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Ewan Couic, Gérard Gruau, Sen Gu, A. Casquin. Variability of phosphorus sorption properties in hydromorphic soils: consequences on P losses in agricultural landscapes. *European Journal of Soil Science*, 2022, 73 (6), pp.e13326. 10.1111/ejss.13326 . insu-03874757

**HAL Id: insu-03874757**

**<https://insu.hal.science/insu-03874757>**

Submitted on 28 Nov 2022

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# Variability of phosphorus sorption properties in hydromorphic soils: consequences on P losses in agricultural landscapes

Running title: High phosphorus sorption variability in wetland domains

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This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process which may lead to differences between this version and the [Version of Record](https://onlinelibrary.wiley.com/doi/10.1111/ejss.13326). Please cite this article as doi: [10.1111/ejss.13326](https://onlinelibrary.wiley.com/doi/10.1111/ejss.13326)

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**Highlights:**

- Wetlands soils in western France show high variability in their phosphorus properties.
- There is a high-risk of dissolved P losses from wetland soils to watercourses.
- The risk can remain high even in soils that are currently not cultivated
- Degree of phosphorus saturation method to assess dissolved P release risk could underestimate it.

**Abstract** - Increasing concerns over water eutrophication due to agricultural phosphorus (P) loss have led to the development of indicators to assess the risk of P release from agricultural soils. Recently, a logarithmic equation linking the degree of phosphorus saturation (DPS) to the simple water-soluble P (WSP) content of soils has been proposed as a universal method to assess this risk based, however, mainly on the analysis of well-drained soils. Here, we studied the P sorption properties and DPS values of 69 hydromorphic soils from cultivated and uncultivated wetland zones located in Brittany, Western France, to test whether the method could also apply to poorly-drained soils. The bulk soil analysis showed that P contents of the studied hydromorphic soils were 30 to 80% higher than P contents normally found in Brittany soils, evidencing a possible P enrichment process. Adsorption isotherms revealed a surprisingly high variability in the P sorption properties as a function of the location of the soil (maximum P adsorption capacity ranging from 500 to 1850 mg kg<sup>-1</sup>), which is

caused by variations in the phases controlling P sorption in soil (from clay to organic matter and/or iron and aluminum oxides, depending on the soil location). Distinct relationships between DPS and WSP values were also obtained depending on the location of the soils. The obtained DPS vs. WSP relationships showed that the P saturation threshold above which the risk of dissolved P release increases markedly is 30% lower on average for hydromorphic soils than for well-drained soils. Hydromorphic soils appear to be more at risk of releasing dissolved P at the same DPS values than well-drained soils. The present study indicates an underestimation of the P release risk from hydromorphic soils by the existing method developed for well-drained soils and calls for the development of specific risk assessment tools for hydromorphic soils, especially given on the strong spatial heterogeneity of their P sorption properties.

**Keywords:** Biogeochemistry; Phosphorus; Degree of phosphorus saturation; Wetlands; Hydromorphic soils; Soil management

## 1. Introduction

Diffuse phosphorus (P) losses from agricultural lands are increasingly contributing to surface water eutrophication, exceeding the contribution of point-source P emissions in many parts of the world (Kleinman, 2017; Bol *et al.*, 2018; Le Moal *et al.*, 2019). Recently, attention has been drawn to the dissolved part of these diffuse P losses because of the high bioavailability of dissolved P species (Bol *et al.*, 2018). A commonly used method to assess the ability of soils to fix or release dissolved P is the adsorption isotherm method (Nair *et al.*, 1984), in which a soil sample is equilibrated with solutions that have increasing P concentrations. Several parameters describing the P

adsorption properties of a soil such as the maximum P adsorption capacity ( $Q_{\max}$ ), the equilibrium P concentration or  $EPC_0$  (i.e. the concentration at which the P adsorption and desorption by soil are equivalent), and the P adsorption constant ( $k$ ) can then be calculated.

At the same time, the degree of P saturation (DPS) has become widely used to predict the potential risk of dissolved P release by soils (Pöthig *et al.*, 2010; Wang *et al.*, 2016; Fischer *et al.*, 2017). The method involves comparing the total amount of P that can be theoretically adsorbed by a soil with the quantity of P effectively adsorbed by this soil. The total number of P adsorbing sites can be determined either (1) indirectly, by measuring the aluminum (Al) and iron (Fe) oxides content, which are major P adsorption sites in soil (Nair *et al.*, 1984; Reddy *et al.*, 1998; Schoumans & Chardon, 2014) or (2) directly, by using the above-mentioned adsorption isotherm method. Thus, Pöthig *et al.* (2010) and Fischer *et al.* (2017) applied the adsorption isotherm method to a large number (> 400) of soils from Germany and Switzerland and reported a logarithmic relationship between the calculated DPS and the measured water-soluble P (WSP) content of soils, which they presented as a universal equation, valid for all types of soils. However, the soils considered in these studies are mainly well-drained soils. A focus is not made on hydromorphic soils whose P adsorption properties can be modified due, for example, to the reductive dissolution of soil Fe (hydr)oxides. Furthermore, the equation used by these authors may not reflect the actual soil saturation rate since the DPS is calculated from the TP concentration, which include P fractions that may not be easily exchangeable with the soil solution, such as the P contained in the crystal lattices of certain soil minerals. Despite these shortcomings, the logarithmic relationship between the calculated DPS and the

measured WSP content of soils as established by Pöthing et al. (2010) and Fischer et al. (2017) remains a reference to consider because of its construction on many soils.

In agricultural landscapes, establishment of vegetated buffer zones in riparian wetlands has long been promoted as an effective way to reduce P transfer to streams (Hoffmann *et al.*, 2009). However, recent studies show that this positive role may be offset by the fact that these areas can become sources of dissolved P for watercourses, due to the periodic rising of the water table that these zones undergo (Dupas *et al.*, 2015; Gu *et al.*, 2017). This offset is even more crucial when wetlands are cultivated and fertilized with P, as is the case in the Brittany region in Western France, where wetlands may represent up to 20% of the cultivated land (Montreuil *et al.*, 2011; Casquin *et al.*, 2021). Hydromorphic soils from wetland areas are also known to be depleted in Fe but enriched in organic matter, which can exacerbate the capacity of these soils to release dissolved and colloidal P (Brand-Klibanski *et al.*, 2007; Wang *et al.*, 2019). These specific physico-chemical characteristics and high hydrological connectivity make hydromorphic soils from wetland domains potentially at high risk for the release of dissolved P into watercourses.

It is necessary to test if the existing P risk assessment tools mostly developed for well-drained soils, such as the logarithmic relationship between DPS and WSP as established by Pöthing et al. (2010), can also be used as a risk assessment tool for hydromorphic soils. For that purpose, 69 samples of currently cultivated and non-cultivated hydromorphic soils from wetland domains set in the Brittany Region, an intensively cultivated region of Western France, were investigated, with three main objectives: i) to determine the P adsorption properties of these hydromorphic soils using the conventional P sorption isotherm method and to identify the primary factors

controlling these properties; ii) to determine whether the simple relationship between the DPS and WSP proposed universally by Pöthig et al. (2010) and Fischer et al. (2017) for agricultural soils also apply to hydromorphic soils which are presumably at high risk for the release of dissolved P; and lastly iii) to evaluate further the risk that hydromorphic soils from wetland domains could constitute an important source of dissolved P emissions in agricultural landscapes.

## 2. Materials and Methods

### 2.1. Study area

The Brittany region of Western France (Fig. 1) spans 27,000 km<sup>2</sup> over basement rock consisting mainly of low-permeability granite and schists (Aquilina *et al.*, 2012). The climate is temperate oceanic with an average annual temperature of around 11.2°C and an annual rainfall varying from 600 to 1400 mm from east to west (Frei *et al.*, 2020). Agriculture in Brittany covers 56% of the surface area and is dominated by indoor pig and poultry farming, as well as dairy production. Agriculture in Brittany is highly intensive, contributing to 22% of the French agricultural production in terms of volume (Gascuel-Oudou *et al.*, 2010; Poisvert *et al.*, 2016; Kim *et al.*, 2019) and characterized by high overall 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>) (Guillemot *et al.*, 2021). These high nutrient surpluses, coupled with a shallow groundwater table, make this region highly sensitive to eutrophication as evidenced by the frequent development of cyanobacteria blooms and green algae tides (Charlier *et al.*, 2007; Schreyers *et al.*, 2021).

Several recent studies conducted in Brittany have shown that wetlands can be sources of dissolved P in streams and rivers (Dupas *et al.*, 2015; Gu *et al.*, 2017, 2019;

Casquin *et al.*, 2021). Two main mechanisms contribute to this release: i) soil rewetting during the water table rise after dry periods (Gu *et al.*, 2017, 2018), and ii) reductive dissolution of soil Fe (hydr)oxides during prolonged periods of water saturation (Gu *et al.*, 2019). Although the dissolved P concentrations in many Brittany rivers have decreased in the past 10 years, the challenge of reducing diffuse P emissions from agricultural soils remains important in this region, as this decrease is mainly attributed to the decrease of domestic and industrial point-source emissions (Dupas *et al.*, 2018).

## 2.2. Sampling strategy

Soil sampling was carried out in five main sectors from three different catchments: the Mauron, Guilliers, and Ploërmel sectors in the Yvel catchment (375 km<sup>2</sup>), the Naizin sector in the Kervidy-Naizin catchment (12 km<sup>2</sup>), and the Languenan sector in the Fremur catchment (58 km<sup>2</sup>). The surface areas of the sampled sectors are 7.3 km<sup>2</sup> (Languenan), 6.9 km<sup>2</sup> (Mauron), 4.6 km<sup>2</sup> (Guilliers), 0.54 km<sup>2</sup> (Naizin), and 0.14 km<sup>2</sup> (Ploërmel). Sectors in the Yvel catchment are separated from each other by a distance less than 15 km.

A total of 69 soil samples was taken (19 in Languenan, 8 in Naizin, 15 in Ploërmel, 17 in Mauron, and 10 in Guilliers), belonging to 27 transects perpendicular to the stream network. Soils were classified as hydromorphic by analyzing basic features typical of hydromorphic soils (iron redistribution, bleaching, clay accumulation; see Baize & Girard, 2009). Each soil was further ranked on a scale of 0 (no sign of hydromorphy) to 10 (maximum hydromorphy intensity) depending on the observed density of the hydromorphy traits (Rivière *et al.* 1992). For each site, a composite sampling of the surface soil (0-20cm) which contains most of the P, was carried out



using an auger, consisting of a mixture of five samples spaced out from each other by 5 m. Approximately 2-3 kg of fresh soil were collected at each site. Soil samples were stored in airtight plastic bags directly in the field and transported to the laboratory for analysis.

The sites selected for hydromorphic soil sampling encompass four main types of land use: i) cultivated wetlands (CW) which correspond to fertilized and tilled plots; ii) vegetated buffer strips (VBS) which correspond to 5 to 10 m grass strips; these VBS were all cultivated and fertilized in the recent past (< 10 years); (iii) permanent grasslands (PG) which correspond to the permanently grazed parts of wetlands; some of these areas may have been cultivated in the past (< 10-20 years); iv) non-cultivated wetlands (NCW) which correspond to portions of wetlands that have never been cultivated; they are usually extremely wet zones located in the immediate vicinity of watercourses; (see Table S1 in the supplementary materials for a complete description of the soil sample hydromorphic intensity, position on the slope, current land use and geographic coordinates).

### 2.3. Soil analysis

After transfer to the laboratory, soils were air-dried in a clean room for 20 days ( $25 \pm 2^\circ\text{C}$ ) and then sieved to < 2mm after removing all visible plant debris. Portions of the sieved air-dried soil samples were sent to the Soil Analysis Laboratory at the French National Research Institute of Agriculture, Food, and Environment (INRAE; Arras, France) to analyze the following parameters: particle size fractions, organic matter (OM)/nitrogen/carbon contents, water pH (1:5 v:v water extraction), labile P contents (i.e. oxalate-P; Tamm, 1922), Dyer-P (Dyer, 1894) and Olsen-P (Olsen *et al.*, 1954),

oxalate Si/Al/Fe contents (ICP-AES after extraction with ammonium oxalate and oxalic acid (Tamm, 1922), and total P content (ICP-AES after total solubilization with hydrofluoric and perchloric acid). Oxalate Al (Al-Ox) and oxalate Fe (Fe-Ox) concentrations are proxies for the poorly crystallized fractions of Al and Fe oxides in soils, which are presumed to be two of the main adsorption phases of P in soils (Börling *et al.*, 2004).

Water soluble P (WSP) was extracted by shaking the soil suspensions (1 g of dry weight soil in 25 ml ultrapure H<sub>2</sub>O) for 24h. After centrifugation at 3000 rpm for 10 minutes, the supernatant was filtered at 0.45 µm using pre-cleaned cellulose acetate filters. WSP was determined colorimetrically via a reaction with ammonium molybdate (Murphy & Riley, 1962). The accuracy of the WSP measurements was  $\pm 4 \mu\text{g l}^{-1}$ .

## 2.4. Phosphorus adsorption properties

Langmuir adsorption isotherms were measured in triplicate following the standard procedure developed by Graetz and Nair in "Methods for phosphorus analysis" (see Pierzynski and Hodges, 2000 (Pierzynski & Hodges, 2000)) by shaking 1.0 g of soil in 25 mL of one of eight P solutions containing either 0, 0.5, 1, 5, 10, 25, 50, 75, or 100 mg P l<sup>-1</sup>. The P solutions were prepared by dissolving KH<sub>2</sub>PO<sub>4</sub> in 0.01 M CaCl<sub>2</sub>. Soil suspensions were filtered using 0.45-µm pre-cleaned cellulose acetate filters. Because of the strong buffering capacity of studied soils, mainly due to their high organic matter content, the soil suspensions exhibited only a limited pH variation during the course of the present P adsorption experiments (maximum variation between 6.4 and 7.1), and no additional pH buffering was performed, as in the experiments previously conducted by Graetz and Nair (2009).

A P Langmuir sorption isotherm can be described by the following equation:

$$SP = \frac{Q_{max} k * EPC}{1 + k * EPC} \quad (1)$$

with a linear simplification:

$$\frac{EPC}{SP} = \frac{EPC}{Q_{max}} + \frac{1}{Q_{max} * k} \quad (2)$$

where SP is the total amount of P sorbed by the soil ( $\text{mg kg}^{-1}$ ) for one given P concentration in solution during the experiment, EPC is the P concentration ( $\text{mg l}^{-1}$ ) in the solution after exchange with the soil,  $Q_{max}$  is the P sorption maximum capacity ( $\text{mg kg}^{-1}$ ), and  $k$  represents the P sorption strength constant ( $\text{L mg}^{-1}$ ).

The equilibrium P concentration at zero net P sorption ( $EPC_0$ ) is defined by the intersection of the P sorption isotherm with the x-axis. It is calculated from the linear relationship between SP and EPC at the initial range of the sorption isotherm (Pöthig et al., 2010; Zhou and Li, 2001).  $Q_{max}$  is calculated from the reciprocal slope obtained by plotting the quotient  $EPC/SP$  versus EPC. By knowing SP, EPC, and  $Q_{max}$ , it is possible to determine the sorption constant  $k$  using equation (1).

The Langmuir model can also be used to evaluate how  $k$  values changed as adsorption proceeds, thereby giving access to the strength of the sites involved in P binding at a given stage of adsorption. Instantaneous  $k$  values can then be used to evaluate the relative proportion of weak and strong sites involved in the overall adsorption process.

## 2.5. DPS calculation

Because one of our objectives in this study was to test the hypothesis that the DPS as calculated by Pöthig et al. (2010) could be universally used to describe the capacity of soils to release dissolved P, we used the same equation proposed by these authors to calculate DPS values for the soils studied in the present study, namely:

$$DPS (\%) = \frac{TP}{PSC} \times 100 \quad (3)$$

where TP is the total P content in the soil ( $\text{mg kg}^{-1}$ ), and PSC the P sorption capacity of the soil which is defined as the sum of  $Q_{\text{max}}$  and TP ( $\text{mg kg}^{-1}$ ).

## 2.6. Statistical analysis

All statistical analysis were realized with R version 4.1.2 (R Core Team, 2021). The normality of soil physico-chemical characteristics and soil P adsorption properties were tested using the Shapiro test that showed that most characteristics could not be considered normal. To assess the statistical significance of differences in these properties between sampling sectors, we relied on non-parametrical tests. First, Kruskal-Wallis rank sum test was performed for each characteristic with the sector as the factor, and the post-hoc Dunn's Test (Dunn, 1964) was used to test differences between every pairs of sectors considering a significant an adjusted p-value (Benjamini & Hochberg, 1995) of 0.05. Kruskal-Wallis rank sum test is part of base R, while Dunn's test and adjusted p-values were computed using dunn.test package version 1.3.5 (Dinno, 2017). Correlations between variables related to P adsorption properties ( $Q_{\text{max}}$ , TP, and WSP) and variables related to proxies of P-sorbing phase concentrations (clay, Fe\_Ox, Al\_Ox, Si oxalate content (Si\_Ox), OM content) were assessed using Pearson correlations.

## 3. Results

### 3.1. Soil composition

The overall compositions of the 69 analyzed soils (see Table S2 in the supplementary materials) are typical of silty loamy luvisol soils which characterize the Brittany region (Curmi *et al.*, 1998). The soil composition showed high variabilities at the intra and inter-sector scales (Table 1; Fig. S1). At inter-sector scales and on average, soils from the Languenan sector were poorer in clay and fine silt than soils from other sectors. At intra-sector scales, the greatest variations were observed for Mauron soils (clay, fine silt, coarse silt, and sand contents), followed by Naizin and Ploërmel soils (clay and coarse sands).

The average organic carbon contents (OC) ranged between 24.4 and 29.6 g kg<sup>-1</sup> for most samples, except for soils from the Languenan and Naizin sectors which had significantly lower (15.3 g kg<sup>-1</sup>) and higher OC contents (39.2 g kg<sup>-1</sup>), respectively.

Al<sub>Ox</sub> and Fe<sub>Ox</sub> contents varied by approximately the same order among the sectors as the clay contents, with samples from the Languenan and Ploërmel sectors showing the lowest and highest Al<sub>Ox</sub> and Fe<sub>Ox</sub> contents, respectively. In addition, intra-sector variations also appeared, with higher variations for the Fe<sub>Ox</sub> contents than for the Al<sub>Ox</sub> contents (Fig. S1).

### 3.2. Phosphorus concentration

Both the average TP and WSP content differed significantly among the sampling sectors: from 0.87 (Guilliers sector) to 2.11 g kg<sup>-1</sup> (Ploërmel sector) for TP; from 2.5 mg (Ploërmel sector) to 14.5 mg l<sup>-1</sup> (Naizin sector) for WSP (Fig. 2). Conversely, the average Olsen-P and Dyer-P contents were comparable from one sector to another (Fig. 2). However, the intra-sectoral variations for the TP, Olsen-P, Dyer-P, and WSP contents

were generally high, with soils from the Mauron sector showing the highest variations (Fig. 2).

Table 2 compares the average TP, Dyer-P, Olsen-P, and WSP concentrations measured in the studied hydromorphic soils with averages calculated from two regional databases gathering cultivated soils mainly from upslope, well-drained domains (Matos-Moreira *et al.*, 2017; Saby *et al.*, 2019). The Olsen-P and Dyer-P contents of the currently cultivated hydromorphic soils (CW + PG) were 30 to 79% higher than the average soil contents in these two databases. The P enrichment of the hydromorphic soils was even clearer when considering the TP contents which were higher in both the studied cultivated and uncultivated soils than in these two databases. On average, the Olsen-P and Dyer-P contents of the studied hydromorphic soils were within the range for good soil fertility (Morel *et al.*, 1992).

### 3.3. Sorption properties

The P adsorption isotherm evidenced particular and specific P adsorption properties depending on the sector of origin of the samples (Fig. 3). Q<sub>max</sub> values showed a strong inter-sector variation (factor of 4 from 468 to 1836 mg kg<sup>-1</sup>) in the order Guilliers < Languenan < Naizin = Mauron < Ploërmel.

The average k values also exhibited differences depending on the geographical sector of origin of the studied soils, although not correlated with variation in Q<sub>max</sub> values (Fig. 3). The average k values were lowest in the Naizin soils (0.03 L mg<sup>-1</sup>), and highest in the Languenan soils (0.39 L mg<sup>-1</sup>). Unlike the Q<sub>max</sub> value, however, only soils from the Naizin sector had k values significantly different from the remaining soils. Average k values of soils from the other four sectors were not statistically different

from each other, basically due to a strong intra-sector heterogeneity (Fig. 3). The average EPC<sub>0</sub> values also differed among the sampling sectors, ranging from 0.03 mg l<sup>-1</sup> for Ploërmel soils to 0.102 and 0.127 mg l<sup>-1</sup> for Languenan and Mauron soils, respectively. However, these variations were not statistically significant due to a high intra-sector variability (Fig. 3). Thus, for both the EPC<sub>0</sub> and k values, the intra-sector variability predominated over the inter-sector variability. Conversely, the Q<sub>max</sub> values showed a clear predominance of inter-sector variability over intra-sector variability.

As illustrated in Fig. 4, the k values showed a marked peak for the Guilliers, Ploërmel and Mauron soils at the beginning of the adsorption experiments, which then decreased as the adsorption proceeded. This suggests the presence in these soils of a mixture of strong and weak P binding sites, the strong sites being first saturated with P before the relay taken over by weak sites. The sharp and rapid decrease in k values for Guilliers soils suggest the presence of a more limited number of strong sites in these soils, as compared to soils from the Ploërmel and Mauron sectors for which the decreases in k values occurred later during the adsorptions. Conversely, the k values in soils from the Naizin sector were consistently low throughout the adsorption process, suggesting that the P sorption sites in these soils are mostly weak sites. These results highlight the occurrence of a diversity of P binding sites in the analyzed soil samples, both in terms of absolute strength and relative proportion of weak and strong sites.

### **3.4. Relationship between DPS, EPC<sub>0</sub> and WSP**

For the soils from each sector, the WSP increased as the DPS increased and there were several critical DPS values above which a slight increase in the DPS values resulted in a strong increase in WSP (Fig. 5). However, contrary to the German and Swiss soils

investigated by Pöthig et al. (2010), the correlation observed is neither unique nor regular. In fact, a dispersion of the points was observed, linked to the fact that i) specific relationships were observed for each sampling sector, and (ii) the critical DPS values were different also depending on the sampling sectors. Thus, in the Naizin soils, the critical DPS value was as low as 30%, whereas this value was around 55-60% for the Guilliers and Ploërmel soils, and around 55% for the Mauron soils. In the absence of a strong overall mathematical relationship for all samples between these parameters, these thresholds are estimated visually.

Also, unlike the soil investigated by Pöthig et al. (2010) the hydromorphic soils analyzed in this study did not produce a unique and regular correlation between the ECP\_0 and DPS values (Fig. 6). Rather, a superposition of different correlations depending on the sampling sectors was observed, with EPC\_0 concentrations starting to rise at different DPS values (between 30 to 50-60%), depending on the sectors.

### **3.5. Relationship between Qmax and soil composition**

Possible relationships between P adsorption properties and P carrier phases in the studied soils can be assessed by considering Table 3 which presents Pearson correlation coefficients between Qmax and soil composition. Table 3 shows that a combined analysis of all the samples pooled together yielded insignificant correlations, except for Fe\_Ox ( $r=0.55$ ). The sector based treatment, by contrast, gave specific and statistically significant correlations. For the Naizin soils, the most significant correlations were obtained with the Fe\_Ox and OC contents ( $r = 0.80$  and  $0.82$ , respectively). The data also highlighted a potential secondary control of Qmax by the Al\_Ox ( $r = 0.48$ ) and/or clay ( $r = 0.47$ ) contents. For the Guilliers soils, a primary control



of  $Q_{\max}$  was observed with clay ( $r = 0.82$ ) and Fe\_Ox ( $r = 0.79$ ), and a secondary control was observed with Si\_Ox ( $r = 0.77$ ) and Al\_Ox ( $r = 0.65$ ) contents. For the Ploërmel soils with the highest  $Q_{\max}$  values, correlation test showed a control of  $Q_{\max}$  exclusively by the Al\_Ox content ( $r = 0.69$ ). Only the Maureon soils showed no obvious control of  $Q_{\max}$ .

## 4. Discussion

### 4.1. Causes of spatial heterogeneity in the P sorption properties of wetland soils

An important result of this study is the richness in P of the hydromorphic soils analyzed, the average concentration in TP being around  $1500 \text{ mg kg}^{-1}$ . Such high TP concentrations are evidence of intensive agriculture in the Brittany region over the past decades. The Dyer-P and Olsen-P contents are also indicative of heavy fertilization. The variations in P content between sectors could be explained by differences in i) soil composition and soil P adsorption properties, ii) land use history and period of conversion to intensive agriculture, and iii) variable P inputs from cultivated upland domains for those of the soils located in lowland wetland domains. The high P contents displayed by the studied soils is regarded as evidence that wetland domains are P enriched zones in agricultural landscapes, at least at the scale of the Brittany region where this study is based. A superposition of two main reasons can be envisaged to explain this overall P enrichment: i) the fact that most wetland domains in Brittany were at some point in their recent history cultivated and fertilized with P; ii) the fact that these domains are domains of P accumulation due to their lowland topographic position.

Another important result is the significant variability in P sorption properties (i.e.  $Q_{\max}$  and  $k$  values) displayed by the investigated hydromorphic soils, both at the intra- and inter-sector scales. Because of this variability, we can deduce that it is a complex task to assess the risk of dissolved P loss in Brittany hydromorphic soils. Indeed, this task requires an understanding of P adsorption processes, and therefore requires a thorough study of the variability of the soil properties studied. Published studies have shown that several phases may control P adsorption in soils, such as clays, Fe and Al oxides or OM (via cationic bridges), each with varying binding strengths (Vistoso *et al.*, 2012; Gérard, 2016; Yang *et al.*, 2019). Therefore, it may be possible that the observed variations in P sorbing properties were due to spatial variations in the nature of the P controlling phases.

The different P carrier phases identified here for each sector (clay, Fe- and Al-Ox, OC; see Table 3) are consistent with the general literature which describes organo-mineral complexes (Gerke, 2010), metal oxides (Yao & Millero, 1996; Antelo *et al.*, 2005), aluminosilicates (Jara *et al.*, 2006), and clays (Manning & Goldberg, 1996; Gérard, 2016) as the main P carrier phases in soils. Interestingly, results from 4 of the 5 sampled sectors are consistent with several previous studies which pointed out that Al-oxides are major P carrier phases in wetland soils (Bridgham *et al.*, 2001; Bruland & Richardson, 2004; Cohen *et al.*, 2007). Thus, the highest  $k$  values were found for the Guiliers and Ploërmel soils for which P sorption appears to be controlled by clays and Al-Ox, two phases that are known to have among the highest affinity constants of all P complexing phases in soils (Rajan & Perrott, 1975; Gérard, 2016). Conversely, for the Naizin soils that exhibit the weakest sites, the sorption of P seems to be dominantly controlled by OM, a compound known to reduce the strength of P sorption in soils and

sediments (Yang *et al.*, 2019). Thus, the spatial variations in P adsorption properties seem to be linked to the differences in the soil mineralogy and soil OM content. For this study, we have not strictly investigated the mineralogy and P-speciation of these soils using, for example, spectroscopic methods such as the XANES or STXM methods, and it is not possible to comment further on the exact nature of these differences.

We explored the hypothesis that agricultural practices could be at the origin, at least in part, of the observed variations in soil P sorption properties. To do that, we performed additional PCA analyses by separating the soils between i) cultivated and uncultivated soils, ii) hydromorphy levels and iii) topographical position. The results (not shown) did not highlight any role of agriculture on the observed variations. Consequently, we conclude that the ultimate causes of the spatial variations in the P sorption properties of the studied soils remain unknown and that further studies are needed to determine these causes.

#### **4.2. Assessing dissolved P release risk in hydromorphic soils: is the DPS vs. WSP correlation a reliable tool?**

The high spatial variability in the P sorption properties observed in the studied hydromorphic soils calls into question the applicability of existing equations to predict the risk of dissolved P release using simple indicators such as the DPS. We found that, unlike in the German and Swiss soils analyzed by Pöthig *et al.* (2010), the hydromorphic soils in the present study defined different WSP vs. DPS correlations and different DPS critical values depending on the sampling sector (Fig. 5). Thus, the idea defended by Pöthig *et al.* (2010) and later taken up by Fischer *et al.* (2017), i.e. that there may be a universal WSP vs. DPS correlation to reliably assess the potential risk of dissolved P

release by soils, is not supported by the present dataset.

Another highlight of the present dataset is that the critical DPS values were much lower (between 30 and 60%) than in the German and Swiss soils studied by Pöthig et al. (2010). The studied hydromorphic soils here are potentially more at risk of releasing dissolved P in soil waters at the same DPS value than the reference soils used by Pöthig et al. (2010), as shown in Figure 5. This greater risk could be partly due to that a large proportion of the P sorption sites present in the studied soils are weak sites. For example, the lowest critical DPS value was found for soils from the Naizin sector ( $\approx 30\%$ ; Fig. 5). The adsorption experiments conducted on the Naizin soils gave the lowest values of the affinity constant  $k$  of all the soils investigated here and did not reveal the presence of strong sites in these soils at the onset of the P sorption process.

The existence of high proportions of weak P binding sites in hydromorphic soils could explain the generally lower critical DPS values we observe in this study as compared to the soils investigated by Pöthig et al. (2010). Although still a controversial issue, the alternation of redox conditions in wetland soils is suggested to have the potential to reduce the strength of Fe-P complexes by its capacity to favor the development of poorly crystalized iron oxides (Reddy *et al.*, 1999). The high OM contents of wetland soils could also be involved, as recent studies have shown that the addition of OM to soils decreased the strength of the P binding sites (Yang *et al.*, 2019).

The variability and geographical dependence of the DPS vs. WSP correlations obtained in this study emphasized the difficulty to use the DPS as a reliable predictor of the risk of P release by hydromorphic soils from wetland domains. We can conclude that, because of high variability, the DPS measurement alone does not make it possible to know a priori the level of risk of dissolved P release by these soils and from the

results it is difficult or impossible to predict the risk without conducting extensive analyses on the soil (sorption isotherm, WSP).

We propose an evaluation of the potential risk of dissolved P release for the investigated hydromorphic soils based on the consideration of two essential sorption properties measured in these soils: the  $Q_{\max}$  value and average affinity constants  $k$  (Table 4). This evaluation is qualitative, and its only purpose is to provide a classification of the main soil P sorption properties encountered in this study on a scale of potential risk of dissolved P release. In this evaluation, we decided to give a maximum weight to the  $Q_{\max}$  value (decreased risk with an increase in the  $Q_{\max}$  value), however with a potential downgrade according to the  $k$  value (increased risk for a high  $Q_{\max}$  value but accompanied by a low  $k$  value). Using these criteria, the potential release risk of hydromorphic soils in the present study was classified as a low risk at Ploërmel, a moderate risk at Mauron and Languenan, and a high and extremely high risk at Guilliers and Naizin, respectively (Table 4).

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

Based on the non-linear regressions reported in Fig. 5, we assessed the proportion of investigated hydromorphic soils that should be considered as high risk of dissolved P release and identified within this proportion the proportion of soils that are currently cultivated and uncultivated (Table 5). The overall proportion of soils at high risk is approximately 50%, within which 70% were from cultivated wetland domains and 30% from uncultivated wetland domains. The proportion of soils at risk in each sampling geographical sector was consistent with the risk classification established based on the

sorption properties of the soils, with the highest proportions being found for the Naizin, Guiliers and Languenan sectors (69-86%, Table 5). This result confirms the recently put forward hypothesis that wetland sectors should be considered as potential hot spot zones of dissolved P emissions in Brittany's agricultural landscapes (Gu *et al.*, 2017; Casquin *et al.*, 2021).

It is notable that the proportion of uncultivated soils presenting a high risk of dissolved P release is not negligible as it represents 30% of the total analyzed soils. Among these uncultivated soils, 55% are VBS which are no longer fertilized. Considering that all these VBS are of comparable width (5-10 m according to the Brittany regulation for water protection), the fact that a significant portion of these zones is at a high risk of dissolved P release is probably due to the fact that most of the VBS analyzed here are only 5 to 10 years old. They were previously cultivated and fertilized with P. As the turnover of P in soil is very slow (Sharpley *et al.*, 2013; Schoumans & Chardon, 2014), this may have generated a legacy P store in the VBS soils with high DPS values. Another cause could be the fact that VBS are able to effectively capture particulate P eroded from upslope cultivated fields and thus limit the flux of P from soils to watercourses (Dorioz *et al.*, 2006; Al-Wadaey *et al.*, 2012; Roberts *et al.*, 2012). Although very useful for reducing the emission of particulate P into watercourses, VBS in the Brittany region may have the negative effect of increasing the DPS value of soils in these areas and potentially transform the accumulated P into dissolved forms, creating a risk of dissolved P release.

Recent studies have reported increases in the dissolved P concentrations in rivers in several agricultural regions of the world, such as the Chesapeake Bay or Lake Erie basins (Daloğlu *et al.*, 2012; Kleinman *et al.*, 2019). These increases have been

attributed to the implementation of conservation agricultural practices, especially no-till practices, in these regions (Jarvie *et al.*, 2017; Kleinman *et al.*, 2019). We emphasize here that another key element of agricultural conservation practices is the systematic implantation of grass strips downslope of cultivated zones to capture particulate P emissions from these zones. Results from the present study clearly show that soils from these VBS may be at high risk of dissolved P release, particularly when the grass strips are set in riparian wetland domains. Consequently, the installation of VBS could also contribute to the increase in dissolved P concentrations observed in rivers in these regions, a hypothesis that would merit further consideration, in our opinion.

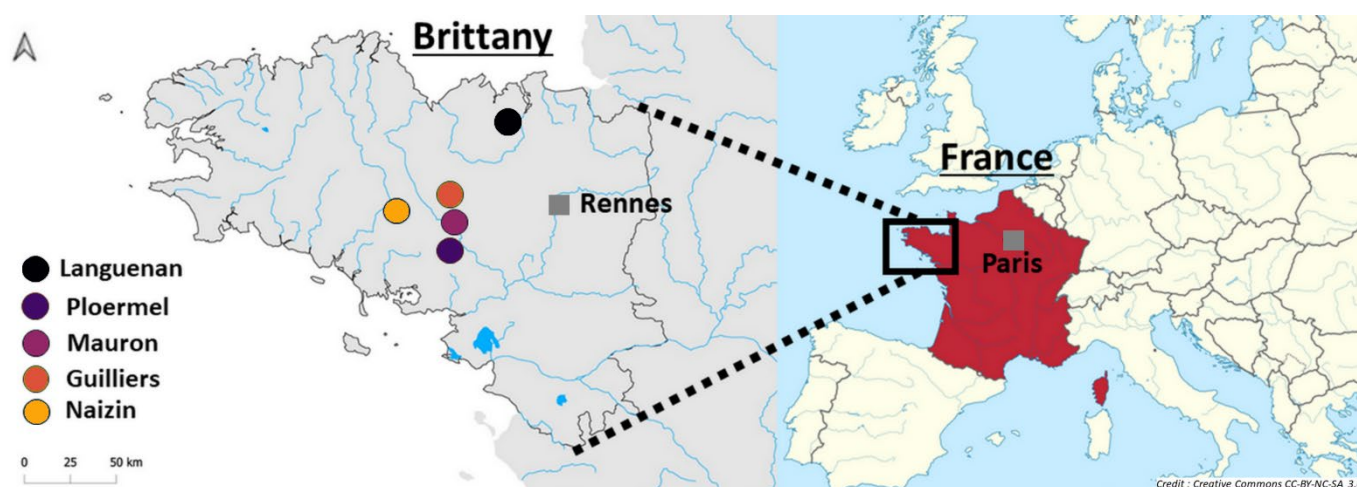
## 5. Conclusion

The present study assessed the P sorption properties of 69 cultivated and uncultivated hydromorphic soils set in wetland domains in the Brittany region. We observed high spatial variability in the P sorption properties both in terms of quantity of P sorption sites and in terms of the nature of the phases involved in sorption. Contrary to well-drained soils, hydromorphic soils in the present study defined specific WSP vs. DPS correlations and specific DPS critical values depending on the nature of the P adsorption phases among the sampling sectors. The critical DPS values above which the risk of dissolved P release increases significantly were lower in hydromorphic soils (30-60%) than those in published studies on well-drained soils (70-80%). For the same DPS value, hydromorphic soils from wetland domains had higher WSP concentrations than that predicted from existing equations based on well-drained soils, indicating that the risk of P release from hydromorphic soils may be underestimated when assessed using these equations.

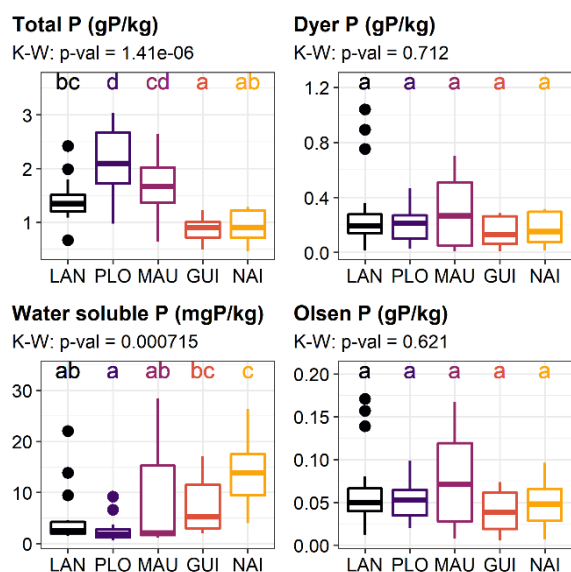
Our results confirm that wetland areas are zones of P accumulation in agricultural landscapes and are potentially high-risk zones in terms of dissolved P losses. We emphasize that great care should be exercised when applying the existing risk assessment method of dissolved P release into hydromorphic soils, and that specific assessment tools able to account for the variability in the P sorption properties should be developed for these high-risk soils.



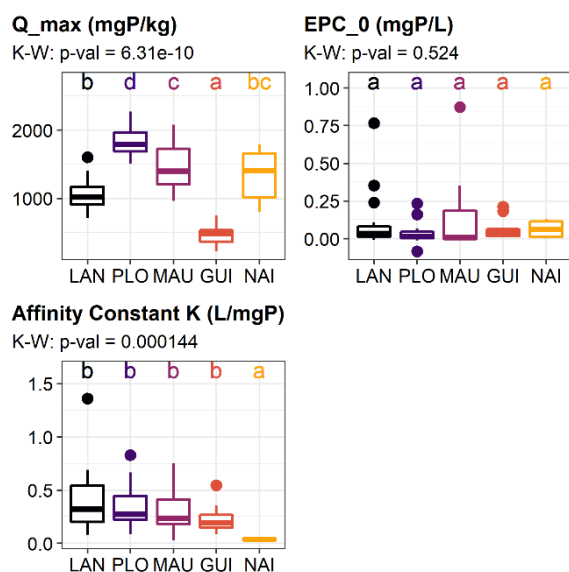
## Figures.



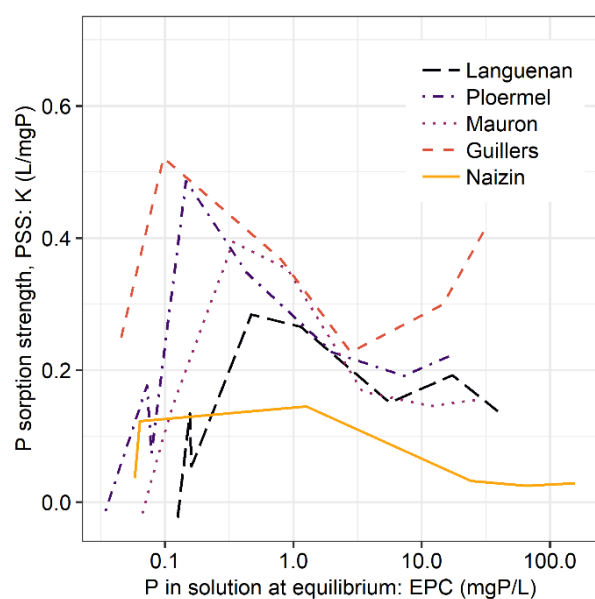
**Figure 1:** Map showing the location of the sectors from which the samples analyzed in this study come from, as well as that of Brittany in France and in the world



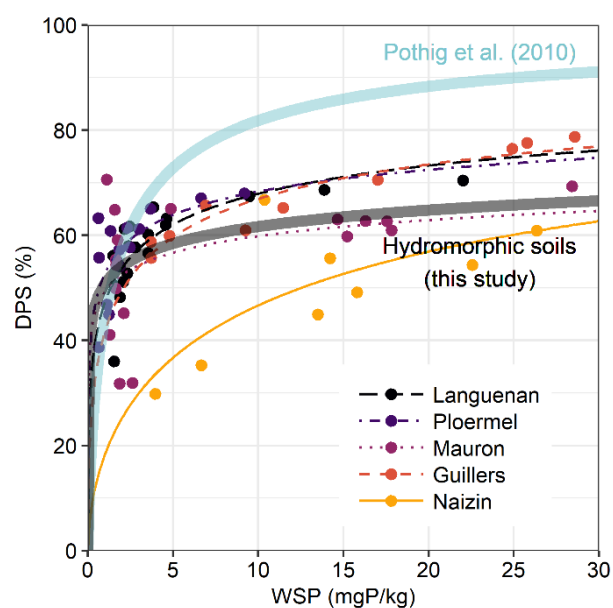
**Figure 2:** Box plot illustrating the inter-sector and intra-sector variability of Total-P, Olsen-P, Dyer-P, and WSP concentrations of the investigated hydromorphic soils. Letters denote significantly different sectors according to Dunn's test (adjusted  $p < 0.05$ ). GUI = Guilliers, LAN = Languenan, MAU = Mauron, NAI = Naizin, PLO = Ploermel.



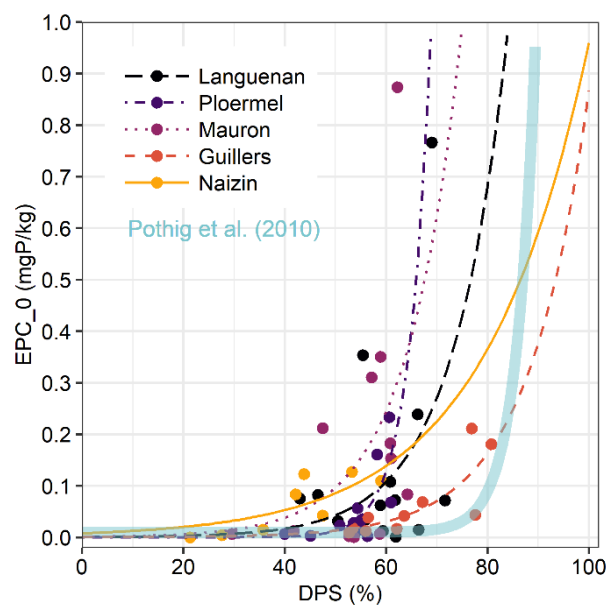
**Figure 3:** Values of the parameters (Q<sub>max</sub>, EPC<sub>0</sub>, affinity constant) describing the adsorption of P by the studied soil samples as calculated from the isotherm experiment results using Langmuir models. Letters denote significantly different sectors according to Dunn's test (adjusted p<0.05). GUI = Guilliers, LAN = Languenan, MAU = Mauron, NAI = Naizin, PLO = Ploermel.



**Figure 4:** Variation of the P sorption strength (PSS) in the investigated soils as adsorption experiments proceeded. PSS are presented as averaged values, for each sampling sector



**Figure 5:** Degree of phosphorus saturation (DPS) as a function of water extractable phosphorus (WSP) values of investigated soils, by sampling sectors and comparison with DPS\_litterature. Bold blue curve corresponds to the equation determined by Pothig et al. (2010) while bold black curve corresponds to the regression computed on all soils of this study.



**Figure 6:** Dependence of the equilibrium P concentration (EPC\_0) on the degree of P saturation (DPS). Bold blue curve corresponds to the equation determined by Pothig et al. (2010).

## Tables.

	Languenan	Ploermel	Mauron	Guilliers	Naizin
Clay	134.3±19.5 <b>a</b>	277.8±47.2 <b>c</b>	201.4±61.7 <b>b</b>	293.4±76.9 <b>c</b>	243.6±53.3 <b>bc</b>
F_loam	189.2±11.8 <b>a</b>	350.5±29.1 <b>bc</b>	336.1±32.2 <b>b</b>	315.2±34.1 <b>b</b>	403.6±42.4 <b>c</b>
C_loam	444.4±39.1 <b>c</b>	156.3±42.91 <b>a</b>	258.3±71.4 <b>b</b>	225.4±72.4 <b>ab</b>	216.9±71.8 <b>ab</b>
F_sand	168.5±19.6 <b>b</b>	93.8±12.4 <b>a</b>	100.2±16.5 <b>a</b>	80.7±19.0 <b>a</b>	72.9±27.4 <b>a</b>
C_sand	63.5±25.7 <b>a</b>	121.6±56.5 <b>b</b>	104.1±36.6 <b>b</b>	85.3±59.5 <b>ab</b>	63.0±27.7 <b>a</b>
OC	15.3±5.3 <b>a</b>	27.8±3.4 <b>b</b>	24.4±4.4 <b>b</b>	29.6±13.8 <b>b</b>	39.2±24.5 <b>b</b>
Al_Ox	1.1±0.2 <b>a</b>	2.0±0.5 <b>c</b>	1.5±0.3 <b>b</b>	2.0±0.3 <b>c</b>	1.9±0.6 <b>bc</b>
Fe_Ox	4.6±1.1 <b>a</b>	8.3±1.7 <b>c</b>	5.5±2.2 <b>ab</b>	7.2±2.8 <b>bc</b>	5.9±2.1 <b>abc</b>
Si_Ox	0.3±0.0 <b>a</b>	0.4±0.1 <b>b</b>	0.27±0.10 <b>a</b>	0.6±0.17 <b>b</b>	0.3±0.0 <b>a</b>

**Table 1.** Summary of the mean±standard deviation of the physico-chemical properties (g/kg) of the surface soils of the 5 sectors. F\_loam = fine loam, C\_loam = coarse loam, F\_sand = fine sand, C\_sand = coarse sand, OC = organic carbon, Al, Fe and Si\_Ox = Al, Fe and Si oxalate. Lowercase letters after each value denote significantly different medians across sectors according to Dunn's test (adjusted  $p < 0.05$ ), in increasing order.


Database Source	Hydromorphic soil database All soils, this study	Cultivated wetlands CW and PG soils, this study	Uncultivated wetlands VBS and NCW soils, this study	Trans P Matos-Moreira et al. (2017)	BDAT Saby et al. (2019)
Sample number	69	41	28	137	> 90 000
Olsen-P	58 ± 41	68 ± 43	44 ± 36	41 ± 26	51 ± 28
Dyer-P	230 ± 210	270 ± 220	174 ± 210	151 ± 104	196 ± 121
Total-P	1.49 ± 0.64	1.62 ± 0.67	1.30 ± 0.53	1.10 ± 0.46	nd
WSP	6.45 ± 6.86	6.99 ± 6.87	5.65 ± 6.86	8.0 ± 6.0	nd

**Table 2.** Comparison between the average concentrations of Olsen-P, Dyer-P, Total-P and WSP of the analyzed wetland soils and average concentrations from the Brittany Trans-P and BDAT databases. CW: Cultivated wetlands, PG: Permanent grasslands, VBS: Vegetated buffer strips, NCW: non-cultivated wetlands. Concentrations are in mg/kg except for Total P (g/kg). nd: not determined.



	Languenan	Ploermel	Mauron	Guilliers	Naizin	All sectors
Clay	0.04	<b>-0.53*</b>	0.06	<b>0.85**</b>	<b>0.47*</b>	0.36
OC	<b>0.73**</b>	-0.39	0.10	-0.16	<b>0.82**</b>	0.36
Al_Ox	<b>0.59*</b>	<b>0.69**</b>	<b>-0.70**</b>	<b>0.65*</b>	<b>0.48*</b>	0.3
Fe_Ox	<b>0.75**</b>	-0.26	0.05	<b>0.79**</b>	<b>0.80**</b>	<b>0.55*</b>
Si_Ox	<b>-0.53*</b>	-0.02	-0.18	<b>0.77**</b>	<b>-0.79**</b>	0.02

**Table 3** Pearson correlation between Qmax and soil potential P carrier phases for each sector and considering the whole dataset (n=69). OC: organic carbon; Al, Fe, and Si\_Ox: oxalate extraction of Al, Fe, and Si. Bold values are significant at p-value < 0.05. \* means a p value < 0.05 and \*\* means a p value < 0.01.

Sector (Catchment)	Ploërmel (Yvel)	Mauron (Yvel)	Languenan (Frémur)	Guilliers (Yvel)	Naizin (Naizin)
Texture	Clay and fine loam	Fine and coarse loam	Fine loam and fine sand	Clay, fine loam and OM	Clay, fine loam and OM
Qmax (mg/kg)	1836	1469	1054	515	1333
Main carrier phase	Al oxides	unknown	Iron oxides and OM	Clay and oxides	Iron oxides and OM
Critical DPS (%)	55	55	60	55	30
Average affinity constant (k)	0,34	0,28	0,39	0,23	0,04
Maximum affinity constant (k)	0,82	0,75	0,69	0,54	0,05
Ratio [strong sites]/[weak sites]	High	Moderate	Moderate	Low	Very low
Release risk					

**Table 4.** Qualitative ranking of the studied soils as regards the risk of P release as estimated from their sorption properties, and depending of their sampling sector. The critical DPS threshold (critical DPS) was estimated graphically from the relationship between DPS and WSP obtained in Figure 5. A premium is given in this ranking to the Qmax values and the estimated ratio [number of strong sites]/[number of weak sites].

Sector	Languenan	Ploërmel	Mauron	Guilliers	Naizin	Total
Number of samples	19	15	17	10	8	69
Total (%)	69	13	47	86	78	51
Cultivated (%)	64	100	75	67	71	69
Uncultivated (%)	36	0	25	33	29	31

**Table 5.** Proportion of wetland soils per sampling locality whose degree of P saturation exceeds the risk thresholds listed in Table 4. The proportions are first calculated for all land uses combined. The proportions are then broken down into soils currently cultivated and soils currently uncultivated.

## Acknowledgments

This work benefited from financial support from the DRP2 project, jointly funded by the Regional Council of Brittany (grant N°18006537) and the Loire-Bretagne Water Agency (grant N°204802). Through the support of the GeOHeLiS analytical platform of Rennes University, this publication is also supported by the European Union through the European Regional Development Fund (FEDER), the French ministry of Higher Education and Research, the French Region of Brittany and Rennes Metropole. We thank Rémi Dupas from INRAE for discussions at the origin of the DPR2 project, and thus of this research work. We also thank two anonymous reviewers for their constructing comments that greatly help us to improve the ideas developed in this paper. Sara Mullin post-edited the English style and grammar of this paper.

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