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Release of dissolved phosphorus from riparian wetlands: Evidence for complex interactions among hydroclimate variability, topography and soil properties

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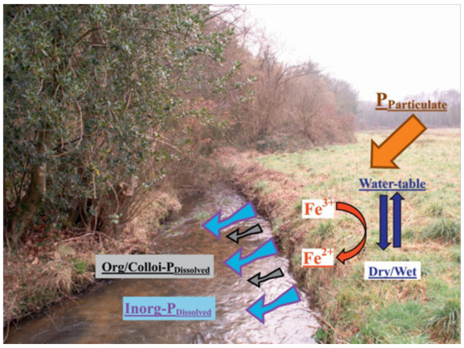
HIGHLIGHTS

- P release dynamics were investigated in natural soil solutions for three years.
- Soil P status and topography control spatial variations of dissolved P.
- Hydroclimate and topography control intra-/interannual variations of dissolved P.
- Retention processes occurred during dissolved P transport from soil to stream.

GRAPHICAL ABSTRACT



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ABSTRACT

In agricultural landscapes, establishment of vegetated buffer zones in riparian wetlands (RWs) is promoted to decrease phosphorus (P) emissions because RWs can trap particulate P from upslope fields. However, long-term accumulation of P risks the release of dissolved P, since the unstable hydrological conditions in these zones may mobilize accumulated particulate P by transforming it into a mobile dissolved P species. This study evaluates how hydroclimate variability, topography and soil properties interact and influence this mobilization, using a three-year dataset of molybdate-reactive dissolved P (MRDP) and total dissolved P (TDP) concentrations in soil water from two RWs located in an agricultural catchment in western France (Kervidy-Naizin), along with stream P concentrations. Two main drivers of seasonal dissolved P release were identified: i) soil rewetting during water-table rise after dry periods and ii) reductive dissolution of soil Fe (hydr)oxides during prolonged water saturation periods. These mechanisms were shown to vary greatly in space (according to topography) and time (according to intra- and interannual hydroclimate variability). The concentration and speciation of the released dissolved P also varied spatially depending on soil chemistry and local topography. Comparison of sites revealed a similar correlation between soil P speciation (percentage of organic P ranging from 35–70%) and the concentration and speciation of the released P (MRDP from <0.10 to 0.40 mg l^{-1}; percentage of MRDP in TDP from 25–70%). These differences propagated to stream water, suggesting that the two RWs investigated were the main

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sources of dissolved P to streams. RWs can be critical areas due to their ability to biogeochemically transform the accumulated P in these zones into highly mobile and highly bioavailable dissolved P forms. Hydroclimate variability, local topography and soil chemistry must be considered to decrease the risk of remobilizing legacy soil P when establishing riparian buffer zones in agricultural landscapes.

1. Introduction

Despite intensive efforts to decrease anthropogenic nutrient inputs to surface water, phosphorus (P) remains an important issue in many water-quality restoration programs worldwide (Jarvie et al., 2013; Sharpley et al., 2013; Smith and Schindler, 2009). As a result of the general reduction in urban and industrial emissions, the percentage of P derived from diffuse agricultural sources has increased over the past two decades in Europe and North America. Agricultural P currently represents >50% of the total P load in many streams and rivers in Western countries (Dupas et al., 2015a; Kronvang et al., 2007). Therefore, research and management efforts in these countries currently focus on decreasing diffuse P losses from agricultural sources (Kleinman et al., 2007; Schoumans et al., 2014; Sharpley et al., 2013).

In agricultural landscapes, establishment of vegetated buffer zones in riparian wetlands (RWs) has long been promoted as an effective way to reduce P transfer to streams. P can be retained through two main mechanisms: i) using vegetation to trap particulate P and ii) retaining dissolved and colloidal P forms via soil adsorption or plant uptake (Dorioz et al., 2006; Haygarth et al., 2006; Vidon et al., 2010). RWs can also be sources of dissolved organic and inorganic P, which is more bioavailable than particulate P, for streams and rivers, in response to geochemical or biogeochemical mediated solubilization of particulate P, or P bound to RW soils (Gächter et al., 1998; Roberts et al., 2012; Stutter et al., 2009). In particular, the water-table fluctuations that seasonally influence these hydrologically unstable zones can induce a succession of drying-rewetting cycles, a situation that is known to trigger the release of dissolved P in soils (Blackwell et al., 2009, 2010, 2013; Turner and Haygarth, 2001). The dissolved P that is released can come from many sources, including lysed microbial cells (Grierson et al., 1998; Turner et al., 2003; Turner and Haygarth, 2001), solutes that soil micro-organisms produce to protect themselves from desiccation (Halverson et al., 2000) and organic matter previously protected in soil micro-aggregates and disrupted by physical stresses caused by drying (Blackwell et al., 2010). The hydrological instability of RWs has also been widely shown to influence redox conditions in soils. The high water table and low velocity flow episodes that usually develop in RWs during the wet season can create anoxic conditions, inducing reductive dissolution of Fe (hydr)oxides (Jeanneau et al., 2014; Knorr, 2013) and thus solubilization of the P previously adsorbed or co-precipitated onto/within these Fe (hydr)oxides (Carlyle and Hill, 2001; Hoffmann et al., 2009; Surridge et al., 2007; Zak and Gelbrecht, 2007).

Thus, it is essential to understand how and under what conditions these biogeochemical processes develop in RWs because they can transform RWs into potential sources of dissolved P in streams. This is a complicated issue due to the diversity of the processes and factors involved, and because of the complex interactions between these processes and factors. In the same way that the speciation and content of P can vary by location in RW soils, both intra- and interannual variations in hydroclimatic conditions can influence groundwater dynamics and consequently the frequency and development of drying-wetting cycles and reducing conditions. Slope gradients and soil composition and structure in RWs may also influence dissolved P release by driving soil-groundwater contact time and soil P adsorption capacity (Darch et al., 2015). The hydroclimate and slope gradient together can influence hydrological connectivity between RWs and streams, ultimately regulating the risk of transfer of released P into streams (Wolf et al., 2013).

Most studies on the release of dissolved P in soils have been performed in the laboratory (e.g. Blackwell et al., 2010; Stutter et al., 2009; Turner and Haygarth, 2001), and little is known about interactions between the above factors and processes under field conditions. Recently, a field study by Dupas et al. (2015b) highlighted the complexity of these interactions by investigating release dynamics of molybdate-reactive (i.e. inorganic) dissolved P (MRDP) in two RWs in a small agricultural catchment (Kervidy-Naizin) in western France. Their results revealed i) a large difference in the ability of two RWs to release MRDP and ii) temporal succession of two P release mechanisms (soil rewetting in autumn and reductive dissolution of soil Fe (hydr)oxides in late winter), which are driven by seasonal fluctuations in water table.

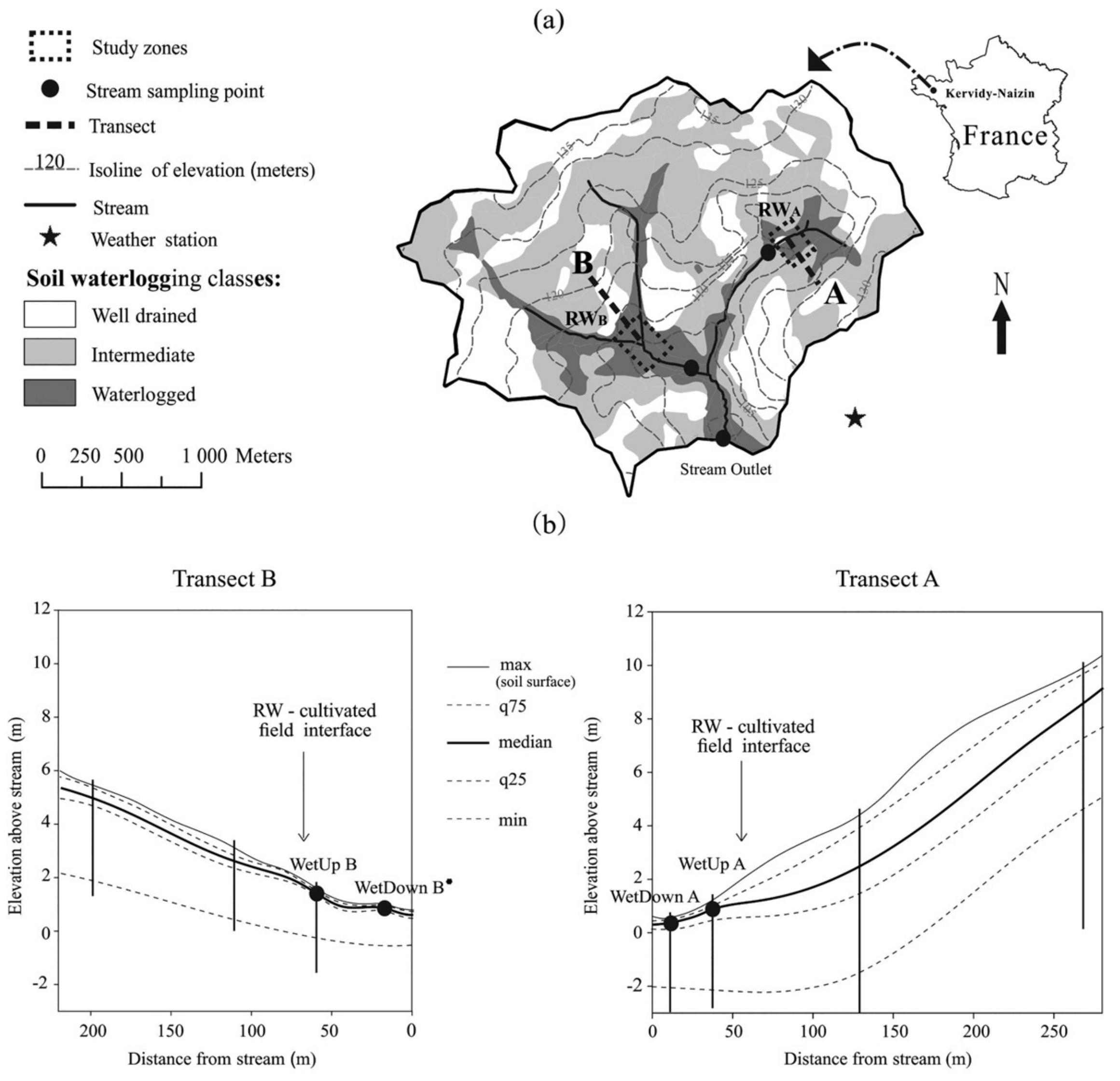
The Dupas et al. (2015b) study, however, monitored dynamics for only one year; thus, it could not examine the influence of interannual hydroclimate variability on P release dynamics. Moreover, little is known about the molybdate-unreactive dissolved P (MUDP) forms in their study because only MRDP concentrations were measured. For the present study, we included a three-year monitoring of the two RWs investigated previously by Dupas et al. (2015b), measuring both MRDP and total dissolved P (TDP) in water from two RW soils, adjacent streams and the outlet stream of the catchment. Our objective was threefold: i) explore the interaction between soil properties and topography that influences the chemical nature (MRDP and MUDP) of the released P, ii) explore interactions among intra- and interannual hydroclimate variability and topography that influence the variations in dissolved P release dynamics and iii) determine whether all of the dissolved P released is quantitatively transferred to the stream.

2. Materials and methods

2.1. Research site

The Kervidy-Naizin catchment is a small (5 km^2) headwater catchment located in central Brittany, western France (48°N, 3°W), that belongs to the AgrHys environmental research observatory (http://www6.inra.fr/ore_agrhys_eng/). The climate is temperate oceanic, with annual temperature and rainfall averaging 10.5 °C and 875 mm, respectively, from 2006 to 2016. The catchment is drained by a second-order stream (Strahler classification) that usually dries up in summer. The substrate lithology consists of impervious Brioverian schists covered with 2–30 m of unconsolidated weathered materials in which a shallow aquifer develops. Soils are silty loamy Luvisols that are well-drained in upland domains and hydromorphic in valley bottoms, where RWs develop. Agricultural practices mainly involve arable crops (cereals, maize and winter barley) and livestock farming (dairy/beef cattle, pigs and poultry).

Many hydrological and biogeochemical research projects have been conducted in this catchment since the AgrHys environmental research observatory was established in 1993 (Aubert et al., 2013; Dupas et al., 2016; Lambert et al., 2013; Molénat et al., 2008), providing detailed knowledge of water chemistry and water pathways during base-flow and storm-flow periods. Water-table depths are recorded every 15 min using 10 piezometers (depth: 2–8 m, equipped with Orpheus OTT pressure probes) installed along two transects (A and B, Fig. 1). Stream discharge is monitored at the outlet at 1-min intervals with an automatic gauge station; rainfall is recorded hourly at the Toullo weather station located to the east of the catchment outlet.



* WetDown B is located ca. 100 m laterally from piezometer transect B

Fig. 1. (a) Map of the Kervidy-Naizin catchment; (b) location of sampling sites (black dots) and variability of water-table level along the two transects, as established from analysis of 15 years of piezometric data. Vertical black lines represent piezometers.

Three hydrological periods have been distinguished on an annual basis in this catchment (Humbert et al., 2015; Lambert et al., 2013; Molénat et al., 2008). Period A sees progressive rewetting of RW soils after the dry summer season. Period B sees the water-table rise in the upland domain, leading to a high hydraulic gradient between upland areas and RWs and strong lateral water flow in RW soils; this period (sub-divided into B1 and B2, depending on the RW soil redox status (Lambert et al., 2013)) is associated with prolonged waterlogging of RW soils on an annual basis. Period C sees drawdown of the water table, which progressively dries catchment soils and decreases stream flow (Humbert et al., 2015; Lambert et al., 2013; Molénat et al., 2008).

RWs located at the foot-slope of transects A and B (RW_A and RW_B) were studied using zero-tension lysimeters installed by Dupas et al. (2015a, b) designed to collect free soil water without disturbing in-situ redox conditions. Twenty-four lysimeters were set in triplicate at two depths (10–15 and 50–55 cm) and at two sites in each RW. The two sites in RW_A (hereafter called "WetUp-A" and "WetDown-A") are located 13 m and 40 m downslope from the RW-Cultivated field interface, respectively, while those in RW_B (hereafter called "WetUp-B" and "WetDown-B") are located 9 m and 52 m downslope from the RW-Cultivated field interface, respectively (Fig. 1). Transects A and B, and therefore RW_A and RW_B, differ morphologically; transect B and RW_B are flatter than transect A and RW_A (mean slope gradient of 2.8% and 3.8%, respectively). RW_A is 51 m wide, with vegetation consisting of unfertilized herbaceous species (*Dactylis glomerata* and *Agrostis canina*), while RW_B is 64 m wide, with vegetation consisting of a mixture of shrubs and trees (Populus negro, *Salix caprea* and *Betula alba*).

Both RWs were managed as unfertilized riparian buffer zones for ca. 20 years, without export of biomass. Before being managed as buffer zones, RW_A was fertilized with pig slurry and mineral fertilizer at amounts up to 60 kg P ha^{-1} yr^{-1}, while RW_B was subjected to unquantified P inputs of cattle manure (assumed to be lower than those in RW_A). Dupas et al. (2015b) measured total P, extractable P (citric acid extractable P, Dyer method), clay, silt, sand, Al, Fe, organic carbon and organic nitrogen concentrations of soils in RW_A and RW_B. Their results indicated a three- to four-fold decrease in mean concentrations of total P and Dyer P with increasing depth (Table S1). They also showed higher total P and Dyer P concentrations in RW_A top-soils (1052–1213 and 242–289 mg/kg, respectively, depending on position in the RW) than in RW_B top-soils at equivalent positions and depths (458–681 and 12–48 mg/kg, respectively). The mean degree of P saturation calculated from oxalate-extractable Al and Fe contents was also higher in RW_A (7–21% depending on depth and position in the RW) than in RW_B (1–3%). Total P and Dyer P concentrations decreased from the top (i.e. near the cultivated fields) to the bottom (i.e. near the stream) of each RW.

2.2. Soil and water sampling

In April 2015, a 75-mm-diameter auger was used to collect soil samples in RW_A and RW_B at depths comparable to those of the lysimeters (i.e. 0–15 cm ("shallow") and 30–40 cm ("deep")) to determine P speciation in soils from these RWs. In RW_A, soil samples were taken at WetUp-A and WetDown-A; in RW_B, only the shallow soil (0–15 cm) at WetUp-B could be sampled due to the extreme moisture conditions in this RW at the time. Soil water samples were collected weekly to biweekly from October 2013 to June 2016. On each sampling date, samples from the triplicate lysimeters from each given depth and location were mixed to increase the amount of soil water available for chemical analysis.

Stream water samples were collected on the same dates as the soil water sampling in the stream reaches adjacent to the two RWs, and daily at the catchment outlet. Because this study focused on the release of P in RW soils and the subsequent transfer of this P to the stream through groundwater flow, samples collected during storms were removed from data analysis to avoid the potential contribution of overland flow to the stream's dissolved P budget (included when calculating annual TDP flux). Note that the storm periods are also important concerning P release from RWs, due to the high hydraulic gradient between RWs and streams which leads to strong exchange of water and solutes. Storm events were identified when discharge exceeded 20 $l\ s^{-1}$ and when increases in discharge over a period of 10 min were >10% (Dupas et al., 2015a). All water samples were passed through <0.45 μm cellulose acetate filters within 6 h after sampling, then kept in a refrigerator in the dark at 4 °C until analysis within 3 days.

2.3. Soil and water chemical analysis

Soil samples were transferred to the laboratory in plastic bags inside a cool box, then homogenized by wet sieving to <5 mm. Soil P speciation was determined using the sequential fractionation method developed by Hedley et al. (1982) and modified by Ivanoff et al. (1998). This method is based on sequential P extraction with different reagents (H_2O, 0.5 M $NaHCO_3$ at pH 8.5, 1 M HCl, and 0.1 M NaOH). P was extracted by shaking soil suspensions (1 g of dry weight soil in 30 ml solution) for 16–21 h. After centrifugation at 10000 RPM for 10 min, the supernatant was removed and analyzed for TDP and MRDP. P extracted by H_2O and $NaHCO_3$ is considered labile P, while HCl- and NaOH- extracted P is defined as moderately labile P. Residual (i.e. non-labile) P, which may contain a mixture of organic and inorganic P forms, was determined as the total P measured after calcination at 550 °C and acid digestion of the residue after the final extraction step. Extraction efficiency was checked by comparing the sum of P extracted using the sequential extraction method with the total P content measured after calcination and acid digestion of the bulk soil samples. All sequential experiments were performed in triplicate.

For all water samples, MRDP was determined colorimetrically via reaction with ammonium molybdate (Murphy and Riley, 1962) applied directly to the <0.45 μm filtrates (natural water) or to the centrifuged solutions (soil extracts). The same method was used for TDP, but after digestion of the filtrates or centrifuged solution in acidic potassium persulfate. The precision of MRDP and TDP measurements was $\pm 4\ \mu g\ l^{-1}$ and $\pm 13\ \mu g\ l^{-1}$, respectively. The difference between TDP and MRDP was assumed to be organic P for soil extracts and MUDP for natural water samples. Development of reducing conditions in soil water was monitored by measuring Fe^{2+} concentrations using the 1.10 phenanthroline colorimetric method (AFNOR NF T90-017, 1997), with a precision of 5%. Fe^{2+} reactants were mixed with samples in situ to avoid the influence of oxidation on Fe^{2+} concentration during sample transport. The potential influence of Fe oxyhydroxide precipitation on MRDP concentrations during sample transport was checked by comparing MRDP concentrations in sample aliquots directly filtrated and acidified on-site to MRDP concentrations in sample aliquots filtrated in the laboratory. The results were found to be comparable with average differences below 12%, suggesting that potential Fe^{2+} oxidation had little influence on MRDP concentrations in the <0.45 μm filtrates (Fig. S1).

3. Results

3.1. Hedley P fractionation

The sums of TDP extracted by Hedley fractionation did not differ significantly (ANOVA, $p > 0.05$) from total P contents measured after digestion of the bulk soil samples, suggesting high efficiency of the selected P fractionation method (see supporting materials, Table S2). Consistent with results of the bulk soil analyses (Table S1), the amount of extracted P content decreased strongly with soil depth and was much higher in RW_A soils than in RW_B soils (Fig. 2). However, the total P content from bulk soil analyses were 1.3–3.1 times as large as those obtained by Hedley fractionation for the same soils (Tables S1, S2). Hedley fractionation may have underestimated total P content for two reasons: i) the difference in sample pretreatment (sieving wet soils at 5 mm for P fractionation vs. sieving air-dried soils at 2 mm for bulk soil analyses); ii) the difference in the acids used for digestion (calcination at 550 °C followed by H_2SO_4 digestion for P fractionation vs. $HF/HClO_4$ digestion for bulk soil analyses).

According to Hedley fractionation, moderately labile P extracted was always the largest P fraction (up to 77%), while labile P and residual P were found in smaller percentages (12–18% and 9–33% of total extracted P, respectively). In the two main fractions (moderately labile and labile P), P speciation in shallow soils differed between RW_A and RW_B. Organic P represented ca. 70% of these two fractions in shallow RW_B soils but <35% of those in shallow RW_A soils. Interestingly, the percentage of MRDP in these two fractions was linearly correlated with the percentage of Dyer P in the total P content from bulk soil analysis at the same sites ($r = 0.9753$, Fig. S2). This indicates that Dyer P content can be considered a proxy for the extracted MRDP (i.e. inorganic P content) in the soils studied; thus, the lower percentage of Dyer P in RW_B soils emphasized that organic P was the dominant P fraction in RW_B soils (Table S1).

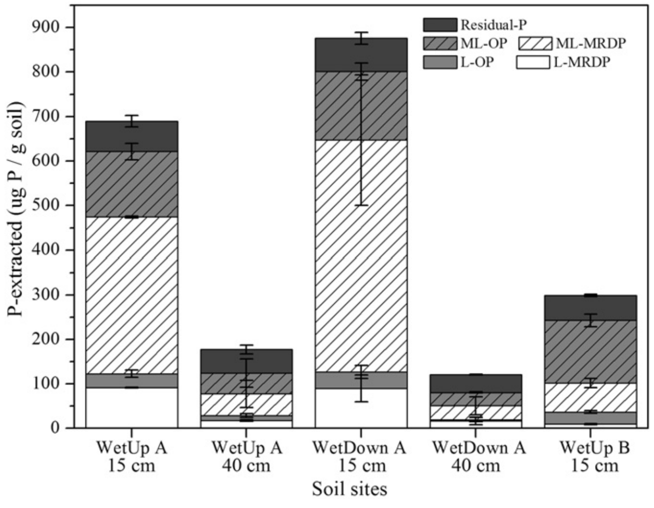


Fig. 2. Amounts of organic and inorganic P in the studied soils as established from the Hedley fractionation results. "ML" and "L" refer to moderately labile and labile P, respectively. "OP" represents organic P, which is the difference between TDP and MRDP. Error bars represent the standard deviation of triplicate samples.

3.2. Rainfall, discharge and water-table variations

In this section, we highlight differences in hydroclimatic and water-table dynamics between the three P-monitored years to clarify their influence on processes that trigger release of different forms of dissolved P in RW soils. For simplification, the hydrological year monitored by Dupas et al. (2015b) (i.e. 2013–2014) is referred to as Y1, and the two hydrological years monitored in the current study (i.e. 2014–2015 and 2015–2016) are referred to as Y2 and Y3.

Cumulative values and distribution of discharge directly reflected rainfall (Fig. 3a). Stream discharge at the catchment outlet in Y1 was nearly 2 times as high as that in Y2 and Y3, especially during the high-flow period B. For each of the three years, the beginning of period B corresponded to an abrupt increase in stream discharge to >100 l s^{-1}. In Y1 and Y3, stream discharge remained >100 l s^{-1} during most of period B, even though the magnitude was relatively lower in Y3. The magnitude of stream discharge in Y2 during period B was much lower, with <30 consecutive days with discharge >100 l s^{-1} (Fig. 3a).

Consequently, water-table fluctuations and the number of days in which RW soils were saturated also varied during the three years (especially for high-flow period B) and between the two RWs (Fig. 3b). The difference in transect topography resulted in a shallower mean water table in RW_B than in RW_A (Fig. 1b). In RW_B, even the shallow soil horizons remained saturated throughout period B, irrespective of interannual rainfall variability. In contrast, due to the steeper topography of RW_A, interannual variability in rainfall amount and frequency resulted in strong spatio-temporal variability in the duration of saturation periods. Shallow soils remained saturated throughout most of period B at WetUp-A and WetDown-A locations in Y1. In contrast, the water table remained quite deep in "dry" Y2; only deep soils remained saturated during period B, while shallow soils experienced a frequent succession of dry/wet episodes. An intermediate situation was observed in Y3: shallow soils in WetDown-A remained saturated during most of period B, as in Y1, while those in WetUp-A experienced a frequent succession of dry/wet episodes, as in Y2 (Fig. S3).

3.3. Soil water chemistry

Soil water chemistry data are reported as time-series plots that compare TDP, MRDP and Fe^{2+} concentrations measured at WetUp-A (Fig. 4.1), WetDown-A (Fig. 4.2), WetUp-B (Fig. 4.3) and WetDown-B (Fig. 4.4). During the three years, MRDP concentrations remained near the detection limit (ca. 0.005 mg l^{-1}) in RW_B lysimeters, except at WetUp-B, where MRDP concentrations in shallow lysimeters rose to 0.1 mg l^{-1} at the end of period B of each year (Fig. 4.3a). These low MRDP concentrations in RW_B lysimeters contrasted with those in RW_A lysimeters, which frequently recorded MRDP concentrations >0.1 mg l^{-1}. MRDP concentrations fluctuated in the same range from Y1 to Y3 in shallow lysimeters in RW_A (0.15–0.40 and 0.05–0.25 mg l^{-1} at WetUp-A and WetDown-A lysimeters, respectively). The positive concentration gradient observed between shallow WetDown-A (0.1 mg l^{-1} < MRDP < 0.2 mg l^{-1}) and WetUp-A (0.2 mg l^{-1} < MRDP < 0.4 mg l^{-1}) lysimeters in Y1 remained constant in Y2 and Y3. Mean TDP concentrations were consistently higher (70%, $n = 250$) than mean MRDP concentrations in all lysimeters, suggesting that MUDP were always present (Fig. 4.1-4). Interestingly, strong TDP concentration peaks (up to 0.3–0.4 mg l^{-1}) were observed in WetUp-B and WetDown-B lysimeters (Fig. 4.3a–b and 4.4a–b). These peaks indicate that the dissolved P released by RW_B soils had a different chemical nature (molybdate unreactive) compared to that released by RW_A soils (molybdate reactive).

The Fe^{2+} concentration peaks varied in amplitude and timing among sampling sites and were in phase with variations in water-table dynamics and soil saturation periods. Deep lysimeters at WetUp-A and WetDown-A recorded Fe^{2+} concentration peaks (up to 17 mg l^{-1}) each year (Fig. 4.1d and 4.2d). In shallow lysimeters, Fe^{2+} concentration peaks were only observed in Y1 and Y3 at WetDown-A (Fig. 4.2c) and in "wet" Y1 at WetUp-A (Fig. 4.1c). In contrast, all lysimeters in RW_B recorded Fe^{2+} peaks at the end of period B of each year (Fig. 4.3c–d and 4.4c–d). Thus, Fe^{2+} concentration peaks in RW_A and RW_B lysimeters depended entirely on water-table dynamics and the topographic position of the lysimeters.

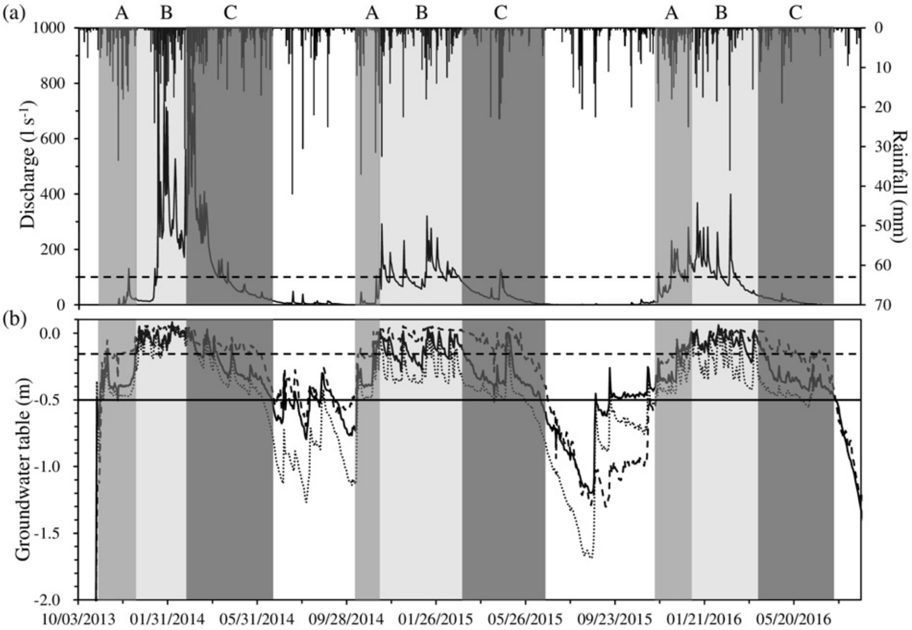
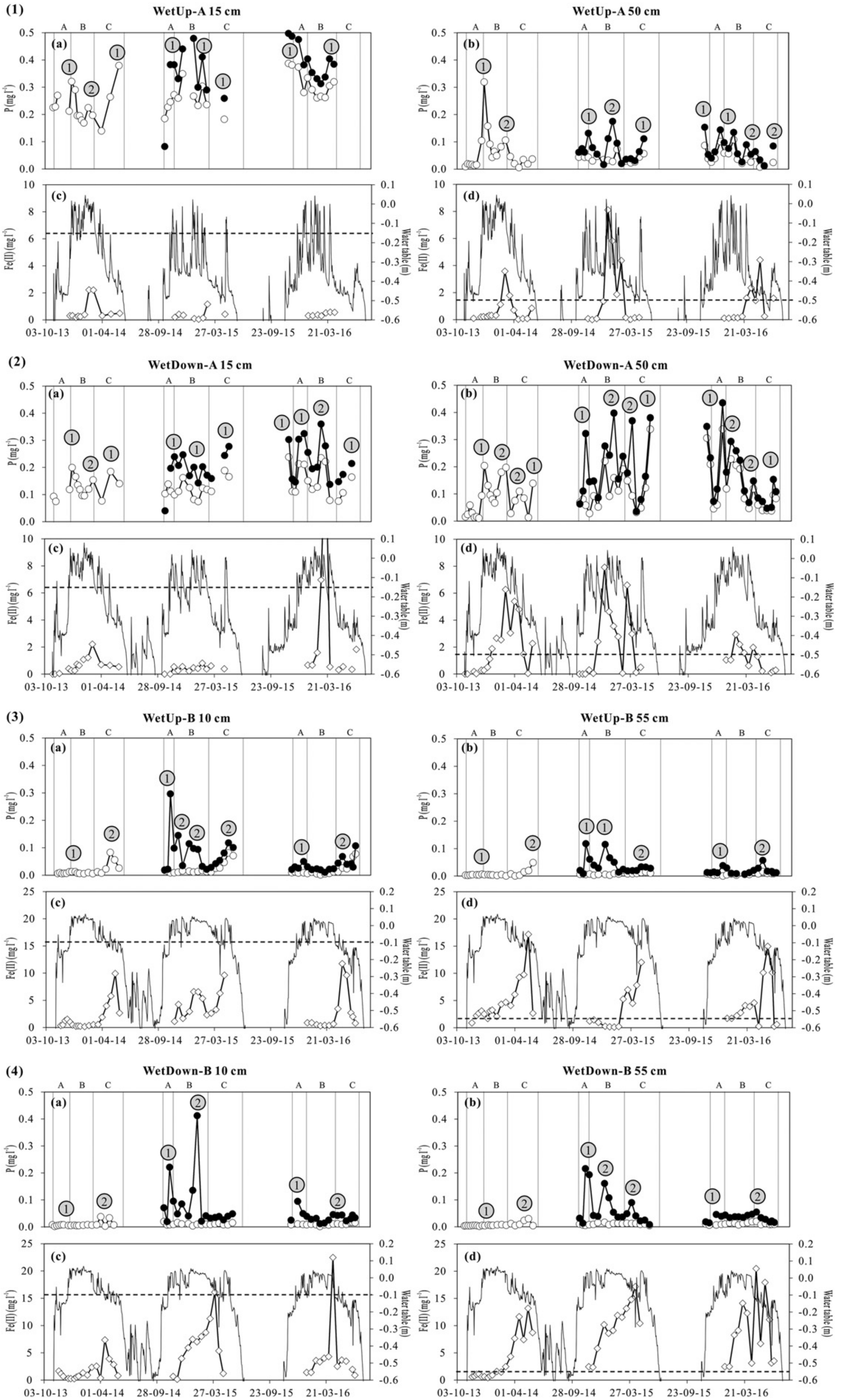


Fig. 3. (a) Discharge (black line) and precipitation (black histogram) time-series data for the Kervidy-Naizin catchment during the three investigated years. Grey, light grey and dark grey areas represent the identified hydrologic periods A, B and C, respectively. Horizontal dashed line represents discharge value of 100 l s^{-1}. (b) Groundwater table of WetUp-A (dotted line), WetDown-A (solid line) and WetUp B (dashed line). Horizontal dashed and solid lines represent the depths of 15 cm and 50 cm lysimeters in RW_A. Due to the flatness of RW_B, the results for WetUp B and WetDown B are based on the same piezometric water-table data, with depths of lysimeters in RW_B at 10 cm and 55 cm, respectively.


(1)
WetUp-A 15 cm
WetUp-A 50 cm
(2)
WetDown-A 15 cm
WetDown-A 50 cm
(3)
WetUp-B 10 cm
WetUp-B 55 cm
(4)
WetDown-B 10 cm
WetDown-B 55 cm
(a)
(b)
(c)
(d)
A
B
C
P (mg l⁻¹)
Fe(II) (mg l⁻¹)
Water table (m)
1
2
03-10-13
01-04-14
28-09-14
27-03-15
23-09-15
21-03-16

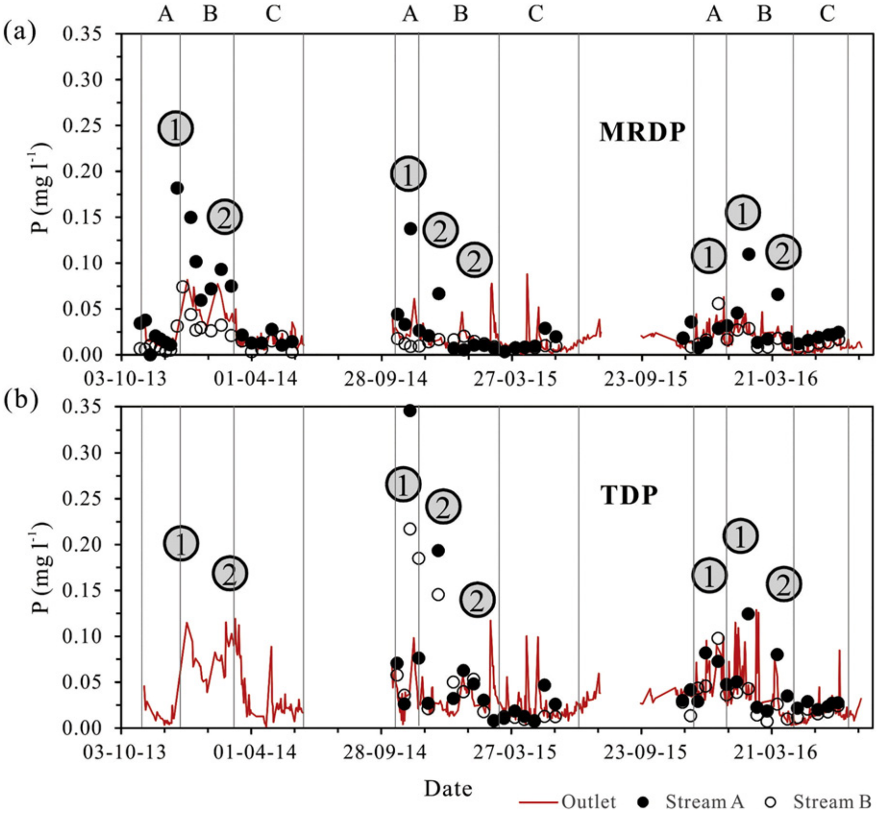


Fig. 5. (a) MRDP and (b) TDP concentrations during baseflow periods (A, B and C) in streams near RW_A, RW_B and at the catchment outlet. Solid circles: MRDP or TDP in stream A waters; empty circles: MRDP or TDP in stream B waters; red line: MRDP or TDP in stream waters at the catchment outlet. Circled numbers in grey (1 and 2) relate concentration peaks to P release mechanisms discussed in text. Vertical grey lines represent the limits between hydrological periods.

By comparing water-table fluctuations to the temporal distribution of MRDP, TDP and Fe^{2+} concentration peaks, one can identify two situations that favored the occurrence of TDP and MRDP peaks in the two RWs. The first situation ("1" in Fig. 4.1-4) corresponds to episodes of water-table rise after dry periods, especially the initial water-table rise event after the dry summer, i.e. at the beginning of period B. The second ("2" in Fig. 4.1-4) corresponds to periods of Fe^{2+} release to soil water, which were particularly well identified in both shallow and deep RW_A lysimeters (Fig. 4.1-2). Thus, our data support a combination of two types of dissolved P release peaks in the RWs studied, as highlighted by Dupas et al. (2015b).

3.4. Stream water chemistry

Stream water chemistry was similar to that of RW_A and RW_B soil water, in terms of differences in P speciation and temporal dynamics of TDP and MRDP concentrations (Fig. 5). In particular, the stream branch that drains RW_A (stream A) had consistently higher MRDP concentrations than the stream branch that drains RW_B (stream B), as observed in the corresponding RW soil water. Concentration peaks observed in streams A and B were similar to those observed in RW soil water. However, stream waters differed from soil water in that MRDP concentrations measured in the stream in Y2 and Y3 were lower than those in Y1. This was particularly evident for stream A, whose mean MRDP concentration of 0.048 mg l^{-1} ($n = 20$) in Y1 decreased to 0.016 ($n = 15$) and 0.029 mg l^{-1} ($n = 17$) in Y2 and Y3, respectively. This interannual decrease in MRDP concentration in stream A differed greatly from the consistently high level or increase in MRDP concentrations in RW_A soil water (Fig. 4.1-2). In contrast, MUDP produced in RW_B soil water in Y2 and Y3 was efficiently transferred to the stream in these years, which indicates that conditions or processes in Y2 and Y3 decreased the transfer of MRDP from soil waters to the stream.

4. Discussion

4.1. Influence of soil P content and soil P speciation

One major finding of the present study is the evidence that release of dissolved P following water-table rise in RWs is not restricted to MRDP (inorganic P). Other P species, which the ammonium molybdate method of Murphy and Riley (1962) cannot detect, are also released. These species include organic P carried by organic molecules such as phytates, sugar phosphates or phospholipids, or organic or inorganic P incorporated into or adsorbed onto colloidal particles (Haygarth and Sharpley, 2000). Release of organic P in RWs is potentially damaging due to the risk of eutrophication, since several P-bearing organic compounds are known to be highly bioavailable (Li and Brett, 2013). Many recent studies have indicated that Fe-rich colloids associated with organic matter are vectors for P transport in soils and watercourses (e.g. Baken et al., 2016; Gottselig et al., 2014; Liu et al., 2014; Regelink et al., 2013; Rick and Arai, 2011) and that increased mobilization of these colloids in

Fig. 4. Time-series plots comparing the evolution of MRDP (empty circles) and TDP (solid circles) concentrations with Fe^{2+} concentrations and water-table depth fluctuations measured in soil solutions at (1) WetUp-A locations (15 cm and 50 cm depth), (2) WetDown-A locations (15 cm and 50 cm depth), (3) WetUp-B locations (10 cm and 55 cm depth), and (4) WetDown-D locations (10 cm and 55 cm depth). Circled numbers in grey (1 and 2) relate concentration peaks to P release mechanisms discussed in text. Horizontal black dashed lines represent the depths of lysimeters. Vertical black lines represent the limits between hydrological periods. Data for hydrological year 2013–2014 are from Dupas et al. (2015b).

RWs can damage the quality of surface water because it could accelerate transfer of P from soils. Based only on our data, we cannot firmly identify the presence of these colloids in the two RWs studied. We can only assume that when they are present, they are likely to mobilize P more in RW_B soil water than in RW_A soil water, where most of the P released is MRDP.

We assume that the differences in P content and speciation observed between RW_A and RW_B soils are the main drivers of the observed spatial differences in dissolved P concentration and speciation. Bulk soil analyses and Hedley fractionation results showed that RW_B soils contained less total P and less easily exchangeable inorganic P than RW_A equivalents. The historical difference in P input ($RW_A > RW_B$) could explain the difference in total P content between RW_B and RW_A soils. There are several explanations for the difference in P speciation, including i) differences in past fertilizer inputs prior to conversion into vegetated buffer zones (pig slurry and mineral fertilizer in RW_A vs. cattle manure in RW_B), since fertilization history is known to play a key role in P speciation in soils (Eriksson et al., 2016; Khatiwada et al., 2014) and ii) differences in vegetation cover (mainly grass species in RW_A and shrubs and trees in RW_B), since vegetation is known to influence the inorganic-P:organic-P ratio in soils (directly or indirectly) through its influence on soil pH (Osborne and Kovacic, 1993; Sugihara et al., 2015). The difference in topography between the two RWs could also explain the difference in P speciation. The interannual recurrence of prolonged saturation periods, as observed in RW_B soils, could have decreased the mineralization of soil organic matter, thereby favoring the release of a larger percentage of organic/colloidal P. Conversely, rapid oscillation of oxic/anoxic conditions induced by frequent water-table fluctuations in RW_A could have increased conversion of organic P into inorganic P forms in the soil, as suggested by recent experimental results (Scalenghe et al., 2012), which ultimately would explain why water leached from RW_A was rich in inorganic P and poorer in organic/colloidal P.

4.2. Key influence of interannual hydroclimatic variability on P release dynamics

Our data indicate that two hydrologically-driven processes influence release of dissolved P in the two RWs studied: i) rewetting of soils after dry periods and ii) reductive dissolution of soil Fe (hydr)oxides in response to soil saturation. The first process is consistent with laboratory experiments showing that soil rewetting after a dry period can release organic and inorganic P as a result of microbial biomass being killed by osmotic shock (Blackwell et al., 2010; Turner et al., 2003; Turner and Haygarth, 2001). This process was triggered each year in RW_A and RW_B during the water-table rise at the beginning of period B, and occasionally occurred in shallow RW_A soils in late period B (Fig. 4.1–4). Concerning the second process, it is well known that reductive dissolution of Fe (hydr)oxides, as observed in saturated RW soils, can cause P release in soil water (Hoffmann et al., 2009; Obour et al., 2011; Roberts et al., 2012; Scalenghe et al., 2012; Surridge et al., 2007; Young and Ross, 2001). Our results show, however, that triggering of this process can vary spatially and temporarily because it depends on the establishment of the anoxic conditions necessary to reduce soil Fe (hydr)oxides. These conditions were spatially and temporary stable in RW_B, where simultaneous reductive dissolution of soil Fe (hydr)oxides and dissolved P release occurred each year in both shallow and deep soils (Fig. 4.3-4). It was unstable in shallow RW_A soils, occurring only in wet Y1 at WetUp-A, and only in Y1 and Y3 at WetDown-A (Fig. 4.1–2). In addition to the amount and frequency of rainfall, topography appears to have a major influence on the temporal stability of reductive dissolution of soil Fe (hydr)oxides. The flat topography of RW_B facilitated saturation of shallow and deep soils for long periods of time, irrespective of the annual weather conditions. In contrast, the steeper slope of RW_A meant that long-term soil saturation only occurred annually in deeper soils, and occurred in shallower soils only in relatively wet years (Y1 and Y3), when they were saturated long enough to allow reductive dissolution of Fe (hydr)oxides.

Using our data, we semi-quantitatively estimated the groundwater conditions required to induce reductive dissolution of Fe (hydr)oxides, i.e. the period of time the soil must remain saturated to generate the anoxic conditions necessary for the reductive dissolution to start. In shallow RW_B soils, 65 and 51 days were required at WetUp-B and WetDown-B, respectively. In shallow WetUp-A soils, Fe^{2+} release began after 26 consecutive days of saturation in Y1, but none was observed in Y2 and Y3 because they had no >5 and 8 consecutive days of saturation, respectively. In shallow WetDown-A soils, Fe^{2+} release began after 48 consecutive days of saturation in Y1 and Y3, but none was observed during Y2 because it had no >26 consecutive days of saturation. In deep soils, longer saturation was required to trigger reductive dissolution in RW_B soils (at least 95 days) than in RW_A soils (at least 66 days). Different mechanisms could explain these spatial variations, such as initial differences in the availability of other electron acceptors (mostly oxygen and nitrate) in the soil. Deep RW_B soils had higher nitrate concentrations than deep RW_A soils at the beginning of period B (data not shown), which could explain why reductive dissolution of Fe (hydr)oxides occurred later in RW_B soils than in RW_A soils.

Hydroclimate variability during the three years and topographic differences between RW_A and RW_B also induced spatio-temporal variations in the triggering of P mobilization through soil rewetting after drying. For example, in shallow WetUp-A soils, at least two release peaks occurred in Y2 and Y3 due to a succession of dry/wet episodes caused by water-table fluctuations, while only one peak occurred in Y1 (between periods A and B); the water table at this location remained near the soil surface throughout period B. This is in contrast to the flatter RW_B, in which P release upon soil rewetting was essentially confined to the transition between periods A and B of each year (Fig. 4.3–4).

Overall, release of MRDP in RW_A soils was sustained by a combination of higher soil P content, predominant inorganic P forms and the less stable hydrological conditions induced by a steeper topography. Although TDP dynamics observed in Y2 and Y3 suggest that RW_B soils can release dissolved P in organic/colloidal forms, the peak magnitudes and mean concentrations in these soil waters were much lower than those observed for MRDP in RW_A waters. MRDP concentrations in RW_A soil water were not only higher on average but also appeared to decrease less rapidly after a water-table rise. Although the MRDP pool in RW_A soils can become exhausted in wet years such as Y1, present results indicate the existence of effective interannual regeneration mechanisms of this pool (Fig. 4.1–2). Irrespective of the nature of these mechanisms, the MRDP pool in RW_A soils appeared much larger and regenerated more rapidly than the pool of exchangeable organic/colloidal P in RW_B soils.

4.3. Topography as the potential ultimate driver of dissolved P release in RW soils

Using the Kervidy-Naizin catchment as an example, a conceptual model was constructed to describe how topography could ultimately drive processes that release P in RWs and the chemical nature and concentrations of the released P. Due to differences in topography, the mean water-table level is deeper in RW_A than in RW_B (Fig. 6). RW_A soils experience more intra- and interannual water-table variations than RW_B soils, where the flatter topography causes the water table to remain in shallow soil horizons even in dry years. These topography-induced unstable groundwater dynamics explain the great spatial and temporal variations in the two main processes of dissolved P release, and why the P release linked to reductive dissolution of Fe (hydr)oxides can be deactivated in dry years in shallow soil horizons in RW_A. As discussed above, the effect of topography on soil moisture and organic matter mineralization rates could explain the higher inorganic-P:organic-P ratio in RW_A soils than in their RW_B equivalents. Overall, shallow RW_A soils have more inorganic P and a frequent, rapid cycle

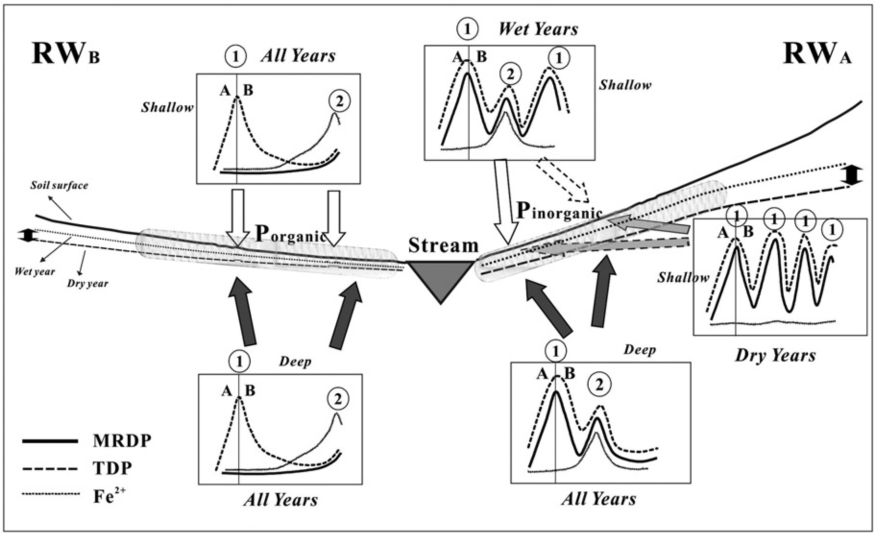


Fig. 6. Sketch diagram summarizing the spatial and temporal variability of P release processes and species in the two studied RWs. The greater diversity of situations encountered in RW_A soils is thought to be primarily due to the steeper slope compared to RW_B, meaning that this RW is more susceptible to inter-annual hydroclimatic variations than RW_B. The circled numbers "1" and "2" given opposite the cycles refer to the release processes discussed in the text. In each inset box, the solid line represents MRDP, the dashed line TDP and the dotted line the Fe^{2+} concentration, vertical line represents the transition between periods A and B. On each RW slope, the solid line represents the soil surface, the dotted line the mean water table in wet years and the dashed line the mean water table in dry years.

of dry/wet episodes. Since topography influences both of these features, this conceptual model provides a suitable explanation for why the steeper RW_A releases more inorganic P than the flatter RW_B.

Steep topography could increase the ability of RW to transform particulate P into bioavailable MRDP at the catchment scale due to its influence on major soil biogeochemical processes involved in the production and release of MRDP. The potential negative influence on water quality could increase because steep topography also facilitates the transport of erosive soil particles from upland cultivated soils into the RWs, thereby providing the particulate P necessary to sustain chemical reactions. In the Kervidy-Naizin catchment, this downward transport of upland P-rich soil particles into the steeper RW_A has been suggested as the main cause for the high P concentrations in RW_A soils, especially at the WetUp-A location (Dupas et al., 2015b), which supports the hypothesis that steeper topography is a potential aggravating factor in RW_A.

4.4. Delivery and retention of mobilized P

A strong connection appears to exist between dissolved P release in RW soil water and delivery of P to streams (Figs. 4.1–4 and 5). We stress, however, that P transfer is not quantitative and that P may be retained in certain years. This is suggested by the lower MRDP concentrations observed at point A in the stream in Y2 and Y3 than in Y1, despite the consistently high MRDP concentrations in RW_A soil water over the three years. At the sampling point in stream A, which is upstream in the catchment (Fig. 1), the RW merges with the drainage area where stream A originates, and it is unlikely that this decrease in MRDP concentrations is related to a change in water pathways between years or to input into the stream of MRDP-poor water of a different origin during Y2 and Y3. Comparison of annual P and water fluxes at the catchment outlet also indicates the existence of retention processes. Using the high-frequency monitoring of water discharge and TDP concentrations at the catchment outlet, total annual TDP fluxes were estimated at 63–185 g P ha^{-1} y^{-1}, depending on the year (Fig. 7), which is in the range of annual P fluxes exported from temperate catchments (e.g. Mellander et al., 2015, 2016; Pärn et al., 2012). Consistent with hydroclimate conditions, TDP and water fluxes were much higher in Y1 than in Y2 and Y3; however, the decrease in TDP fluxes between Y1 and Y2/Y3 was 1.5 times as large as the decrease in water fluxes (2 times as high).

These two observations suggest that some of the TDP released from RW soils does not transfer to the stream and that this retention may have peaked in Y2 and Y3. Re-oxidation of Fe^{2+} released from RW soils is a potential retention mechanism. Precipitation of Fe (hydr)oxides is a commonly observed phenomenon that traps P when reduced water flows over oxic interfaces (Baken et al., 2015; van der Grift et al., 2014). It most likely occurs on stream banks because they are oxic interfaces that RW water must cross before reaching the stream. This process may have been more active in Y2 and Y3, because the decreased groundwater flow rates caused by the lower hydraulic gradient could have increased Fe^{2+} oxidation reactions at the stream bank, thus causing re-adsorption of some of the TDP transported by the groundwater.

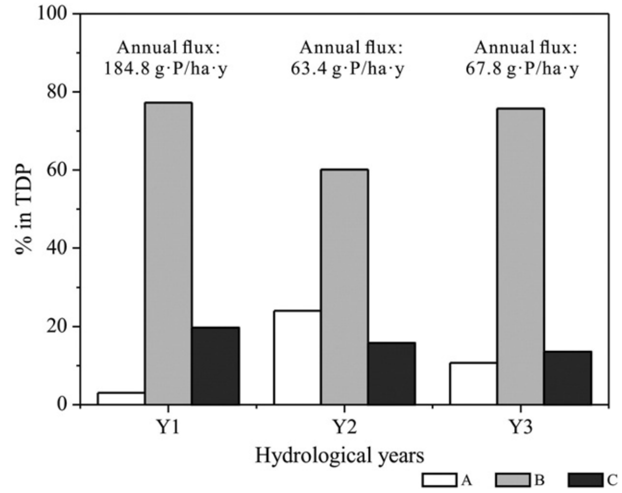


Fig. 7. Relative contribution of each hydrological years and periods within each hydrological years to the total annual flux of TDP exported at the outlet of the Kervidy-Naizin catchment during the study period.

5. Conclusions

Establishment of vegetated buffer zones in RWs is a valuable strategy to reduce diffuse P transfer in agricultural areas (Schoumans et al., 2014) due to the ability of these zones to trap particulate P. However, biogeochemical processes can transform accumulated P in these zones into highly mobile and highly bioavailable dissolved P forms. Our study indicates that RW soils are hotspots of dissolved P release in an agricultural catchment in western France. We confirm the generalizability of the two mechanisms suggested to explain the release of dissolved P in RW soils: rewetting of soils after dry periods and reductive dissolution of soil Fe (hydr)oxides in response to soil saturation. This study provides three new major findings: i) differences in soil properties and topography can induce spatial variations in the chemical nature (inorganic vs. organic/colloidal) of the released P; ii) distinct intra- and inter-annual variations in dissolved P release dynamics can occur in RW soils as a function of the frequency of drying-rewetting cycles and the duration of soil saturation, both of which depend on the hydroclimate and local topography; and iii) the triggering of retention processes at the RW-stream interface can decrease P export from RW soils to streams.

Overall, the study reveals a complex interactions among soil chemistry, hydroclimate variability and topography in determining the location of hotspots of dissolved P release in RWs at the catchment scale. Topography is identified as the key driver due to its influence on the spatio-temporal variability of drying-rewetting cycles and subsequent redox oscillations. Steeper topography increases input of particulate P into zones able to efficiently transform particular P into bioavailable dissolved P. When developing management strategies for RWs with steep topography, the first consideration must be to decrease P mobilization due to erosion from upslope fields in order to prevent further accumulation of particulate P in RWs.

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Appendix A. Supplementary data

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