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# Conventional soil test phosphorus failed to accurately predict dissolved phosphorus release in agricultural hydromorphic soils in Brittany, Western France

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**Abstract:** Researches have proved that agricultural phosphorus (P) loss contributes significantly to surface water eutrophication. Various soil test P (STP) methods have been developed to assess the P loss risk from agricultural soils. In the intensively-cultivated Brittany region of Western France, hydromorphic soils in wetland domains exhibit high risks of leaching and transferring dissolved P - the most bio-available form of P - to surface

waters. It remains unclear whether STP conventionally developed for well-drained soils can accurately predict the risk of dissolved P release from these hydromorphic soils. In this study, we measured the dissolved reactive P (DRP) concentrations in soil solutions sampled in situ from 26 hydromorphic soils in the Brittany region and examined their relationship with several STPs available on the corresponding soils, such as the degree of soil P saturation, the equilibrium soil P concentration, or the soil Olsen P, Dyer P, and water extractable P contents. DRP concentrations ranged from 0.01 to 0.310 mg P l<sup>-1</sup> (mean = 0.075 mg P l<sup>-1</sup>), highlighting the potential of hydromorphic soils as hotspots for DRP release in agricultural landscapes. Correlations between DRP concentrations and STPs were relatively weak ( $0.09 < r^2 < 0.64$ ), indicating that conventional STPs are generally unable to accurately predict the DRP release risks in hydromorphic soils. Tentatively, Olsen P showed promises as a useful risk indicator, with a relatively high  $r^2$  value of 0.6 and wide inclusion in the current STP database, especially in the Brittany region. Nevertheless, this hypothesis requires further evaluation with additional data. This study confirms the high risk of dissolved P release from hydromorphic soils in agricultural wetland domains and emphasizes the need for developing specific risk assessment tools to these hydromorphic soils.

**Keywords:** Gleysols, dissolved phosphorus, agricultural wetland, eutrophication, risk assessment

**Abbreviations:** DRP, dissolved reactive phosphorus; STP, soil test phosphorus; DPS, degree of phosphorus saturation; ECP<sub>0</sub>, equilibrium phosphorus concentration; CW, cultivated wetlands; VBS, vegetated buffer strips; PG, permanent grassland; NCW, non-cultivated wetlands; OM, organic matter; Q<sub>max</sub>, maximum phosphorus sorption capacity of soil.

## 1 Introduction

Understanding the environmental fate of phosphorus (P) is of concern as diffuse P losses from agricultural sources can potentially favor the eutrophication of surface waters (Smith and Schindler, 2009; Sharpley et al., 2013; Jarvie et al., 2017; Kleinman et al., 2015; Bol et al., 2018; Le Moal et al., 2019). Of all the agricultural areas, those containing hydromorphic soils constitute a particular risk from this point of view. The presence of hydromorphic soils indicates a rise in the water table, which can lead to mobilization of P stored in the soil in a dissolved form and its potential transfer to watercourses (Stutter et al., 2009; Vidon et al., 2010; Dupas et al., 2015b; Gu et al., 2017; Walton et al., 2020). Moreover, many hydromorphic soils are located in lowland areas, often co-occurring with places where vegetated strips are established to prevent the flux of erosive P coming from upland domains from reaching watercourses (Casquin et al., 2021; Dupas et al., 2023). One undesirable effect of this situation over the long term is the enrichment of P in these soils, thereby creating a risk of releasing dissolved P into the nearby watercourses (Dorioz et al., 2006; Hoffmann et al., 2009; Al-wadaey et al., 2012; Li et al., 2013; Roberts et al., 2013; Habibiandehkordi et al., 2018).

Despite these reasons for pinpointing hydromorphic soils as hotspots of dissolved P release in agricultural landscapes, direct evidence remains scarce. Several studies conducted on the Kervidy-Naizin catchment in Brittany, Western France, have underpinned this hypothesis by demonstrating that hydromorphic soils in the lowland domains of this catchment were sources of dissolved P found in the stream network (Dupas et al., 2015a, b; Gu et al., 2017, 2020). Two main mechanisms contribute to the release of dissolved P in these hydromorphic soils: i) rewetting of dry soil during the water table rise after dry periods (Turner and Haygarth, 2001; Gu et al., 2018), and ii) development of reducing conditions in soils during prolonged waterlogging that leads to the reductive

dissolution of soil Fe (hydr)oxides (Gu et al., 2017, 2019). However, the Kervidy-Naizin catchment is a very small catchment (5 km<sup>2</sup>), whether the phenomenon underpinned in this catchment also occurs elsewhere is unclear. This is critical to be confirmed because P emissions from agricultural sources are progressively becoming the main cause of surface water eutrophication in Brittany, due to the marked decrease of domestic and industrial point-source contributions (Dupas et al., 2018).

Concurrently, the need for rational P fertilization and the increasing pressure of agricultural practices on surface water eutrophication led to the development of soil test P (STP) methods to assess the P available for plants and the risk of dissolved P release from soils (Sharpley et al., 1995, 2012; Pöthig et al., 2010; Wang et al., 2016; Fisher et al., 2017; Kleinman, 2017). The most commonly used methods include: i) STPs initially developed for agronomic purposes such as the soil Olsen P (Olsen et al., 1954) and Dyer P (Dyer, 1894), which are reported to perform well in representing the risk of dissolved P release in cultivated soils (Sims et al., 2000a, b), but may not be appropriate for soils with contrasting chemical and mineralogical composition (Sharpley 1995); ii) degree of P saturation (DPS), which considers both the amount of adsorbed P in a soil and the soil's total P sorption capacity and is increasingly used worldwide (Sharpley, 1995; Hooda et al., 2000; Wang et al., 2016); iii) equilibrium P concentration (ECP<sub>0</sub>), which represents the concentration at which no net sorption or desorption of P occurs between the soil and solution (Pöthig et al., 2010; Fisher et al., 2017). However, these STPs were developed for soils that are usually well drained. It is unclear if they could also be used in hydromorphic soils for which the P sorption properties may be markedly different from those of well-drained soils (Khalid et al., 1977; Reddy et al., 1998; Brigham et al., 2001; Couic, et al., 2022).

Thus, our main objectives were i) to evaluate on a larger scale the hypothesis that hydromorphic soils of wetland domains are potential sources of dissolved P in agricultural

landscapes; and ii) to determine whether the STPs commonly used on well-drained soils to assess the risk of dissolved P release also apply to hydromorphic soils from wetland areas. With these objectives in mind, we analyzed the potential release of dissolved P in 26 hydromorphic soils distributed in three catchments in Brittany, Western France, and compared these in-situ dissolved P concentrations with STPs and other soils analyses.

## **2 Materials and methods**

### **2.1 Study area sampling locations**

The studied soils were from the Brittany region which spans a surface area of 27,000 km<sup>2</sup> in Western France (**Fig. 1**).

The Brittany region is an intensive agricultural area on the scale of France and even Europe, contributing 22% of the total French agricultural production with only 5% of the country's surface area (Gascuel-Oudou et al., 2010; Poisvert et al., 2017). One consequence of this high agriculture pressure is the high overall soil nitrogen (N) and P surpluses (about  $50.0 \pm 26.6$  kg N ha<sup>-1</sup> yr<sup>-1</sup> and  $22.5 \pm 12.7$  kg P ha<sup>-1</sup> yr<sup>-1</sup>, respectively) in Brittany (Guillemot et al., 2021), leading to high stocks in soils. Associated with a globally impermeable bedrock resulting in shallow water circulation and spatially extended wetland areas (Dupas et al., 2013), these high surpluses are causing the widespread eutrophication of both its continental and coastal waters (Charlier et al., 2007; Pitois et al., 2014; Guillemot et al., 2021; Schreyers et al., 2021).

The 26 hydromorphic soil sites come from a larger collection of 69 sites previously investigated by Couic et al. (2022) for soil properties. These 26 sites are located in wetland domains found in three catchments: the Languenan domain in the Fremur catchment (6 sites) in northern Brittany, the Guiliers (6 sites), Maun (7 sites) and Ploërmel (3 sites) domains located in the Yvel catchment in central Brittany, and the Naizin domain (4 sites) located in the Kervidy-Naizn catchment in central-western Brittany (**Fig. 1**). Four main

types of land use are encompassed by these 26 sites including: i) cultivated wetlands (CW) which correspond to fertilized and tilled plots (10 sites); ii) vegetated buffer strips (VBS) which correspond to 5 to 10 m grass strips (6 sites); these VBS have not been cultivated and fertilized in recent 10 years; (iii) permanent grasslands (PG; 2 sites); these are grassland areas that are currently extensively managed without the addition of fertilizer, but which may have been cultivated in the past 10-20 years; iv) non-cultivated wetlands (NCW), corresponding to portions of wetlands that have never been cultivated (8 sites); they are usually extremely wet zones located in the immediate vicinity of watercourses. In the 26 investigated sites, in total, 38% of sites are currently cultivated and fertilized (CW) versus 62% of sites that are currently non-cultivated (VBS, PG, NCW).

## 2.2 Soil characteristics

Surface soils (0-20 cm) at each site were sampled with an auger. Five samples spaced out from each other by 5 m (approximately 2-3 kg) were mixed, air-dried in the laboratory and sieved to <2 mm before analysis. The soils studied are classified as silty loamy Luvisols. Couic et al. (2022) reported detailed information about the chemical and mineral composition of these soils including particle size fractions, organic matter (OM), organic nitrogen and carbon (OC) contents, water pH, extractable P contents (oxalate P, Dyer P, Olsen P, water extractable P), oxalate Si/ Al/Fe contents, and total P content. Mean values, domain by domain, are presented in Table 1 (the full mineralogical and chemical analyzes of the 26 soils studied can be found in **Table S1** in the Supplementary Materials). The main differences in-between the domains concern the clay/loam ratio which is comparatively lower in soils from the Languenan domain (0.2), as compared to soils from the other four domains (> 0.6). Another peculiarity is the high OC content of soils from the Naizin domain (57 g kg<sup>-1</sup>), which contrasts with the low OC of soils from the Languenan domain (18 g kg<sup>-1</sup>), and the moderate OC content of soils from the three other

domains (27 to 34 g kg<sup>-1</sup>). On average, the total P, Olsen P and Dyer P contents of soils from the 26 sampled sites (1.32, 0.057, and 0.237 g kg<sup>-1</sup>, respectively) are higher than the mean contents of cultivated soils in Brittany as established from soil analyses collected from the regional BDAT and Trans-P databases (1.1, 0.04-0.05, and 0.150-0.200 g kg<sup>-1</sup> for the total P, Olsen P and Dyer P contents, respectively; also see Couic et al., 2022). When compared to the mean P content in cultivated soils across Brittany, this P enrichment in the 26 soils studied is even higher when only the 10 soils of the CW sites are considered. In this case, the mean total P, Olsen P and Dyer P contents are 1.41, 0.077, and 0.272 g P kg<sup>-1</sup>, respectively. These Olsen P contents were significantly higher than the agronomic optimum Olsen P contents for the main crops grown in the Brittany region, which were 0.012 g kg<sup>-1</sup> for winter wheat, 0.014 g kg<sup>-1</sup> for maize, and 0.018 g kg<sup>-1</sup> for rapeseed, respectively (Steinfurth et al., 2022). These comparisons confirm the point already raised by Couic et al. (2022) that wetland domains in Brittany are regionally P-enriched zones.

Soils were classified as hydromorphic soils by examining characteristic features, such as iron redistribution, bleaching, and clay accumulation (as described in Baize and Girard, 2009). Each soil was then rated on a scale of 0 (no sign of hydromorphy) to 10 (maximum intensity of hydromorphy) depending on the observed density of hydromorphy traits (Rivière et al., 1992).

P sorption properties of the 26 soils studied were obtained by fitting their P sorption isotherms to the Langmuir equation (Couic et al., 2022), including i) the maximum P adsorption capacity (Q<sub>max</sub>; mg P kg<sup>-1</sup>), ii) the constant K characterizing the mean strength of the adsorption sites of P (l mg<sup>-1</sup>), and iii) the concentration of the net zero sorption value (EPC<sub>0</sub>; mg P l<sup>-1</sup>) (see **Table 2** for the mean values, domain by domain). DPS values using three commonly applied methods were calculated as follow:

- i) the method proposed by Wang et al. (2016) in which:



$$DPS_{Wang} = \frac{Olsen\ P}{Q_{max}} * 100 \quad (1)$$

where Olsen P is the Olsen P content of the soil (mg P kg<sup>-1</sup>) and Q<sub>max</sub> is the maximum P sorption capacity of the soil (mg P kg<sup>-1</sup>).

ii) the method proposed by Pöthig et al. (2010) in which:

$$DPS_{Pöthig} = \frac{total\ P}{(total\ P) + Q_{max}} * 100 \quad (2)$$

where total P is the total P content of the soil (mg P kg<sup>-1</sup>) and Q<sub>max</sub> is the maximum P sorption capacity of the soil (mg P kg<sup>-1</sup>).

and, finally iii) the method based on the acid ammonium oxalate test for acidic soils (see the review in Kleinman et al., 2017 and references therein) in which:

$$DPS_{Oxalate} = \frac{oxalate\ P}{0.5 * (oxalate\ Fe + oxalate\ Al)} * 100 \quad (3)$$

where oxalate P/Fe/Al are the molar P/Fe/Al contents extracted from the soils using an acid ammonium oxalate solution.

Table 2 highlighted a significant variation in Q<sub>max</sub> values among soils from the five investigated wetland domains, as previously noted by Couic et al. (2022). Soils from the Ploërmel wetland domain exhibit adsorption capacities (mean Q<sub>max</sub> ≈ 1800 mg P kg<sup>-1</sup>) that are approximately four times higher than in soils from the Guilliers domain (mean Q<sub>max</sub> ≈ 500 mg P kg<sup>-1</sup>). Table 2 also shows variations in the mean strength of the P absorption sites (k values), with soils from the Naizin domain showing particularly low K values (0.04 l mg<sup>-1</sup>).

The DPS values in the studied wetland domains range from 36 to 66% (DPS<sub>Pöthig</sub>), 3.1 to 11.7% (DPS<sub>Wang</sub>), and 4.8 to 17.7% (DPS<sub>Oxalate</sub>), depending on the calculation method used. Note that the oxalate P/Fe/Al data are not available for soils from the Guilliers domain, and therefore an mean DPS<sub>Oxalate</sub> value cannot be calculated for these soils.

### 2.3 Soil water sampling and analysis

Soil waters were sampled twice during two field campaigns: November 28 to December 18, 2019, and February 4 to 11, 2020, at the same sites as the studied hydromorphic soils. Those samplings occurred during the wettest period of the year, during which surface soils of the wetland domains in this region can be consecutively waterlogged for 2-3 months and is more prone to dissolved P transfer from the wetlands to the streams with the water table rises (Gu et al. 2017). For the collection of soil water samples, PVC tubes measuring 50 cm long and 5 cm in diameter were pushed into the ground using a mallet after the uppermost 20 cm of the soil was taken out using a dagger (see **Fig. S1** in the Supplementary Materials). The sunken part (0-20 cm) of the tubes was perforated to allow ground water to enter. The soil water samples are composite samples resulting from the mixture of several samples (usually 5 to 6) collected within a 5-m diameter circle. Approximately 1 l of water was collected at each site, which requires a wait of approximately one hour between the insertion of the tubes and their filling. At certain points or on certain dates where the water table was not high enough to fill the tubes, no samples could be collected.

After collection, water samples were transported in a cooler to the laboratory and passed through 0.45- $\mu$ m, pre-cleaned cellulose acetate filters within 12h after sampling, and then kept in a refrigerator in the dark at 4°C until analysis within 3 days. For all filtered water samples, dissolved reactive P (DRP) concentration was determined colorimetrically via a reaction with ammonium molybdate (Murphy and Riley, 1962). Precision of the DRP measurements was  $\pm 4 \mu\text{g P l}^{-1}$ , using repeated measurements of the DRP standard solution.

## **2.4 Statistical analysis**

We examined the quality of the correlations between the water DRP concentrations and seven STPs, including soil Olsen P, Dyer P, WEP, EPC<sub>0</sub>, as well as DPS<sub>Pöthig</sub>, DPS<sub>Wang</sub>, and DPS<sub>Oxalate</sub>. For each test, we considered the possibility that the correlation is linear or

exponential. In the end, we retained the correlation for which the  $r^2$  value was closest to 1.0.

One or more of the seven tested STPs could serve to reliably predict the soil DRP concentration in hydromorphic soil waters, based on soil data only. By comparing the predicted concentration with the reference concentration of DRP above which there is a risk of eutrophication of the surface water ( $0.03 \text{ mg P l}^{-1}$ ; Carey and Ridyn, 2011; Nemery, 2018), the corresponding STP(s) could then be used to identify which hydromorphic domains are the most critical with regards to the risk of dissolved P release, thereby guiding the remediation strategies needed to reduce this risk.

To compare the DRP concentrations across land use types and soil hydromorphy classes, a one-way analysis of variance with Tukey's post hoc test was performed using SPSS software (IBM Statistics version 22) at a significance level of  $p < 0.05$ .

### **3 Results**

#### **3.1 DRP concentration of soil waters**

The DRP concentrations were variable among sampling sites, ranging from 0.004 to  $0.310 \text{ mg P l}^{-1}$  for the November-December 2019 samples, and from 0.004 to  $0.298 \text{ mg P l}^{-1}$  for the February 2020 samples (**Fig. 2a**; **Table S2**). DRP concentrations remained relatively constant at a given site between the sampling dates, as illustrated by their nearly 1:1 linear correlation (**Fig. 2b**). The highest concentrations were observed in the Mauron and Languenan domains, whereas the lowest were observed in the Naizin and Ploërmel domains. Spatial variation of DRP concentrations was high within a single transect and greater than the variability of mean DRP concentrations in-between transects (**Fig. 2a**). All the installed tubes except one provided water for the November-December 2019 campaign, whereas only 65% of the tubes provided water during the February 2020 campaign, indicating a shallower water table in November-December 2019 than in February 2020.

The measured DRP concentrations are compared with the reference concentration of  $0.03 \text{ mg P l}^{-1}$  (**Fig. 2a**). Sixty percent of the samples collected in November-December had a concentration higher than this limit, and the proportion was similar in February 2020 (67%).

The distribution of the DRP concentrations closely follows the current land use (**Fig. 3**). On average, the samples from the CW and VBS sites have higher DRP concentrations (mean  $\pm$  SD =  $0.106 \pm 0.111$  and  $0.112 \pm 0.093 \text{ mg P l}^{-1}$ , respectively) than the samples from the PG and NCW sites (mean  $\pm$  SD =  $0.026 \pm 0.021$  and  $0.027 \pm 0.025 \text{ mg P l}^{-1}$ , respectively). Note that the DRP concentrations from the currently non-cultivated VBS sites were also higher on average than the limit of  $0.03 \text{ mg P l}^{-1}$  (**Fig. 3**).

### **3.2 Correlation between soil water DRP and the soil test P values**

As shown in Figs. 4 and 5, the best correlations turned out to be the linear correlations for all tests. The best fits (most variance explained) were obtained for the correlations with  $\text{EPC}_0$ ,  $\text{DPS}_{\text{Oxalate}}$ , and Olsen P ( $r^2 = 0.64$ ,  $0.59$ , and  $0.57$ , respectively; **Figs. 4a,b and 5**). The other correlations gave worse fits, with the worst being obtained for the correlations with  $\text{DPS}_{\text{Pöthig}}$  and  $\text{DPS}_{\text{Wang}}$  ( $r^2 = 0.09$  for both; **Fig. 4e,f**).

## **4 Discussion**

### **4.1 Wetlands as potential hotspots of dissolved P release in agricultural landscapes**

One major finding of the present study is the direct confirmation in the field that wetland domains are potential dissolved P release hotspots in the agricultural landscapes of Brittany. The peak DRP concentrations observed in the present study are similar to those observed in soil waters of wetland areas of the Kervidy-Naizin catchment ( $5 \text{ km}^2$ ), which peaked at values around  $0.2\text{-}0.4 \text{ mg P l}^{-1}$  (Dupas et al., 2015b; Gu et al., 2017). Furthermore, the range of DRP concentrations, between  $0.004\text{-}0.310 \text{ mg P l}^{-1}$  in this study, is comparable to the range of  $0.005\text{-}0.400 \text{ mg P l}^{-1}$  in the Kervidy-Naizin catchment. Thus, this study

confirms that what is observed in the wetlands of a small catchment area can be extrapolated to the wetlands of Brittany as a whole.

In the Kervidy-Naizin catchment, a strong connection existed between dissolved P release in wetland soil waters and the supply of the released dissolved P to the stream network (Gu et al., 2017). In the present study, we have not monitored the P concentrations of the streams draining the 26 sampled sites because we did not have the equipment or financial resources to do so. To accurately determine the representative DRP concentrations/loads in streams, high temporal-resolution measurements need to be taken at least once a week or more frequently (Cassidy and Jordan, 2011). Therefore, we cannot provide direct evidence of the transfer of dissolved P from the studied wetland domains to watercourses. However, it is likely that such a transfer occurs, as hydrological connection of wetlands and streams during the wet season is well-documented in Brittany and other regions worldwide and controls the transfer not only of DRP but also of dissolved OC, sulfate and to a lesser extent nitrate (Vidon et al., 2010; Aubert et al., 2013; Lambert et al., 2013, 2014; Jeanneau et al., 2015; Fovet et al., 2018; Walton et al., 2020).

Even if the DRP concentrations of  $0.310 \text{ mg P l}^{-1}$  already constitute high concentrations, posing a high risk of eutrophication for surface waters, it is important to note that these concentrations likely only reflect a portion of the dissolved P ( $< 0.45 \text{ }\mu\text{m}$ ) released in the soil water studied. Many studies have established that a significant part of the operationally-defined dissolved P ( $< 0.45 \text{ }\mu\text{m}$ ) in soil waters exists in organic or colloidal forms (Gotsselig, 2014, 2017; Baken et al., 2016; Jiang et al., 2017; River and Richardson, 2019; Gu et al., 2020) that is not detected by the Murphy and Riley's (1962) ammonium molybdate method. This leads to an underestimation of the real P concentration in the  $< 0.45 \text{ }\mu\text{m}$  filtrates, which can be problematic since some organic P species and colloidal P may be bioavailable to algae, similar to DRP (Li and Brett, 2013; Van Moorleghem et al.,

2013). In the Kervidy-Naizin catchment, where the proportion of colloidal P was assessed in both wetland soil waters and stream waters, Gu et al. (2020) showed that this proportion may represent up to 30 to 45% of the total dissolved P content ( $< 0.45 \mu\text{m}$ ). Thus, the assumption of an equivalent proportion of organic or colloidal P in the analyzed waters in the present study could raise the maximum observed dissolved P concentration to approximately  $0.46 \text{ mg P l}^{-1}$ .

#### **4.2 Weak prediction of soil test P on dissolved P release in soil water**

We found that conventional STPs generally fail to accurately predict the risks of DRP release in hydromorphic soils, as evidenced by the weak correlations between DRP concentrations and STPs ( $0.09 < r^2 < 0.64$ ) compared to previous studies evaluating soil P leaching risks in agricultural soils by STPs (Zheng et al., 2015; Wang et al., 2016). It is widely accepted that adsorption/desorption is the major process controlling the P release into soil waters (Gérard, 2016). Consequently, STPs that reflect soil P sorption properties are expected to give good prediction on soil water P (Sims et al., 2000a, b; Wang et al., 2016). However, the biogeochemical processes that hydromorphic soils of wetland domains frequently experience can potentially disturb this control. The process that most likely exerted an influence in the present study is the reducing conditions generated by the prolonged water saturation of hydromorphic soils, which can lead to the dissolution of Fe (hydr)oxides and thus solubilizing 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; Gu et al., 2019). By grouping the water samples by hydromorphy class of the corresponding soils, we tested the influence of soil hydromorphy class on DRP concentrations (**Fig. 6**). The results showed that the distribution of the DRP concentrations were significantly influenced by soil hydromorphy class, with soils of hydromorphy class [6-10] showing significantly higher DRP concentrations than those of lower hydromorphy

class ([2-4] and [4-6]). Under reducing conditions, the quantity of dissolved P released is not only controlled by the soil P sorption properties, notably the strength of the P-binding sites, but also by the labile P content of the soil, such as the oxalate P contents, as indicated by the comparatively high  $r^2$  for  $DPS_{Oxalate}$ .

On the other hand, we found that the distribution of the DRP concentrations closely follows the current land use, with waters from CW or VBS areas showing mean DRP concentrations higher than those from PG or NCW (**Fig. 3**). The case for the VBS is interesting because the surveys carried out among farmers have shown that these VBS were managed for 10 years, on average, and had not been supplied with any P-rich fertilizers since this time. The continued release of dissolved P from these VBS highlights the concept of legacy P, i.e. the accumulation of P in soil from over-fertilization that remains present even after fertilization has stopped (Sharpley et al., 2013; Kleinman et al., 2019). Furthermore, VBS are often located in valleys bottoms, where P-rich soils from hillslopes can be deposited, providing additional P for VBS soils (Dorioz et al., 2006).

#### **4.3 Assessing and mitigating the risk of dissolved P release from wetland soils**

It should be noted that the present study used only STPs available for the soils studied, which limits the possibility of finding the other better indicators. As potential biogeochemical processes would switch the main controller of dissolved P release from soil P sorption properties to soil labile P content, more aggressive STPs such as Mehlich-3 would probably give better prediction on P release from hydromorphic soils (Kleinman and Sharpley, 2002). In the present study, the linear relationship between STPs and soil water P has also been applied in numerous previous studies and has demonstrated a high level of prediction effectiveness on soil leachate P (Li et al., 2015; Zheng et al., 2015; Jalali and Jalali, 2017). The best linear-correlation coefficients observed in the present study ( $EPC_0$ ,  $DPS_{Oxalate}$ , and Olsen P;  $0.57 < r^2 < 0.64$ ) are lower than many previous studies but

are comparable to some previous studies on agricultural soils (Wang et al., 2016; Jalali and Jalali, 2017). Unlike  $\text{EPC}_0$  and  $\text{DPS}_{\text{Oxalate}}$ , which are either time-consuming or expensive to determine, Olsen P is a convenient and rapid method for analysis. Although Olsen P was initially developed to assess plant-available P and may not directly predict the potential for P loss from a soil (Dodd et al., 2012), the present study tentatively proposed Olsen P as a risk indicator for P loss in hydromorphic soils, especially considering its widespread inclusion in soil test databases, such as the Brittany region of France (Lemercier et al., 2008).

Using the correlation equation between DRP and Olsen P (**Fig. 4**), a ceiling Olsen P content of  $34.0 \text{ mg P kg}^{-1}$  of soil is calculated to keep DRP concentration in soil water below the eutrophication threshold, i.e.  $[\text{DRP}] < 0.03 \text{ mg P l}^{-1}$ . However, it should be noted that assigning this concentration limit to soil waters is probably overly strict as these waters are often diluted by mixing with deeper, P-poor groundwaters in watercourses (Dupas et al., 2015b). P retention in stream banks can also contribute to this same dilution effect. Stream banks are oxic interfaces that wetland soil waters cross before reaching streams. However, due to reducing conditions, wetland soil waters are often enriched in  $\text{Fe}^{2+}$ , leading to the precipitation of Fe (hydr)oxides when they cross stream banks, a process that is very efficient in trapping P (Baken et al., 2015; Van der Grift et al., 2014). In the case of the Kervidy-Naizin catchment where the relationship between the dissolved P in the wetland soil waters and the stream has been studied in detail, a dilution by a factor of 3 was observed, likely due to a conjunction of these two processes (Dupas et al., 2015b; Gu et al., 2017). Assuming this dilution factor is applicable to Brittany as a whole, the ceiling Olsen P content in wetland soils would increase to  $68.7 \text{ mg P kg}^{-1}$  (**Fig. 5**), much higher than the agronomic requirements for optimal yields of common crops in Europe (Steinfurth et al., 2022). Given the poor quality of the correlation on which these calculations are based,



these ceiling Olsen P contents should be considered with caution. However, it does suggest that Olsen P can serve as a guide in addressing and mitigating the risk of dissolved P release from wetland domains.

Expanding and contracting zones of surface soil water saturation, known as potential wetland domains, dominates the lowland areas of agricultural landscapes in Brittany (Mérot et al., 1995; Montreuil et al., 2011). The present study, combined with previous research in the Kervidy-Naizin catchment (Dupas et al., 2015a, b; Gu et al., 2017), suggest that when these areas coincide with high soil labile P content, they can serve as a potential source area of dissolved P that may enter the stream network. This finding aligns with recent studies that used an inverse method to identify critical sources of P in streams at the regional scale in Brittany (Casquin et al., 2021; Dupas et al., 2023). Given that the temporary waterlogged nature of soils (only during the winter wet season), many wetland domains in Brittany have been, or still being, cultivated, resulting in the buildup of legacy P reserves in the soils. Additionally, lowland wetlands domains are also areas where VBS is set up to prevent particulate P from reaching watercourses (Dorioz et al., 2006). This strategy is beneficial for erosion management but could also contribute to building up legacy P reserves in the soils by deposition of P-rich soil from the hillslope. It is urgent to find solutions to these concurrent problems so that the legacy P reserves in these soils do not act as a time bomb for eutrophication by releasing large amounts of dissolved P into watercourses in the future. Smarter P fertilization regimes, phytomining strategies of legacy P, and moving anti-erosion barriers higher up the slopes, are possible options that should be considered in water quality protection programs.

## **5 Conclusion**

The present study evaluated the risk of dissolved P release in 26 cultivated and uncultivated hydromorphic soils set in wetland domains in the Brittany, Western France,

and assessed the prediction of conventional STPs on the DRP concentrations in natural soil waters. The results indicate that hydromorphic soils from wetland domains are potential hotspots of dissolved P release in agricultural landscapes, with DRP concentrations ranging from 0.01 to 0.310 mg P l<sup>-1</sup> (mean = 0.075 mg P l<sup>-1</sup>). Most correlations between DRP concentration and common STPs were poor ( $0.09 < r^2 < 0.64$ ), suggesting that conventional STPs are generally unable to accurately predict the DRP release risks in hydromorphic soils. Olsen P is tentatively proposed as a useful risk indicator, as it gives a relatively high correlation coefficient ( $r^2 = 0.57$ ) and is widely included in the current STP database, especially in the Brittany region. This study confirms that wetland areas in agricultural landscapes are at-risk zones regarding diffuse P emissions and the general inability of conventional STPs to accurately assess this risk. We emphasize the need to prevent accumulations of P in the soils of wetland areas, and if accumulations have already occurred, to implement management strategies to export the accumulated P.

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**Table 1.** Mean composition of the surface soils (0-20 cm) from the five investigated wetland domains. OC: organic carbon; Ox: Oxalate; WEP: water extractable phosphorus. SD: standard deviation. All data are expressed in g kg<sup>-1</sup>, except for the WEP which is given in mg P kg<sup>-1</sup>.

	<b>Languenan</b>		<b>Ploërmel</b>		<b>Mauron</b>		<b>Guilliers</b>		<b>Naizin</b>	
	<i>Mean</i>	<i>SD</i>	<i>Mean</i>	<i>SD</i>	<i>Mean</i>	<i>SD</i>	<i>Mean</i>	<i>SD</i>	<i>Mean</i>	<i>SD</i>
<b>Clay</b>	131	18	260	26	203	57	326	79	281	53
<b>Fine loam</b>	193	10	348	19	335	41	320	35	442	11
<b>Coarse loam</b>	462	54	199	79	259	59	204	38	162	11
<b>Fine sand</b>	166	30	91	13	97	15	74	19	64	27
<b>Coarse Sand</b>	48	28	102	39	106	29	76	65	51	26
<b>OC</b>	17.6	7.5	29.3	3.7	27.0	4.4	34.0	16.4	57.0	23.6
<b>Al_Ox</b>	0.97	0.20	1.85	0.08	1.56	0.34	2.01	0.33	1.53	0.22
<b>Fe_Ox</b>	5.06	1.46	8.73	1.86	5.16	2.43	7.81	3.00	7.04	2.54
<b>Si_Ox</b>	0.26	0.06	0.44	0.10	0.26	0.09	0.61	0.18	0.28	0.02
<b>Total P</b>	1.43	0.19	2.09	0.34	1.52	0.42	0.92	0.19	0.86	0.30
<b>P_Ox</b>	0.32	0.13	0.44	0.07	0.34	0.17	<i>n.d</i>	<i>n.d</i>	0.11	0.09
<b>Olsen P</b>	0.07	0.04	0.05	0.01	0.07	0.05	0.04	0.03	0.04	0.03
<b>Dyer P</b>	0.37	0.31	0.24	0.03	0.24	0.22	0.15	0.11	0.17	0.14
<b>WEP</b>	5.10	3.98	2.22	0.25	8.09	7.28	9.14	5.58	14.88	9.71

**Table 2.** Mean phosphorus (P) sorption properties and P saturation indexes of soils from the five investigated wetland domains. Qmax: maximum P sorption capacity of soil; ECP<sub>0</sub>: equilibrium P concentration; K: soil P affinity constant; DPS: degree of P saturation; SD: standard deviation.

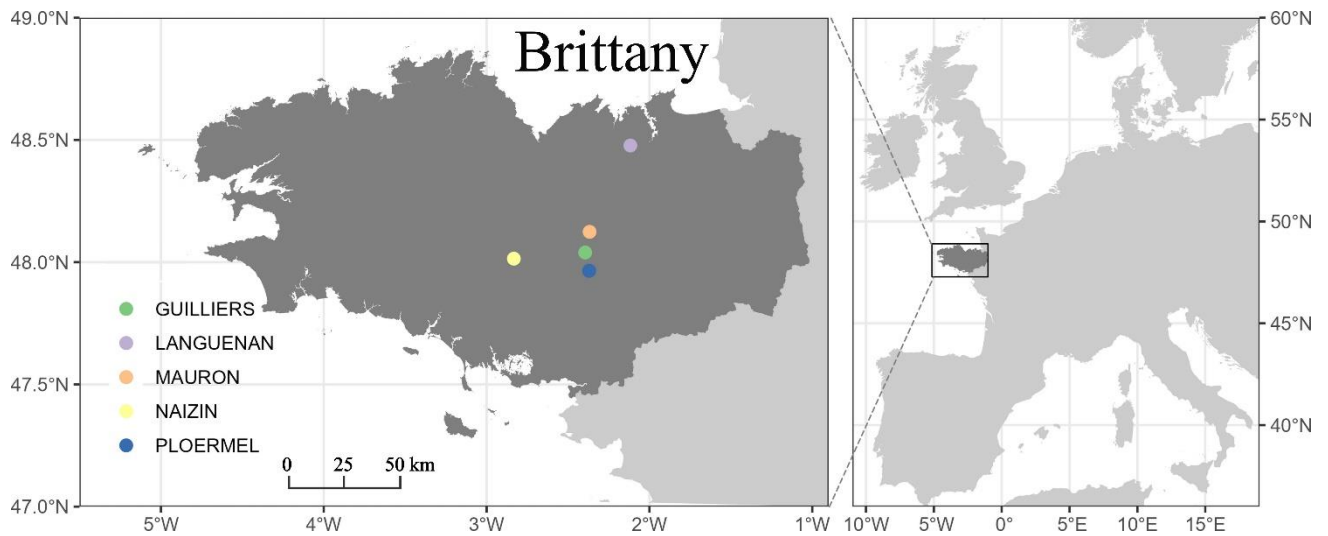
	<b>Languenan</b>		<b>Ploërmel</b>		<b>Mauron</b>		<b>Guilliers</b>		<b>Naizin</b>	
	<i>Mean</i>	<i>SD</i>	<i>Mean</i>	<i>SD</i>	<i>Mean</i>	<i>SD</i>	<i>Mean</i>	<i>SD</i>	<i>Mean</i>	<i>SD</i>
<b>Qmax (mg P kg<sup>-1</sup>)</b>	988	180	1792	156	1493	217	482	193	1502	321
<b>EPC<sub>0</sub> (mg P l<sup>-1</sup>)</b>	0.104	0.123	0.018	0.014	0.121	0.158	0.089	0.086	0.054	0.062
<b>K (l mg<sup>-1</sup>)</b>	0.337	0.182	0.311	0.019	0.344	0.205	0.174	0.072	0.040	0.010
<b>DPS<sub>Pöthig</sub> (%)</b> *	59.0	7.2	53.6	2.7	49.7	11.3	66.1	11.0	36.1	14.4
<b>DPS<sub>Wang</sub> (%)</b> **	8.3	6.9	2.9	0.5	4.9	4.1	11.7	11.6	3.1	3.1
<b>DPS<sub>Oxalate</sub> (%)</b> ***	17.7	10.8	12.8	0.5	16.8	11.8	n.d.	n.d.	4.8	5.1

\*Calculated from Pöthig et al. (2010) as  $DPS = [Total\ P]/([Total\ P] + Q_{max})$

\*\*Calculated from Wang et al. (2016) as  $DPS = ([Olsen\ P]/Q_{max})*100$

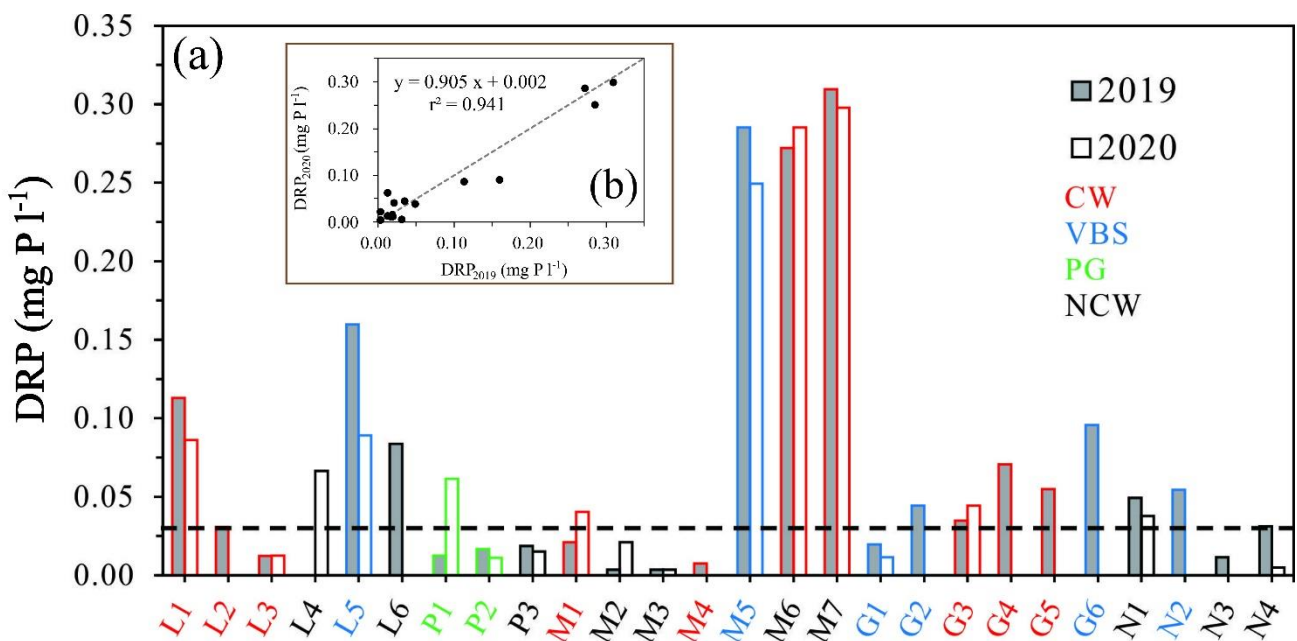
\*\*\*Calculated from Kleinman et al. (2017) as  $DPS = ([Oxalate\ P]/(0.5*([Oxalate\ Fe] + [Oxalate\ Al]))) * 100$

**Figure 1.** Location map of the studied wetland domains and of the Brittany region in France and in the world. The Languenan domain belongs to the Fremur catchment. The Guilliers, Mauron, and Ploërmel domains belong to the Yvel catchment. The Naizin domain belongs to the Kervidy-Naizin catchment.

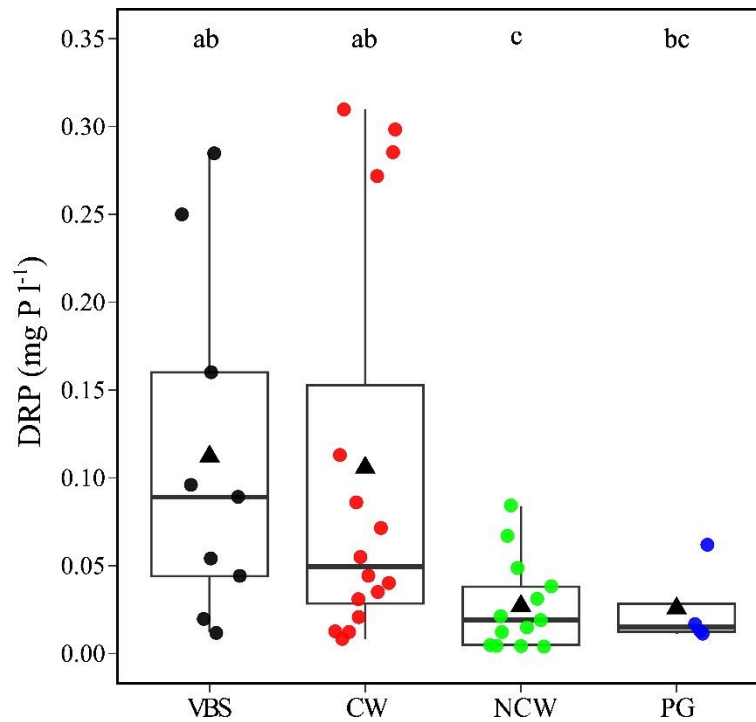




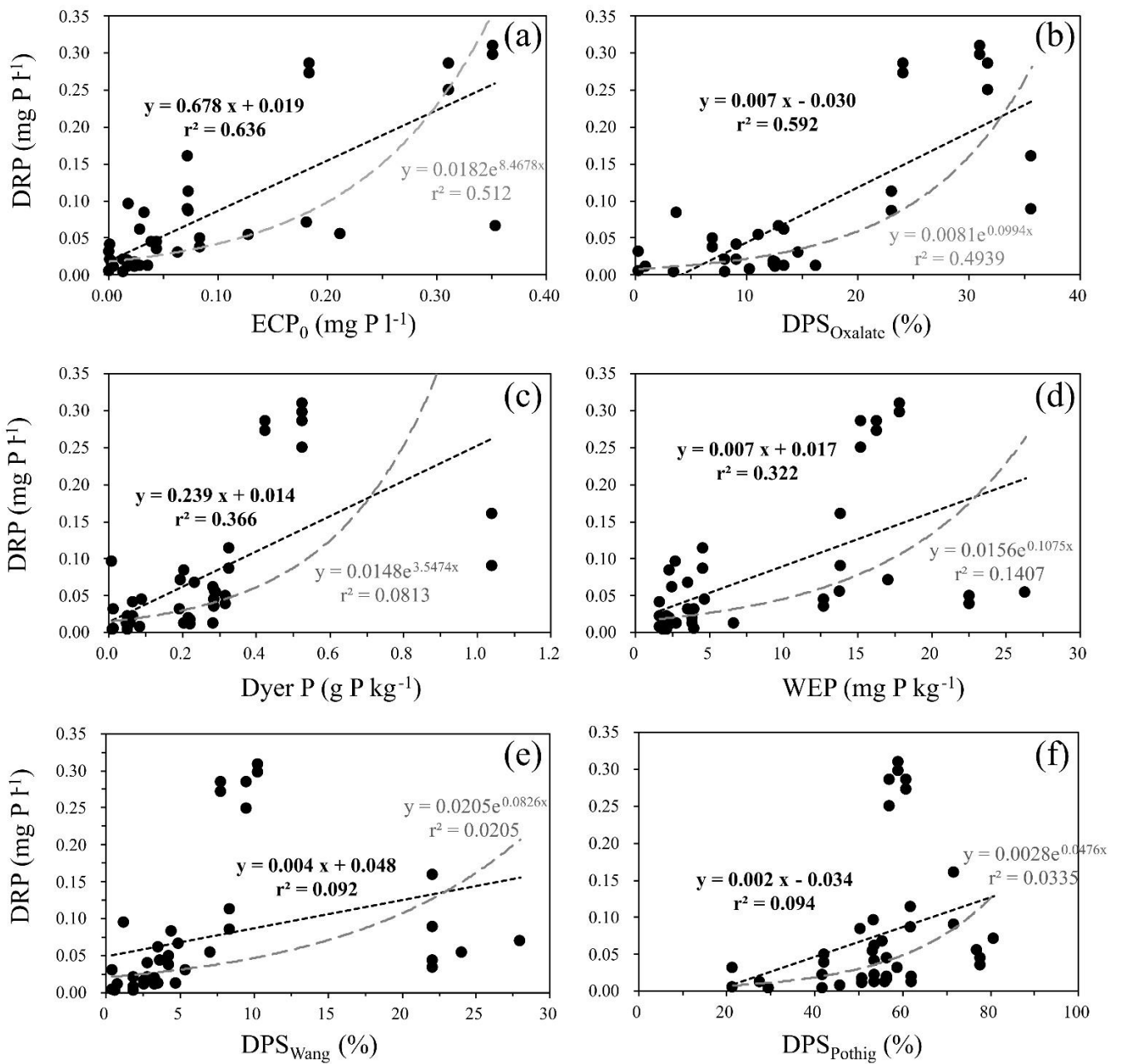
**Figure 2.** (a) Dissolved reactive P (DRP) concentrations in the waters collected in the soils of the studied wetland domains. The horizontal dashed line stands for the P concentration limit above which there is a risk of eutrophication of the surface waters ( $0.03 \text{ mg P l}^{-1}$ ). L: Languenan; P: Ploërmel; M: Mauron; G: Guilliers; N: Naizin. (b) Linear correlation illustrating the high temporal stability of the DRP concentrations in sites where soil waters could be sampled both in November-December 2019 and February 2020.



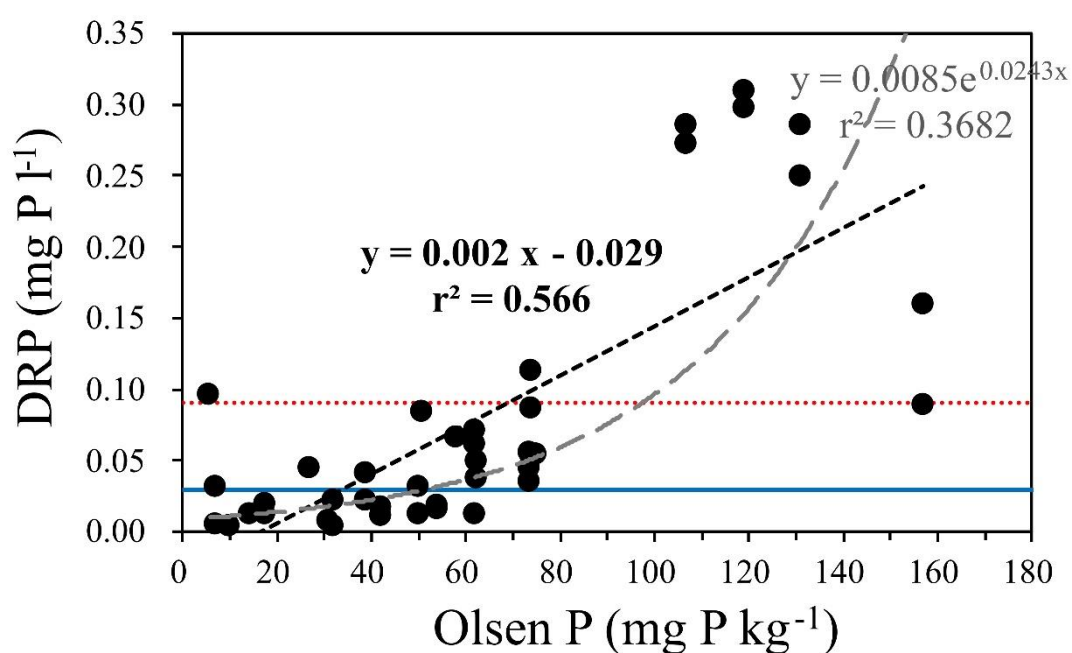
**Figure 3.** Comparison of the dissolved reactive P (DRP) concentration in the soil waters depending on the current land use of the corresponding wetland domains (CW: cultivated wetland; PG: permanent grassland; NCW: non-cultivated wetland; VBS: vegetated buffer strip). Triangle in each box represents the mean DRP concentration of each land use type. Different letters above each box indicate significant differences in means at  $p < 0.05$ .



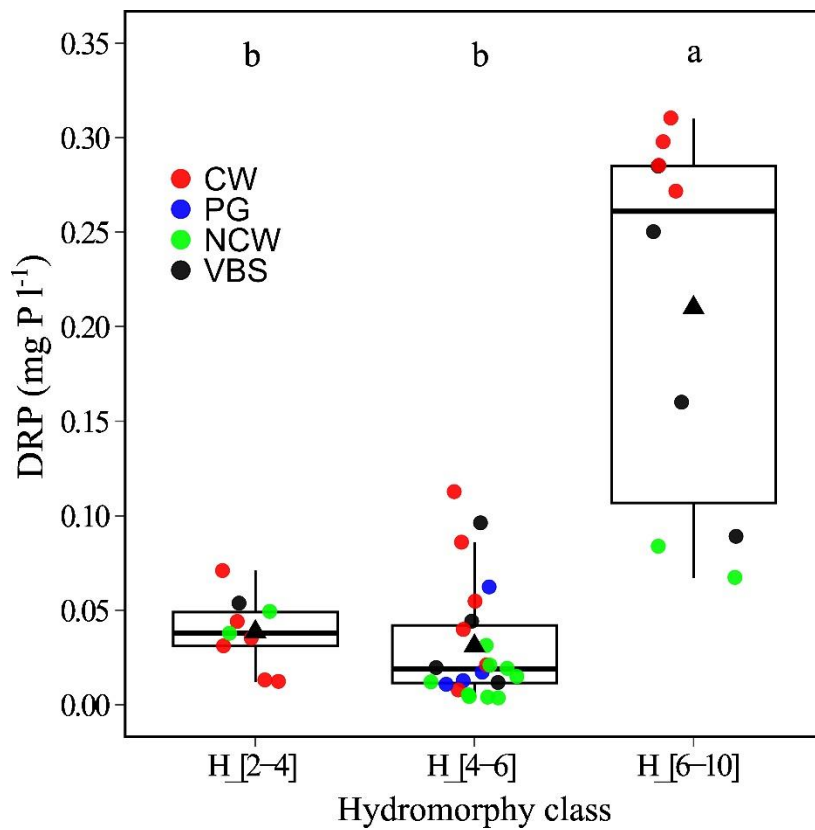
**Figure 4.** Correlations between the dissolved reactive P (DRP) concentrations of soil waters and values of equilibrium P concentration ( $ECP_0$ ), Dyer P, water extractable P (WEP), and the degree of P saturation calculated from Kleinman et al. (2017) [ $DPS_{Oxalate}$ ], from Wang et al. (2016) [ $DPS_{Wang}$ ], and from Pöthig et al. (2010) [ $DPS_{Pöthig}$ ] the corresponding soils. Regression line and equation in grey represent exponential correlation and those in black represent linear correlation.



**Figure 5.** Correlation between the dissolved reactive P (DRP) concentrations of soil waters and the Olsen P contents of the corresponding soils. The horizontal solid line stands for the DRP eutrophication limit of the surface waters ( $0.03 \text{ mg P l}^{-1}$ ). The horizontal dashed line stands for this limit assuming a dilution factor of 3 of the soil waters once in the watercourses ( $0.09 \text{ mg P l}^{-1}$ ). Regression line and equation in grey represent exponential correlation and those in black represent linear correlation.



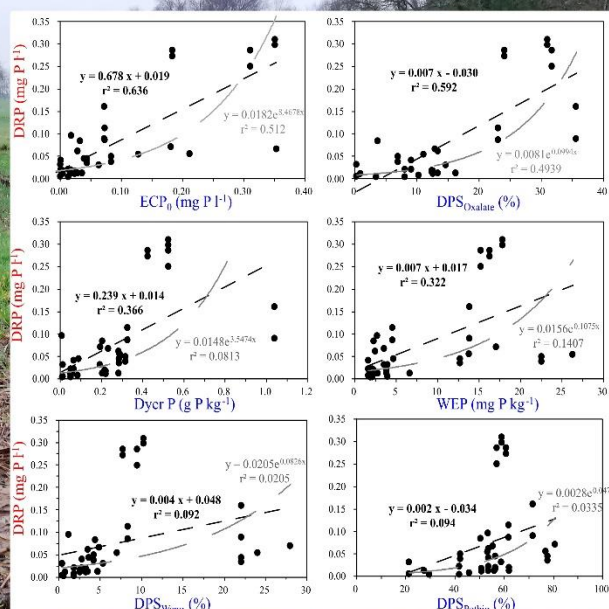
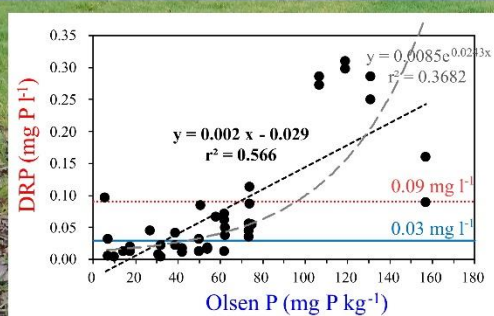
**Figure 6.** Comparison of the dissolved reactive P (DRP) concentration in the soil waters depending on the hydromorphy class ([2-4], [4-6], [6-10]) of the corresponding site. CW: cultivated wetland; PG: permanent grassland; NCW: non-cultivated wetland; VBS: vegetated buffer strip. Triangle in each box represents the mean DRP concentration of each hydromorphy class. Different letters above each box indicate significant differences in means at  $p < 0.05$ .



## Graphic abstract

### Conventional soil test P to indicate dissolved P release risk in natural soil water from agricultural hydromorphic soils

Weak correlations ( $0.09 < r^2 < 0.64$ ) between STPs and DRP in soil water



High dissolved reactive P in natural soil waters ( $\sim 0.3 \text{ mg l}^{-1}$ )

**Brittany, Western France**

## **Highlights**

- High dissolved reactive P concentrations in natural wetland soil waters were found
- Conventional soil P tests fail to accurately predict the dissolved P release risk
- The dissolved P release potential is dependent on soil hydromorphic class
- It is imperative to take measures to avoid the accumulation of P in wetlands