns analyzed in Enxoé, clockwise hysteretic loops represented 46.2% of sediment
452 transport from river deposited sediments and nearby source areas, while anticlockwise
453 loops represented 42.9% of sediment transport from distant source areas. The remaining
454 materials arrived at the outlet in a mixed trajectory, thus the source of these sediments
455 was unclear.

456 Annual sediment yield varied between 9.3 and 338.2 kg ha⁻¹ (Table VI). The
457 lower value was determined during a dry year. Since no major flood events were
458 registered soil erosion was minimal. The value determined in 2010/2011 (338.2 kg ha⁻¹)
459 may be viewed as notably low considering that was obtained in a humid year, but is

460 within the same order of magnitude of the values registered for other catchments in the
461 Iberian Peninsula. Rovira and Batalla (2006) estimated a sediment loss of 500 kg ha^{-1} in
462 a catchment located in Cataluña, Spain. In this catchment, more than 90% of the annual
463 sediment load was transported during flood events. Casalí *et al.* (2010) also reported
464 sediment losses of $550\text{-}700 \text{ kg ha}^{-1} \text{ yr}^{-1}$ in two catchments located in Navarre, Spain.
465 Nonetheless, Walling and Webb (1996) described sediment losses between $1000\text{-}2000$
466 $\text{kg ha}^{-1} \text{ yr}^{-1}$ for other Mediterranean basins of the Iberian Peninsula. The values
467 determined in Enxoé also fall within the lower values obtained by de Vente *et al.* (2006)
468 for 44 Mediterranean basins in Italy. Oeurng *et al.* (2010a) also reported sediment losses
469 of $150\text{-}700 \text{ kg ha}^{-1}$ for a catchment located in the south of France, in which 85-95% of
470 the annual sediment load was transported during flood events.

471 The Enxoé catchment presents a significant area with agro-forestry of holm-oaks
472 “Montado” (1760 ha) that plays an important role in protecting soil surface from soil
473 erosion due to the reduced number of tillage operations carried out there. It explains
474 mostly the low sediment yield losses registered in Enxoé. Rovira and Batalla (2006),
475 Casalí *et al.* (2010), and Oeurng *et al.* (2010a) also reported significant areas with
476 forests or pastures that contributed similarly to soil protection. While sediment losses in
477 Enxoé were within the threshold limits ($1000\text{-}2000 \text{ kg ha}^{-1} \text{ yr}^{-1}$) suggested by Huber *et*
478 *al.* (2007) to be considered as tolerable for the south of Europe, results represent an
479 average value for the entire catchment. Naturally, sediment yield was higher in areas
480 with arable land than in areas with agro-forestry systems or even olive groves. It is
481 therefore important to adopt preventing measures for reducing soil erosion in those
482 arable areas. Reduced tillage (or no-till) can be effective in reducing sediment losses by
483 maintaining crop residue on the soil surface and minimizing soil particle movement
484 during storms. These techniques are also known to improve water infiltration by

485 promoting soil aggregation which would obviously contribute to reducing runoff. On
486 the other hand, hysteresis patterns showed that there is a significant contribution
487 (46.2%) from nearby sources to sediment loads during storm events. Therefore, river
488 banks need simply to be protected from pasturing with consequent improvement of
489 bank stability and cohesion.

490

491 **4.2.2. Phosphorous forms**

492 Total and particulate phosphorous dynamics revealed the same patterns as observed for
493 SSC since both were obtained from turbidity measurements. The same clockwise and
494 anticlockwise flushing effects referred earlier for SSC were also observed here (Table
495 V). SRP increase during autumn was mostly related to the application of P to crops.
496 During spring, P may also be supplied (Table I). Nonetheless, the clockwise trajectory
497 observed during winter and spring floods seems to be mostly justified by the return of
498 the cattle pasturing near the stream and eventual increase of SRP concentration in the
499 river (Table VI).

500 Annual phosphorous losses varied between 0.03 and 0.65 kg ha⁻¹ during the
501 monitored period (0.2-4.4% of P inputs; Table VI). The lower value was again
502 determined when no major flood events were registered (2011/2012). P loads observed
503 in 2010/2011 and 2012/2013 can be considered within the average of reported P losses.
504 Casalí *et al.* (2010) presented slightly higher values (0.76 kg P ha⁻¹ yr⁻¹) in one of the
505 catchments studied in Navarra (Spain), but found lower P exports (0.35 kg P ha⁻¹ yr⁻¹) in
506 the other catchment studied in the same region. Tzoraki and Nikolaidis (2007) only
507 found loads of 0.10 kg P ha⁻¹ (1.2% of input) in a mountain forested catchment in
508 Greece. Probst (1985) reported equally low exportation rates (1%) for his case study.
509 Klein and Koelmans (2011) reported data on P exports (0.08-0.88 kg P ha⁻¹ yr⁻¹) for 13

510 central European basins, in which the Enxoé values would fall within the mean.
511 Nonetheless, all these values are much lower than the 1.2-1.7 kg P ha⁻¹ yr⁻¹ loads
512 reported in the UK by Brazier *et al.* (2005).

513 Although phosphorous loads to the Enxoé reservoir were within the average of
514 reported values, they may help explaining the frequent toxic algae bloom observed in
515 the reservoir since its construction. However, the most significant part arrived at the
516 reservoir in the particulate form and was therefore deposited at the bottom being only
517 available to algae after mineralization. The same practices (reduced tillage and river
518 bank protection) recommended earlier for controlling soil erosion can also be adopted
519 for reducing P loads to the reservoir. Specifically, preserving the riparian vegetation will
520 play here a fundamental role in retaining part of the phosphorous particles deposited in
521 the river.

522

523 **4.2.3. Nitrate**

524 Hydrology was the most important factor influencing the processes responsible for the
525 removal of the nitrate resulting from agricultural practices (Sánchez-Pérez *et al.*, 2003;
526 Ocampo *et al.*, 2006). Rainfall and soil hydraulic characteristics were here the main
527 characteristics influencing nitrate transport. On the other hand, land management,
528 namely crop fertilization periods, influenced nitrate availability.

529 Nitrate losses were mostly monitored during autumn and spring. These two
530 seasons registered the most important rainfall events and corresponded to crop
531 fertilization periods. During autumn, fertilization was applied to annual winter crops
532 during sowing, which normally involved burying fertilizers, thus preventing N losses by
533 runoff. During late-winter/spring, fertilization was applied to summer crops also during
534 sowing. Additionally, annual winter crops were fertilized to promote tillering

535 (February/March) and increase crop yield. However, fertilizers were here usually
536 applied to the soil surface, increasing the odds of N losses by runoff (e.g., event n° 7) as
537 well as leaching with rainfall.

538 Hysteresis patterns observed during the monitored events showed predominantly
539 anticlockwise trajectories. NO_3^- infiltrated first in the soil only reaching later the water
540 stream through subsurface flow. Nitrate transport was thus dependent of the soil
541 physical and hydraulic characteristics, i.e., soil texture, soil porosity, soil water
542 retention, and soil hydraulic conductivity, which influenced water flow and mass
543 transport and produced a delay in the concentration-discharge peak. Buda and DeWalle
544 (2009), Oeurng *et al.* (2010b), Zhu *et al.* (2012) registered similar preferential flowpaths
545 with nitrate losses being associated to either subsurface flow or baseflow.

546 Hence, peak discharges were not directly associated to nitrate transport with only
547 15.2-18.7% of the annual yield being monitored during flood events (Table III). The
548 flushing effect and the anticlockwise loops observed during autumn (Figure 9) showed
549 that significant amounts of nitrate were transported from distant areas of the catchment
550 in the days after those flood events, namely from the agricultural fields where
551 fertilization occurred. This flushing mechanism was explained by the successive rainfall
552 events registered during that period, soil moisture close to saturation, and the medium to
553 coarse textures of the relatively shallow soils in the catchment, namely Luvisols and
554 Cambisols which totalize 78% of the area. This characteristics favored subsurface water
555 flow from a significant part of the area, removing significant amounts of nitrate applied
556 to annual winter crops during sowing.

557 During winter and spring the flushing mechanism switched to a dilution behavior
558 (Table V). Nitrate concentrations in the river always decreased with the arrival of the
559 discharge peak, that is, nitrate concentration in surface runoff was lower than in

560 subsurface flow. Hence, there was no nitrate being transported across the catchment
561 with the exception of that due to the soil leaching had origin in the annual winter crop
562 areas. The arrival of “clean” water from non-fertilized areas, such as agro-forestry of
563 holm-oaks “Montado” and permanent pastures partially diluted river flow.

564 Nitrogen inputs to the catchment amounted $51.10 \text{ kg N ha}^{-1}$, applied under
565 different N forms either from fertilization or livestock (Table I). Besides nutrient
566 uptake, various N transformation processes then occurred in soils mostly due to
567 microbial activity which was controlled by soil environmental conditions such as soil
568 water and temperature (Lillebø *et al.*, 2007). From the initial inputs, between 0.73 and
569 $7.61 \text{ kg N ha}^{-1}$ arrived at the reservoir in the nitrate form, i.e., between 3.24 and 33.70
570 $\text{kg NO}_3^- \text{ ha}^{-1}$. Nitrate exports in Enxoé can thus be considered low since agriculture and
571 pasturing are not very intensive. Nitrate loads fall within the same order of magnitude as
572 those found by Oeurng *et al.* (2010b) and Probst (1985) for catchments in the south of
573 France. There, nitrate loads varied from 10-50 $\text{kg NO}_3^- \text{ ha}^{-1}$. Casalí *et al.* (2010) also
574 reported values ranging from 22-54 $\text{kg NO}_3^- \text{ ha}^{-1}$ in the two catchments studied in
575 Navarre (Spain). In terms of N units, Tzoraki and Niolaidis (2007) reported losses of
576 $2.73 \text{ kg N ha}^{-1}$ (11% of input) in their case study (forested areas were here the dominant
577 land use with 75.4% of the area). But, compared with the values Klein and Koelmans
578 (2011) for catchments in Central Europe ($0.8\text{-}42.6 \text{ kg N ha}^{-1} \text{ yr}^{-1}$), N exports in the
579 Enxoé catchment are within the lowest values.

580 The identification of nitrate sources in the Enxoé catchment using hysteresis
581 patterns was relatively clear due to the small size of the catchment and predominant
582 land uses and land management. Nitrate losses were associated to non-point sources but
583 the periods where higher exports were observed always corresponded to fertilization
584 periods of annual winter and summer crops. Nitrate losses were low though but could be

585 further minimized by increasing fertilization efficiency (by reducing applications during
586 rainy years) or by preserving riparian vegetation which would use most of the nitrate
587 exported to the river before it reached the reservoir.

588

589 **5. CONCLUSIONS**

590 Sediment and nutrient dynamics in the Enxoé catchment showed a strong seasonal and
591 annual variability during the monitored period. Annual discharge varied between 1.2
592 and 28.7 hm³ depending on the amount of rainfall registered in each hydrological year.

593 Annual sediment losses were relatively low (9.3–338.2 kg ha⁻¹ y⁻¹) and were
594 related with the amount of rainfall registered each year. Flood events were responsible
595 for 55.8–76.8% of the annual loads to the reservoir. Likewise, annual phosphorous
596 transport was considered to be within the average of reported values (0.03–0.65 kg ha⁻¹
597 y⁻¹), with flood events being responsible for most of P transport (80.2–82.4%). During
598 the monitored period, 46.2% of the sediment and P losses had origin in river bed
599 deposits that had resulted from pasturing the river bed and river banks, while 42.9%
600 were originated from the enhancement of soil erosion due to tillage operations carried
601 out in agricultural fields. Sediment and phosphorous dynamics in the catchment were
602 thus associated to the stream transport capacity and particle availability throughout the
603 seasons.

604 The behavior of the soluble elements was in general different from the particulate
605 ones. SRP was mostly originated near the river banks. However, a larger number of
606 SRP-*Q* response for Enxoé river is still necessary in order to better identify a “most
607 probable SRP response. Annual nitrate loads were also low (3.24–33.70 kg ha⁻¹ y⁻¹),
608 with the highest exports being observed in autumn and spring. However, the
609 contribution of flood events to NO₃⁻ loads reached only 15.2–18.7% of the annual

610 losses. The most significant part was transported from agricultural fields during non-
611 flood events, through subsurface flow depending on the soil hydraulic characteristics.

612 Based on the conceptual model developed for Enxoé, the most feasible measure
613 towards reducing eutrophication in the Enxoé reservoir would be the adoption of non-
614 tillage practices which would improve soil stability and increase water infiltration, thus
615 reducing runoff. Also, the protection of the river banks from pasturing, with the
616 consequence preservation of the riparian vegetation, would retain a significant part of
617 the nutrients in the river, improve banks aggregation and stability, and reduce sediment
618 deposits in the river bed.

619

620 **ACKNOWLEDGEMENTS**

621 This research was performed within the framework of the EU Interreg SUDOE IVB
622 program (SOE1/P2/F146 AguaFlash project, <http://www.aguaflash-sudoe.eu>), and the
623 Project EUTROPHOS (PTDC/AGR-AAM/098100/2008) of the Fundação para a
624 Ciência e a Tecnologia (FCT).

625

626 **REFERENCES**

627 Alexandrov Y, Laronne JB, Reid I. 2003. Suspended sediment concentration and its
628 variation with water discharge in a dryland ephemeral channel, northern Negev,
629 Israel. *Journal of Arid Environments* **53**: 73-84.

630 Asselman NEM. 1999. Suspended sediment dynamics in a large drainage basin: the
631 River Rhine. *Hydrological Processes* **13**: 1437-1450.

632 APHA. 1995. Standard methods. 19th Edition. American Public Health Association,
633 Washington, DC.

634 Bowes MJ, House WA, Hodgkinson RA, Leach DV. 2005. Phosphorus-discharge
635 hysteresis during storm events along a river catchment: the River Swale, U.K. *Water*
636 *Research* **39**: 751-762.

637 Brazier RE, Heathwaite AL, Liu S. 2005. Scaling issues relating to phosphorous
638 transfer from land to water in agricultural catchments. *Journal of Hydrology* **304**:
639 330-342.

640 Buda AR, DeWalle DR. 2009. Dynamics of stream nitrate sources and flow pathways
641 during stormflows on urban, forest and agricultural watersheds in central
642 Pennsylvania, USA. *Hydrological Processes* **23**: 3292-3305.

643 Bull LJ. 1997. Magnitude and variation in the contribution of bank erosion to the
644 suspended sediment load of the river Severn, UK. *Earth Surface Processes and*
645 *Landforms* **22**: 1109-1123.

646 Burt TP. 2003. Monitoring change in hydrological systems. *The Science of the Total*
647 *Environment* **310**: 9-16.

648 Butturini A, Gallart F, Latron J, Vazquez E, Sabater F. 2006. Cross-site comparison of
649 variability of DOC and nitrate C-Q hysteresis during the autumn-winter period in
650 three Mediterranean headwater streams: a synthetic approach. *Biogeochemistry* **77**:
651 327-349.

652 Butturini A, Alvarez M, Bernal S, Vazquez E, Sabater F. 2008. Diversity and temporal
653 sequences of forms of DOC and NO₃-discharge responses in an intermittent stream:
654 Predictable or random succession? *Journal of Geophysical Research* **113**, G03016.
655 doi:10.1029/2008JG000721.

656 Casalí J, Giménez R, Díez J, Álvarez-Mozos J, Del Valle de Lersundi J, Goñi M,
657 Campo MA, Chahor Y, Gastesi R, López J. 2010. Sediment production and water

658 quality of watersheds with contrasting land use in Navarre (Spain). *Agricultural*
659 *Water Management* **97**: 1683-1694.

660 Cerro I, Sánchez-Pérez JM, Ruiz-Romera E, Antigüedad, I. 2013. Variability of
661 particulate (SS; POC) and dissolved (DOC, NO₃) matter during storm events in the
662 Alegria agricultural watershed. *Hydrological Processes*. doi:10.1002/hyp.9850.

663 CCDR Alentejo. 2005. Anuário de recursos hídricos do Alentejo. Ano Hidrológico
664 2003/2004. MAOTDR, Évora, Portugal.

665 de Vente J, Poesen J, Bazzoffi P, van Rompaey A, Verstraeten G. 2006. Predicting
666 catchment sediment yield in Mediterranean environments: the importance of
667 sediment sources and connectivity in Italian drainage basins. *Earth Surface*
668 *Processes and Landforms* **31**: 1017-1034.

669 Eder A, Strauss P, Krueger T, Quinton JN. 2010. Comparative calculation of suspended
670 sediment loads with respect to hysteresis effects (in the Petzenkirchen catchment,
671 Austria). *Journal of Hydrology* **389**: 168-176.

672 Hendriksen A, Selmer-Olsen AR. 1970. Automatic methods for determination of nitrate
673 and nitrite in water and soil extracts. *The Analyst* **95**: 514-518.

674 House WA, Warwick MS. 1998. Hysteresis of the solute concentration/discharge
675 relationship in rivers during storms. *Water Resources* **32**: 2279–2290.

676 Huber S, Prokop G, Arrouays D, Banko G, Bispo A, Jones RJA, Kibblewhite MG,
677 Lexer W, Möller A, Rickson RJ, Shishkov T, Stephens M, Toth G, Van den Akker
678 JJH, Varallyay G, Verheijen FGA, Jones AR (eds). 2008. Environmental
679 Assessment of Soil for Monitoring: Volume I Indicators & Criteria. EUR 23490
680 EN/1, Office for the Official Publications of the European Communities,
681 Luxembourg, 339pp.

682 Instituto da Água. 2008. Poluição provocada por nitratos de origem agrícola. Directiva
683 91/676/CEE, de 12 de Dezembro de 1991. Relatório (2004-2007). Publicação
684 conjunta do MAOTDR e MADRP, Lisboa, Portugal.

685 Klein JJM, Koelmans AA. 2011. Quantifying seasonal export and retention of nutrients
686 in West European lowland rivers at catchment scale. *Hydrological Processes* **25**:
687 2102-2111.

688 Langlois JL, Johnson DW, Mehuys GR. 2005. Suspended sediment dynamics
689 associated with snowmelt runoff in a small mountain stream of Lake Tahoe
690 (Nevada). *Hydrological Processes* **19**: 3569-3580.

691 Lefrançois J, Grimaldi C, Gascuel-Oudou C, Gilliet N. 2007. Suspended sediment and
692 discharge relationships to identify bank degradation as a main sediment source on
693 small agricultural catchments. *Hydrological Processes* **21**: 2923-2933.

694 Lillebø AI, Morais M, Guilherme P, Fonseca R, Serafim A, Neves R. 2007. Nutrient
695 dynamics in Mediterranean temporary streams: A case study in Pardiela catchment
696 (Degebe River, Portugal). *Limnologica* **37**: 337-348.

697 López-Tarazón JA, Batalla RJ, Vericat D, Francke T. 2009. Suspended sediment
698 transport in a highly erodible catchment: The River Isábena (Southern Pyrenees).
699 *Geomorphology* **109**: 210-221.

700 MADRP. 2010. Análise dos impactos no solo resultantes da introdução de novos olivais
701 regados no Alentejo. 2º Relatório do Grupo de Trabalho do Olival. INRB, MADRP,
702 Lisboa.

703 Nadal-Romero E, Regues D, Latron J. 2008. Relationships among rainfall, runoff, and
704 suspended sediment in a small catchment with badlands. *Catena* **74**: 127-136.

705 Ocampo CJ, Oldham CE, Sivapalan M, Turner JV. 2006. Hydrological versus
706 biogeochemical controls on catchment nitrate export: a test of the flushing
707 mechanism. *Hydrological Processes* **20**: 4269-4286.

708 Oeurng C, Sauvage S, Sánchez-Pérez JM. 2010a. Dynamics of suspended sediment
709 transport and yield in a large agricultural catchment, southwest France. *Earth*
710 *Surface Processes and Landforms* **35**: 1289–1301.

711 Oeurng C, Sauvage S, Sánchez-Pérez JM. 2010b. Temporal variability of nitrate
712 transport through hydrological response during flood events within a large
713 agricultural catchment in south-west France. *Science of the Total Environment* **409**:
714 140-149.

715 Probst JL. 1985. Nitrogen and phosphorous exportation in the Garonne Basin (France).
716 *Journal of Hydrology* **76**: 281-305.

717 Rovira A, Batalla RJ. 2006. Temporal distribution of suspended sediment transport in a
718 Mediterranean basin: The Lower Tordera (NE Spain). *Geomorphology* **79**: 58-71.

719 Sánchez-Pérez JM, Vervier P, Garabétian F, Sauvage S, Loubet M, Rols JL, Bariac T,
720 Weng P. 2003. Nitrogen dynamics in the shallow groundwater of a riparian wetland
721 zone of the Garonne, SW France: nitrate inputs, bacterial densities, organic matter
722 supply and denitrification measurements. *Hydrology and Earth System Sciences* **7**,
723 97-107.

724 Skoulidakis N, Amaxidis Y. 2009. Origin and dynamics of dissolved and particulate
725 nutrients in a minimally disturbed Mediterranean river with intermittent flow.
726 *Journal of Hydrology* **373**: 218-229.

727 Torrent J, Barberis E, Gil-Sotres F. 2007. Agriculture as a source of phosphorus for
728 eutrophication in southern Europe. *Soil Use and Management* **23**: 25-35.

729 Tzoraki O, Nikolaidis NP. 2007. A generalized framework for modeling the hydrologic
730 and biochemical response of a Mediterranean temporary river basin. *Journal of*
731 *Hydrology* **346**: 112-121.

732 Walling DA, Webb BW. 1996. Erosion and sediment yield: A global overview. IAHS
733 Publications 236. IAHS Press: Wallingford, 3-19.

734 Yevenes MA, Mannaerts CM. 2011. Seasonal and land use impacts on the nitrate
735 budget and export of a mesoscale catchment in Southern Portugal. *Agricultural*
736 *Water Management* **102**: 54-65.

737 Zhu Q, Schmidt JP, Bryant RB. 2012. Hot moments and hot spots of nutrient losses
738 from a mixed land use watershed. *Journal of Hydrology* **414-415**: 393-404.

739

List of Tables

740

741

742 **Table I.** Summary description of the main agricultural practices carried out in the
743 Enxoé catchment area.

744

745 **Table II.** General characteristics of the flood events observed in the Enxoé catchment
746 between September, 2010 and August, 2013.

747

748 **Table III.** Water yield and sediment and nutrient loads at the outlet between September,
749 2010 and August, 2013.

750

751 **Table IV.** Pearson correlation matrix between the variables associated to flood events.

752

753 **Table V.** Conceptual model of the source and transport of sediments and nutrients in the
754 river Enxoé catchment area.

755

756 **Table VI.** Annual water, sediment, and nutrient yields in the Enxoé catchment between
757 September, 2010 and August, 2013.

758

Table I. Summary description of the main agricultural practices carried out in the Enxoé catchment area.

Land use	Tillage operations	Fertilization inputs ^a	Livestock
Olive groves	Traditional olive groves (<100 trees/ha): Harrowing (October) Intensive olive groves (300-500 trees/ha): No tillage; average irrigation depths 200 mm (MADRP, 2010)	Traditional olive groves (<100 trees/ha): 24 units of N (April and May) Intensive olive groves (300-500 trees/ha): 60 units of N (April to July) 15 units of P (April to July) 30 units of K (April to July)	Sheep (0.1 LSU ^b)
Agro-forestry of holm-oaks “Montado”	Areas with >30 trees/ha: Harrowing (May) Areas with <30 trees/ha: Include also annual winter crops Harrowing (October)	Annual winter crops: Triticale and Oats 40-80 units of N (October to November) 60 units of P (October to November)	Cows, sheep, goats, and pigs (0.4 LSU, which increase to 0.6 LSU for 3 months during holm-oaks fructification period)
Annual winter crops: Rotation 1 (sunflower + wheat or triticale + barley or oats) Rotation 2 (wheat or triticale + oats + fallow) Rotation 3 (oats + fallow)	Sunflower: Moldboard plowing (April) Harrowing (April) Heavy rolling (April) Sowing (April) Harvest (September) Wheat, Triticale and Barley: Harrowing (November) Sowing (November) Harvest (June) Oats: Harrowing (November) Sowing (October) Harvest (June)	Sunflower: 22 units of P (April) 42 units of K (April) Wheat, Triticale and Barley: 20 units of N (November) 18 units of P (November) 50-90 units of N (January to February) Oats: 40 units of N (March)	Cows and sheep (0.6 LSU)
Permanent Pastures	No tillage operations	18 units of P (October)	Cows and sheep (0.6 LSU)

^a values obtained by inquiring the farmers in the region.

^b LSU – Livestock units

Table II. General characteristics of the flood events observed in the Enxoé catchment between September, 2010 and August, 2013^a.

Flood Events		Rainfall								Discharge				
N°	Date	FD (h)	W (dam ³)	RA (mm)	RD (h)	R1 (mm)	R2 (mm)	R5 (mm)	R10 (mm)	Mean (m ³ s ⁻¹)	Peak N°	P _{max} (m ³ s ⁻¹)	T _{peak} (h)	R _{peak} (mm)
Year: 2010/2011														
1	08/10 - 11/10	51.6	44.7	41.3	3.6	31.4	31.4	31.5	40.6	1.3	1 st	3.6	6.0	33.0
2	29/10 - 02/11	81.2	969.2	48.1	2.7	16.6	16.6	16.6	16.7	5.7	1 st	5.2	3.0	18.2
											2 nd	10.5	15.0	43.4
											3 rd	8.2	17.0	46.6
3	18/12 - 23/12	127.1	622.7	84.1	3.7	28.0	28.0	28.3	29	4.7	1 st	28.0	24.0	28.0
											2 nd	8.3	81.0	51.2
											3 rd	8.9	113.0	84.1
4	30/12 - 02/01	92.3	497.3	21.7	3.4	18.8	18.8	18.9	55.9	1.5	1 st	4.2	21.0	18.8
5	07/01 - 09/01	70.3	265.1	19.5	2.3	6.4	7.4	13.1	34.8	1.0	1 st	3.5	7.0	6.5
6	28/01 - 31/01	90.1	347.4	25.6	3.6	6.4	11.0	13.5	25.5	1.1	1 st	5.5	19.0	19.0
7	15/02 - 17/02	71.8	1473.1	28.0	7.2	18.5	19.5	23.5	23.6	5.0	1 st	7.2	17.0	10.0
											2 nd	9.5	23.0	16.2
											3 rd	13.8	45.0	18.7
8	14/03 - 15/03	47.9	975.2	26.0	3.2	27.8	33.0	52.7	93.2	5.7	1 st	10.6	7.0	12.6
											2 nd	19.7	15.0	24.6
9	19/04 - 21/04	48.0	170.9	75.9	6.6	45.6	45.8	45.8	45.8	0.8	1 st	6.2	12.0	38.4
Year: 2011/2012														
10	26/10 - 28/10	29.4	68.6	68.2	4.1	29.3	30.3	30.3	32	0.7	1 st	2.4	2.0	65.9
11	09/11 - 10/11	35.5	153.3	40.2	3.5	2.6	2.8	2.9	40.2	0.8	1 st	2.4	5.0	40.2
Year: 2012/2013														
12	24/10 - 24/10	1.8	10.0	26.9	1.3	26.9	26.9	27.8	45.9	1.6	1 st	3.0	1.0	47.0
13	03/11 - 05/11	59.4	278.1	19.7	5.1	8.4	22.1	33.4	42.8	3.0	1 st	4.3	2.0	42.8
14	08/11 - 10/11	45.3	433.2	33.8	2.7	24.2	32.0	43.3	76.7	2.9	1 st	12.8	4.5	32.0
											2 nd	4.9	37.0	41.5
15	16/11 - 17/11	37.8	145.1	49.4	2.4	40.3	49.2	49.2	90.8	1.1	1 st	3.1	2.3	49.2
											2 nd	2.7	21.0	58.3
16	15/12 - 17/12	61.0	262.0	18.3	4.7	14.7	17.0	17.4	29.1	1.3	1 st	4.2	10.3	17.4
											2 nd	2.5	54.8	21.0
17	19/01 - 20-01	20.3	108.9	21.0	1.3	15.7	16.2	17.4	20.5	1.6	1 st	3.7	3.0	16.2
18	04/03 - 14/03	210.5	2823.7	85.4	2.1	11.7	12.5	12.7	18.1	2.9	1 st	6.4	12.3	12.5
											2 nd	5.9	62.7	45.7
											3 rd	17.6	91.3	57.6
											4 th	5.3	181.0	86.2
19	19/03 - 21/03	51.0	353.8	21.1	2.9	21.1	21.1	23.8	53.5	2.1	1 st	8.3	5.8	21.1
20	23/03 - 25/03	51.5	429.4	12.8	2.1	9.8	21.8	42.9	45.6	2.3	1 st	4.3	2.5	9.8
21	31/03 - 05/04	124.6	1331.7	45.8	4.7	32.3	32.3	36.7	66.2	3.0	1 st	16.4	11.3	32.3

^a FD, flood duration; W, water yield; RA, rainfall amount between the rising and recession limbs of a flood event; RD, rainfall duration in a flood event; R1, R5, and R10, cumulative precipitation in the 24h, five and ten days before the first discharge peak, respectively; P_{max}, discharge peak; T_{peak} and R_{peak} correspond to the duration and amount of rain accumulated since the beginning of the rain event until the discharge peak of a flood event, respectively.

Table III. Water yield and sediment and nutrient loads at the outlet between September, 2010 and August, 2013.

Flood event	Water yield		Sediment		P		NO ₃ ⁻	
	(dam ³)	(%)	(t)	(%)	(kg)	(%)	(t)	(%)
Year: 2010/2011								
1	44.7	0.2	25.5	1.2	76.4	1.9	0.3	0.1
2	969.2	3.4	205.2	10.0	615.5	15.5	10.2	5.0
3	622.7	2.2	233.8	11.4	696.3	17.5	9.9	4.9
4	497.3	1.7	16.2	0.8	45.9	1.2	2.8	0.1
5	265.1	0.9	7.2	0.4	20.1	0.5	1.1	0.6
6	347.4	1.2	13.4	0.7	38.4	1.0	0.3	0.2
7	1473.1	5.1	317.5	15.4	812.1	20.4	7.4	3.6
8	975.2	3.4	255.9	12.4	758.3	19.1	0.6	0.3
9	170.9	0.6	72.2	3.5	216.4	5.4	7.5	0.4
Total (flood events)	5365.6	18.7	1146.9	55.8	3279.4	82.4	30.9	15.2
Total (year)	28737.9	–	2056.0	–	3978.0	–	204.8	–
Year: 2011/2012								
10	68.6	5.4	1.4	2.5	4.2	2.5	0.1	0.2
11	159.8	12.6	1.8	3.2	4.6	2.7	3.2	16.7
Total (flood events)	228.4	18.0	3.2	5.7	8.8	5.2	3.3	16.9
Total (year)	1269.8	–	56.3	–	168.0	–	19.7	–
Year: 2012/2013								
12	10.0	0.1	5.7	0.3	17	0.4	0.3	0.5
13	278.1	2.7	33.8	2.0	101.5	2.7	0.0	0.1
14	433.2	4.3	458.7	27.6	1356.3	35.8	0.7	1.0
15	145.1	1.4	27.5	1.7	82.5	2.2	0.5	0.7
16	262.0	2.6	35.2	2.1	105.7	2.8	1.5	2.2
17	108.9	1.1	41.1	2.5	123.4	3.3	3.0	4.4
18	2823.7	27.9	543.4	32.7	860.3	22.7	2.6	3.9
19	353.8	3.5	31	1.9	93.1	2.5	0.	0.8
20	429.4	4.2	61.8	3.7	185.4	4.9	2.0	2.9
21	1331.7	13.1	39.3	2.4	117.8	3.1	1.5	2.2
Total (flood events)	6175.9	60.9	1277.5	76.8	3043.0	80.4	12.7	18.7
Total (year)	10138.8	–	1662.4	–	3783.6	–	67.8	–

Table IV. Pearson correlation matrix between the variables associated to flood events^a.

	FD	W	TR	RD	R1	R5	R10	P_{aver}	P_{max}	T_{peak}
FD	1.00									
W	0.83	1.00								
TR	0.48	0.37	1.00							
RD	0.16	0.19	-0.11	1.00						
R1	-0.17	-0.13	0.46	-0.13	1.00					
R5	-0.26	-0.13	0.08	-0.08	0.71	1.00				
R10	-0.28	-0.17	-0.16	-0.11	0.49	0.74	1.00			
P_{aver}	0.33	0.55	0.10	0.32	0.00	0.19	0.03	1.00		
P_{max}	0.43	0.28	0.40	0.18	0.28	0.24	0.14	0.54	1.00	
T_{peak}	0.60	0.34	0.26	0.35	0.00	-0.23	-0.21	0.19	0.53	1.00

^a FD, flood duration; W, water yield; RA, rainfall amount between the rising and recession limbs of a flood event; RD, rainfall duration in a flood event; R1, R5, and R10, cumulative precipitation in the 24h, five and ten days before the first discharge peak, respectively; P_{max}, discharge peak; T_{peak} and R_{peak} correspond to the duration and amount of rain accumulated since the beginning of the rain event until the discharge peak of a flood event, respectively.

Table V. Conceptual model of the source and transport of sediments and nutrients in the river Enxoé catchment area.

	Autumn			Winter			Spring			Summer		
	Source	Transfer	Hysteresis pattern	Source	Transfer	Hysteresis pattern	Source	Transfer	Hysteresis pattern	Source	Transfer	Hysteresis pattern
Particulate elements												
– SSC, TP, and PP	River banks	Runoff	Flushing Clockwise	Agricultural fields	Runoff	Flushing Mixed	River banks Agricultural fields	Runoff	Flushing Mixed	No flow	–	–
Soluble elements												
– SRP	River banks Agricultural fields	Runoff Lateral flow	Dilution Mixed	River banks	Runoff	Flushing Clockwise	River banks	Runoff	Flushing Clockwise	No flow	–	–
– NO ₃ ⁻	Agricultural fields	Lateral flow	Flushing Anticlockwise	Agricultural fields	Lateral flow	Dilution Mixed	Agricultural fields	Lateral flow	Dilution Anticlockwise	No flow	–	–

SSC, suspended sediment concentration, TP, total phosphorous, PP, particulate phosphorous, SRP, soluble reactive phosphorous, NO₃⁻, nitrate.

Table VI. Annual water, sediment, and nutrient yields in the Enxoé catchment between September, 2010 and August, 2013.

	2010/2011		Outputs 2011/2012		2012/2013	
Water yield (mm)						
– river discharge	473	(62.6%)	21	(6.5%)	167	(26.5%)
Sediments (kg ha⁻¹)	338.2		9.3		273.4	
P (kg ha⁻¹)	0.65	(4.4%)	0.03	(0.2%)	0.62	(4.2%)
N (kg ha⁻¹)	7.61	(14.9%)	0.73	(1.4%)	2.52	(4.9%)

List of Figures

Figure 1. Location and land use (top), major soil units (middle), and digital elevation model (bottom) in Enxoé catchment area.

Figure 2. Precipitation (mm) and discharge ($\text{m}^3 \text{s}^{-1}$) at the river Enxoé outlet between September, 2010 and August, 2013. Line in light grey represents a period of 22 days when the equipment malfunctioned.

Figure 3. Discharge, suspended solid concentration (SSC), and turbidity monitored between September, 2010 and August, 2013. Line in light grey represents a period of 22 days when the equipment malfunctioned.

Figure 4. Discharge, nitrate (NO_3^-), total (TP), particulate (PP) and soluble reactive (SRP) phosphorous concentrations observed between September, 2010 and August, 2013. Line in light grey represents a period of 22 days when the equipment malfunctioned.

Figure 5. Regression analysis between (a) suspended solid concentration (SSC) and turbidity; (b) total phosphorous (TP) and SSC; (c) particulate phosphorous (PP) and SSC; and (d) TP and turbidity.

Figure 6. Cumulative water yield (mm), suspended sediments (t), phosphorous (t), and nitrate transport in the Enxoé catchment between September, 2010 and August, 2013.

Figure 7. Relations between suspended sediment loads (SSL), or total phosphorous (TP) loads, and discharge (Q) in the Enxoé catchment.

Figure 8. Unity plane ΔC vs. ΔR for the C - Q hysteresis loops of suspended solid concentration (SSC), total phosphorous (TP), and particulate phosphorous (PP). The marks i,j correspond to the i^{th} flood event monitored (1-21) and the j^{th} discharge peak (1-4) monitored during autumn (A), winter (W), and spring (S). Typical C - Q relations are presented for each region of the unity plane ΔC vs. ΔR .

Figure 9. Unity plane ΔC vs. ΔR for the C - Q hysteresis loops of soluble reactive phosphorous (SRP), and nitrate (NO_3^-). The marks i,j correspond to the i^{th} flood event monitored (1-21) and the j^{th} discharge peak (1-4) monitored during autumn (A), winter (W), and spring (S). Typical C - Q relations are presented for each region of the unity plane ΔC vs. ΔR .

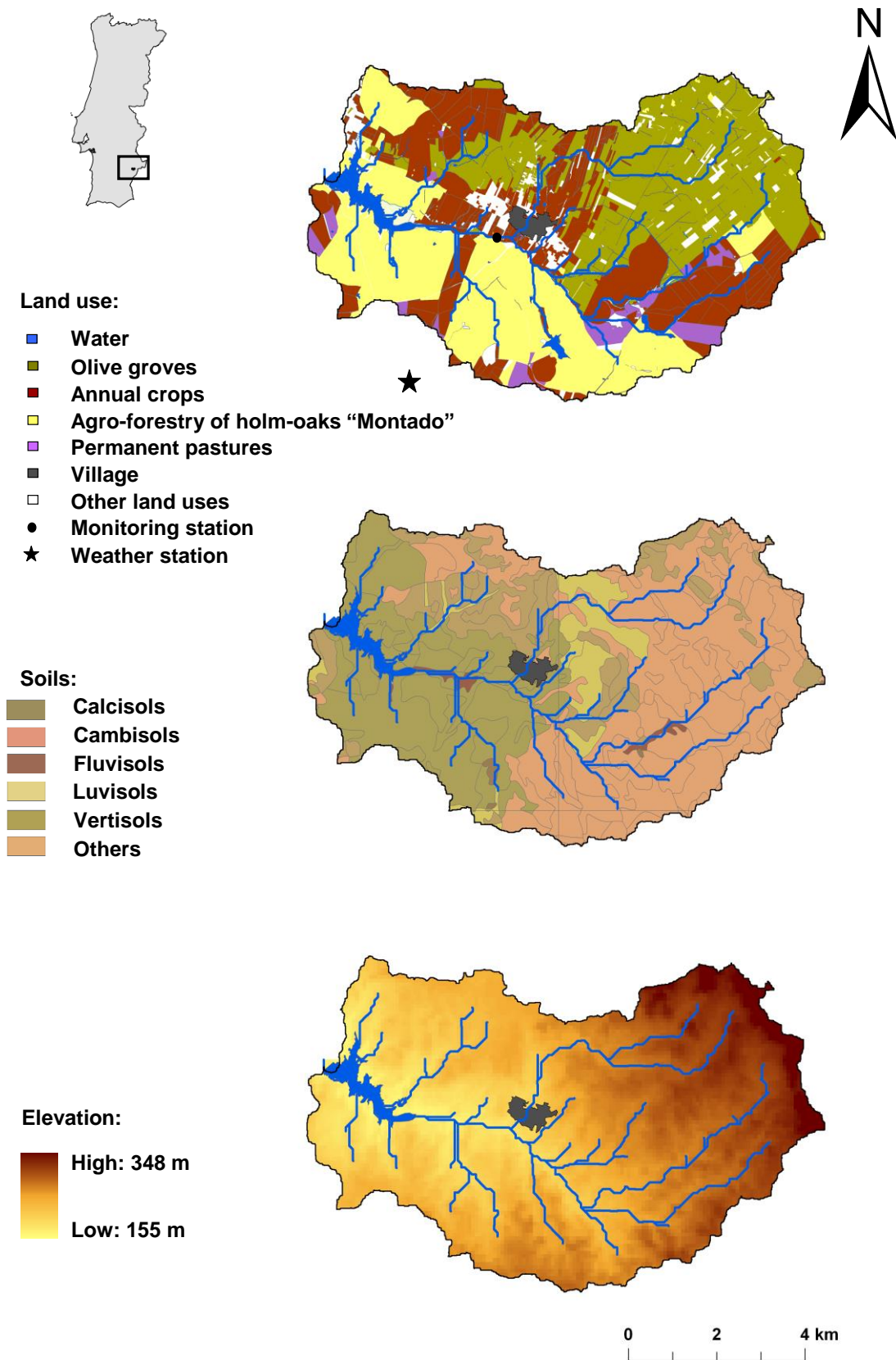


Figure 1. Location and land use (top), major soil units (middle), and digital elevation model (bottom) in Enxoé catchment area.

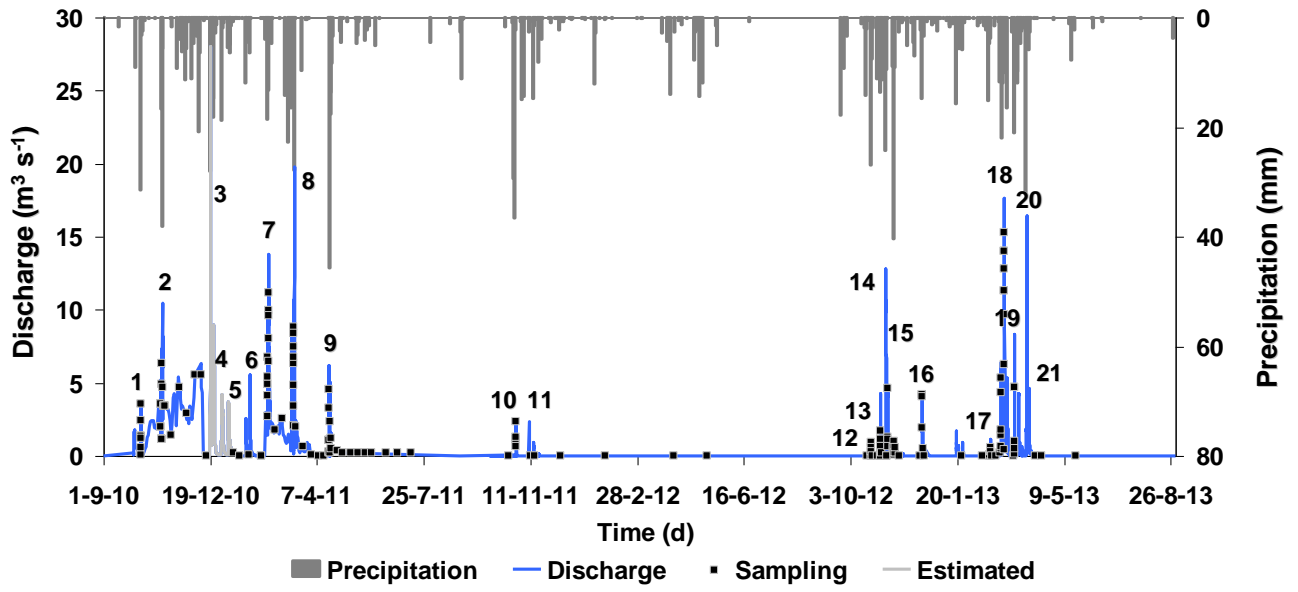


Figure 2. Precipitation (mm) and discharge ($\text{m}^3 \text{s}^{-1}$) at the river Enxoé outlet between September, 2010 and August, 2013. Line in light grey represents a period of 22 days when the equipment malfunctioned.

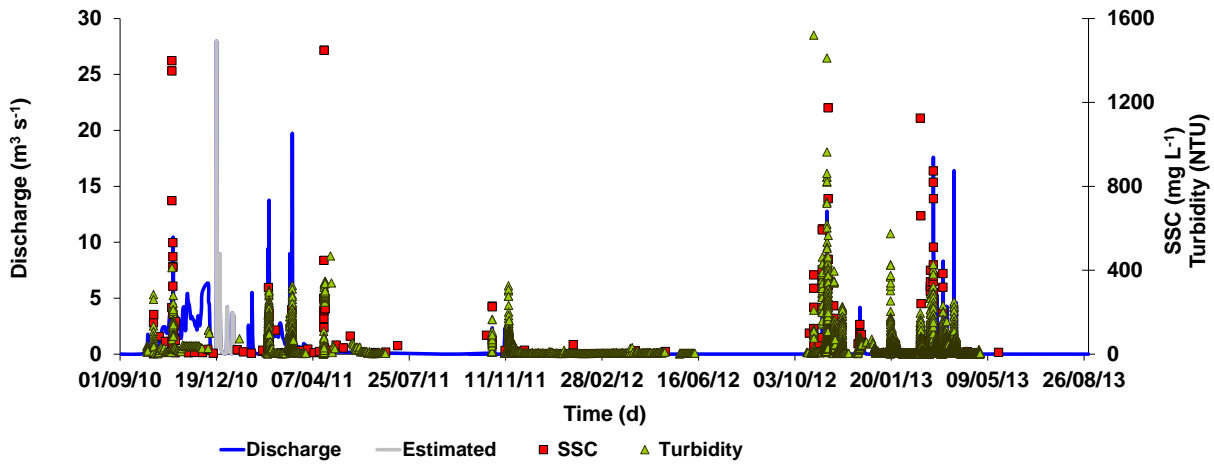


Figure 3. Discharge, suspended solid concentration (SSC), and turbidity monitored between September, 2010 and August, 2013. Line in light grey represents a period of 22 days when the equipment malfunctioned.

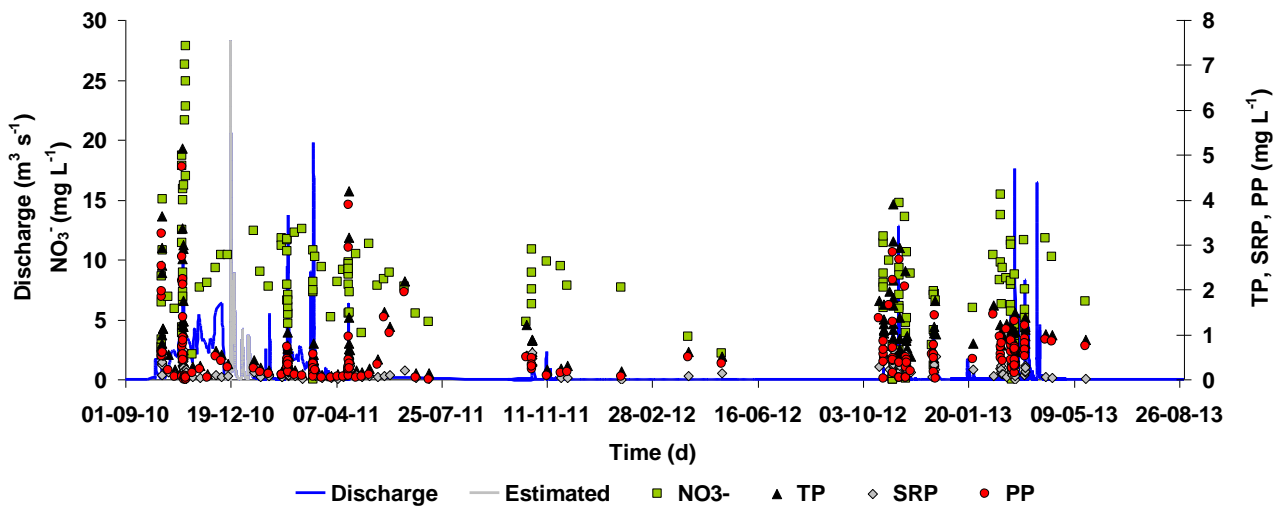


Figure 4. Discharge, nitrate (NO_3^-), total (TP), particulate (PP) and soluble reactive (SRP) phosphorous concentrations observed between September, 2010 and August, 2013. Line in light grey represent a period of 22 days when the equipment malfunctioned.

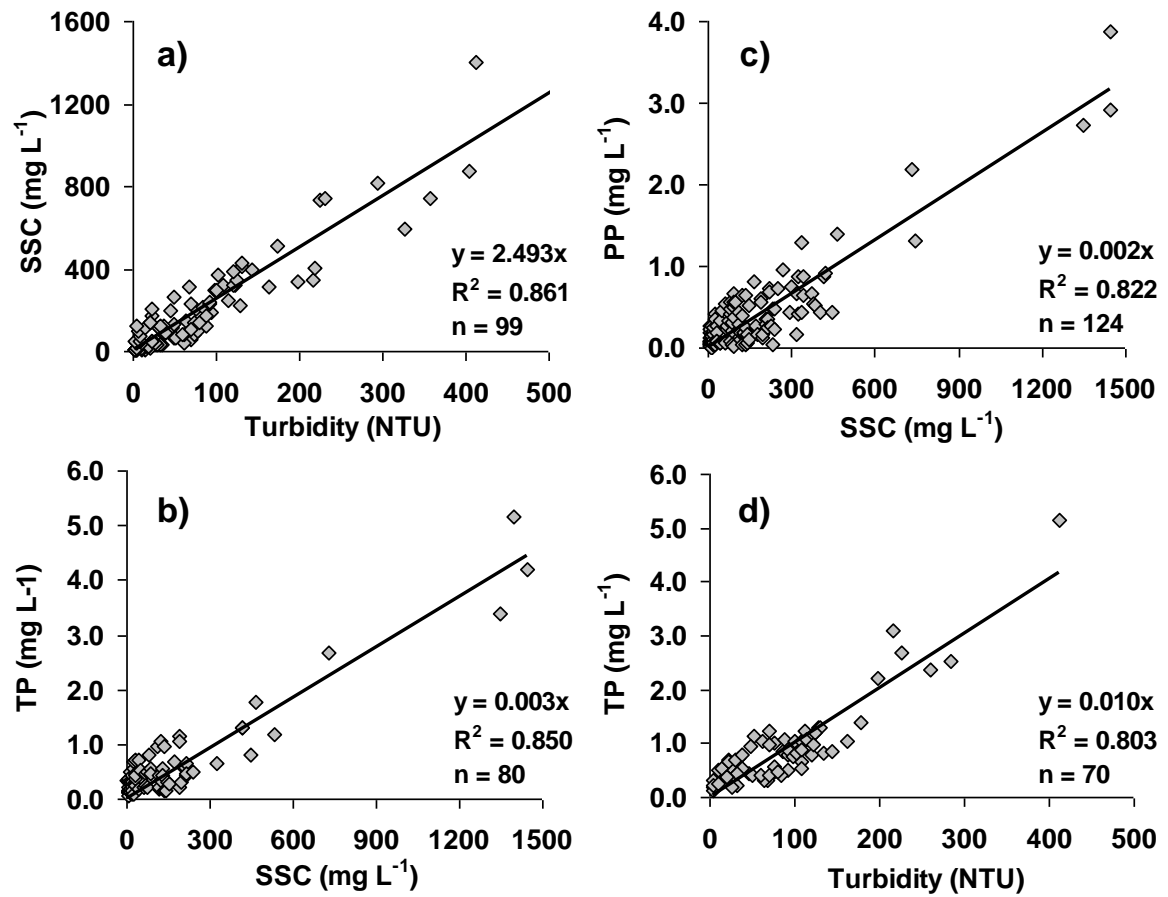


Figure 5. Regression analysis between (a) suspended solid concentration (SSC) and turbidity; (b) total phosphorous (TP) and SSC; (c) particulate phosphorous (PP) and SSC; and (d) TP and turbidity.

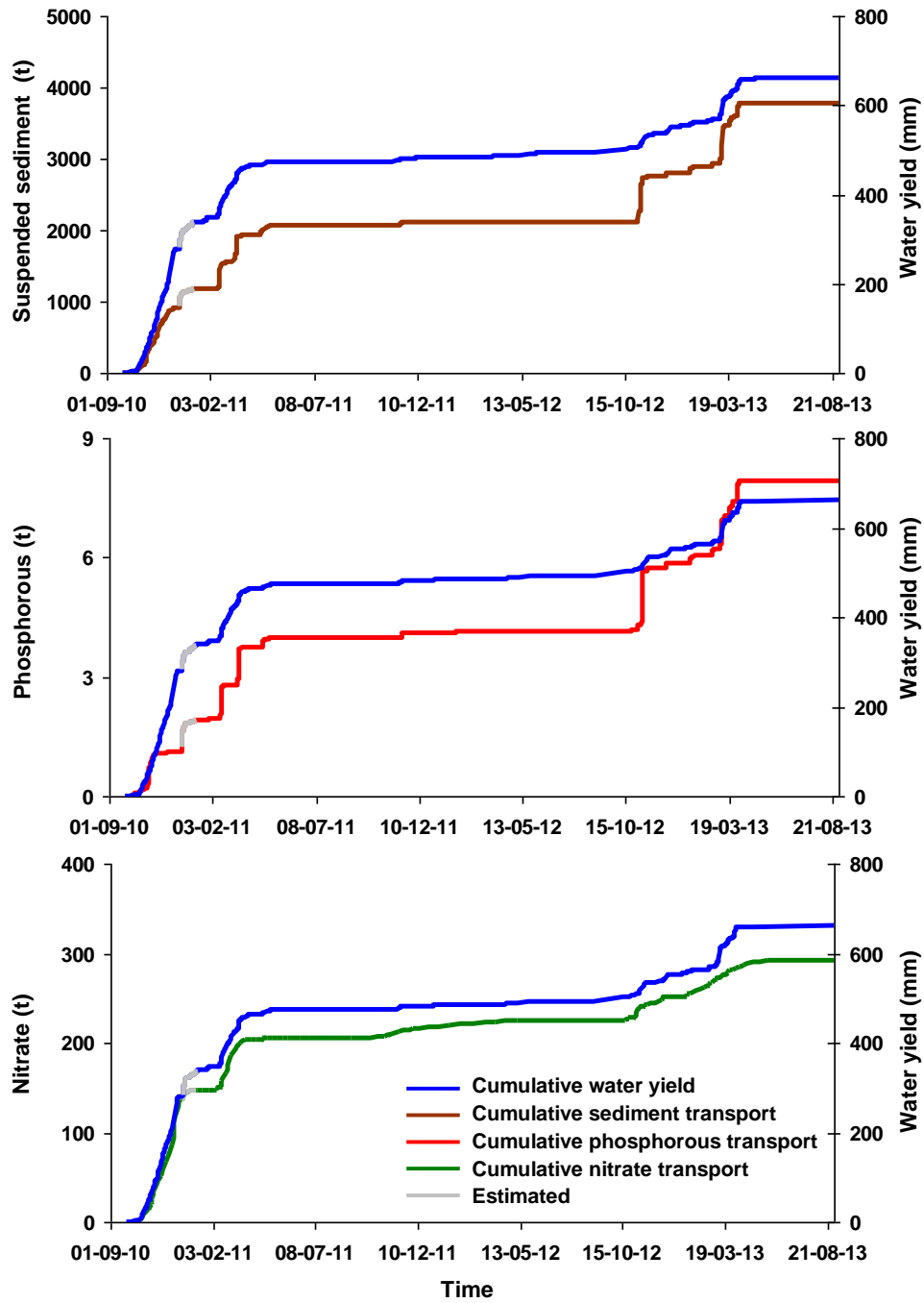


Figure 6. Cumulative water yield (mm), suspended sediments (t), phosphorous (t), and nitrate transport in the Enxoé catchment between September, 2010 and August, 2013.

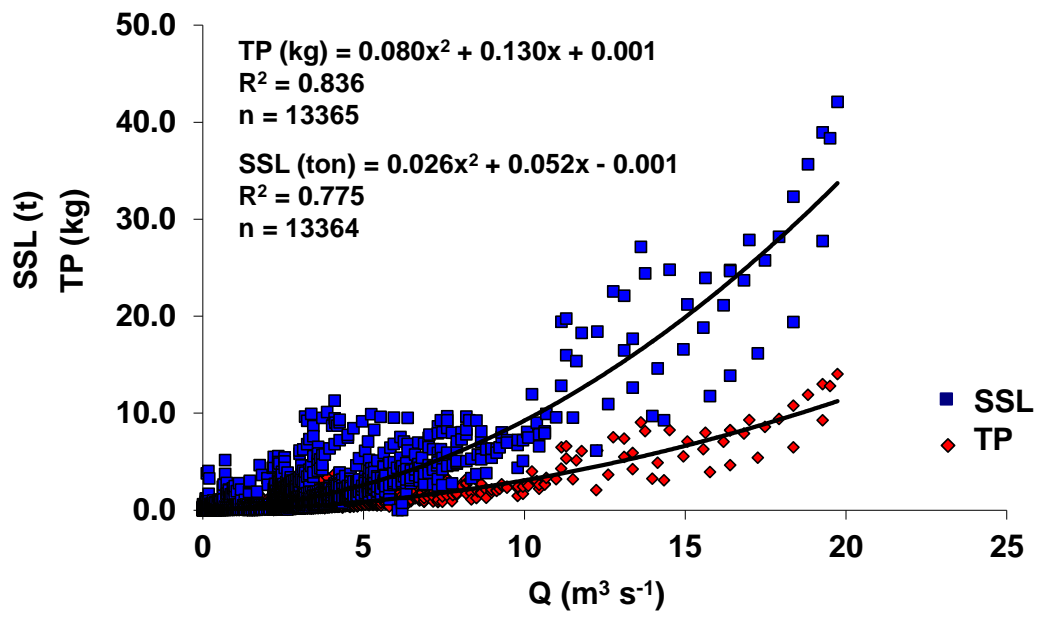


Figure 7. Relations between suspended sediment loads (SSL), or total phosphorous (TP) loads, and discharge (Q) in the Enxoé catchment.

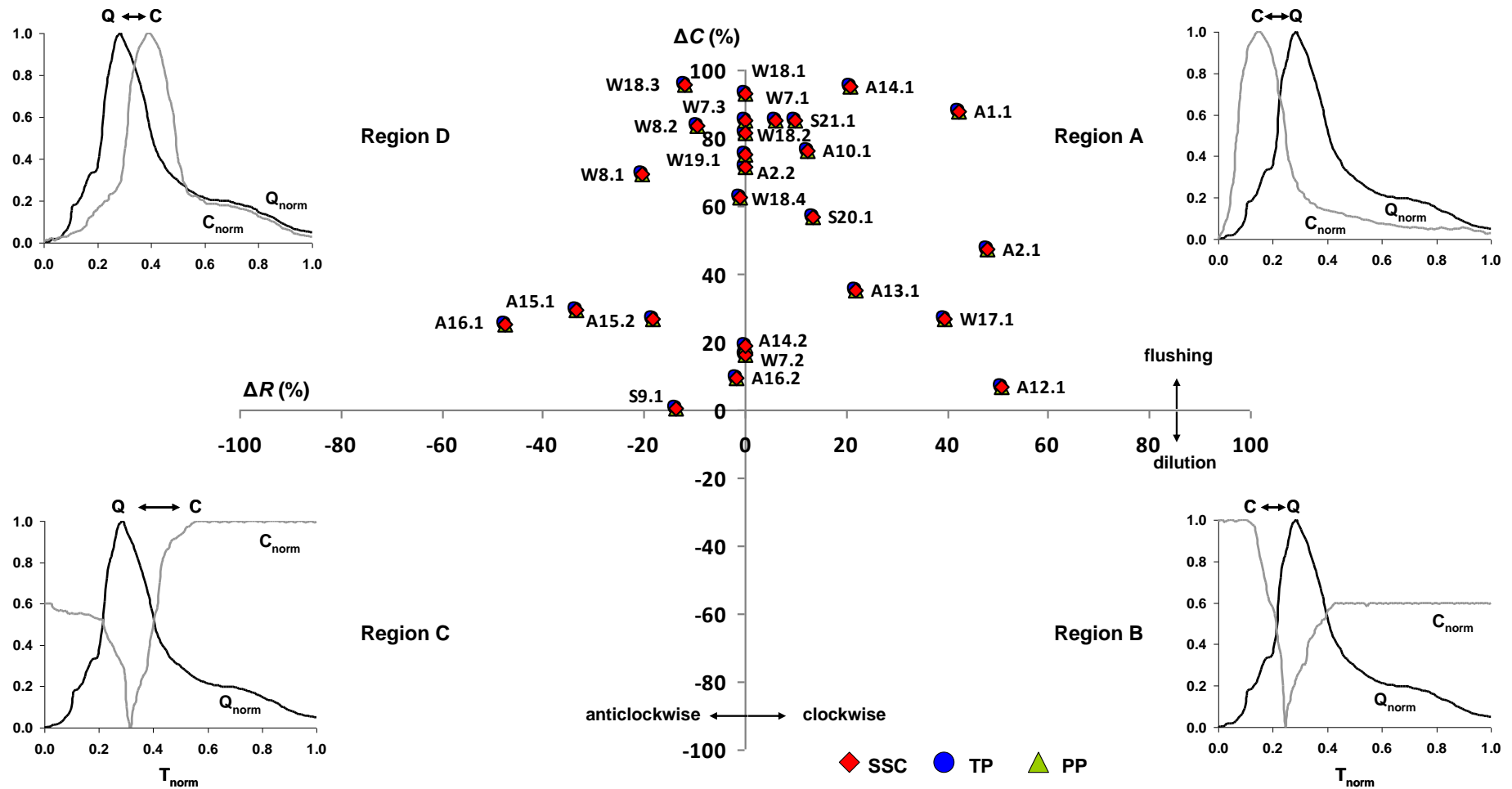


Figure 8. Unity plane ΔC vs. ΔR for the $C-Q$ hysteresis loops of suspended solid concentration (SSC), total phosphorous (TP), and particulate phosphorous (PP). The marks i,j correspond to the i^{th} flood event monitored (1-21) and the j^{th} discharge peak (1-4) monitored during autumn (A), winter (W), and spring (S). Typical $C-Q$ relations are presented for each region of the unity plane ΔC vs. ΔR .

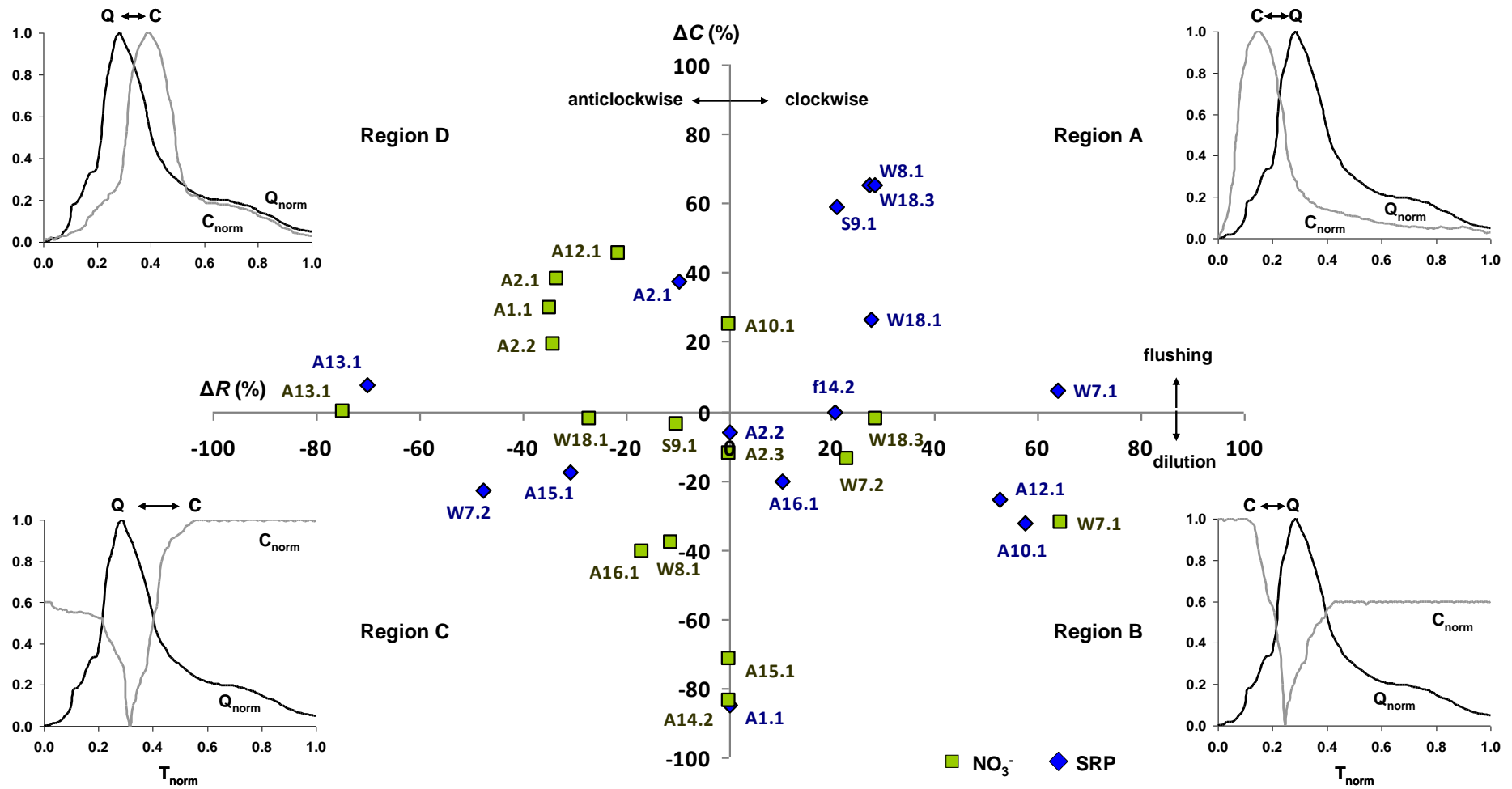


Figure 9. Unity plane ΔC vs. ΔR for the C - Q hysteresis loops of soluble reactive phosphorous (SRP), and nitrate (NO_3^-). The marks i,j correspond to the i^{th} flood event monitored (1-21) and the j^{th} discharge peak (1-4) monitored during autumn (A), winter (W), and spring (S). Typical C - Q relations are presented for each region of the unity plane ΔC vs. ΔR .