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**EVIDENCE OF COLLOIDS AS IMPORTANT PHOSPHORUS CARRIERS IN
NATURAL SOIL/STREAM WATERS IN AN AGRICULTURAL
CATCHMENT**

Sen Gu^{a, b, *}, Gérard Gruau^b, Rémi Dupas^c, Laurent Jeanneau^b

^aInstitute of Hydrobiology, Chinese Academy of Sciences, Wuhan 430072, China

^bUniv Rennes, CNRS, OSUR, Géosciences Rennes - UMR 6118, F-35000 Rennes,
France

^cUMR SAS, INRAE, AGROCAMPUS OUEST, F-35000 Rennes, France

*Corresponding author. E-mail address: gusengreat@gmail.com

Core ideas:

- We studied colloidal P in natural soil waters and their adjacent stream waters
- Colloidal P represented ca. 39% of total P in all the soil/stream waters studied
- Riparian wetlands are hotspot zones for the production of P-bearing colloids
- Colloidal P have great potential to be transported from soils to adjacent streams

Abbreviations: DOC, dissolved organic carbon; ICP-MS, inductively coupled plasma mass spectrometer; MRP, molybdate-reactive P; MUP, molybdate-unreactive P; RW, riparian wetland; TP, total P.

ABSTRACT

Colloids (1-1000 nm) are important phosphorus (P) carriers in agricultural soils. However, most studies are based on colloids from soil waters extracted in the laboratory, thus limiting the understanding of the natural transfer of colloidal P along the soil-to-stream continuum. Here, we conducted a field study on the colloidal P in both natural soilwaters and their adjacent stream waters in an agricultural catchment (Kervidy-Naizin, western France). Soil waters (10-15 cm, Albeluvisol) of two riparian wetlands and the adjacent stream waters were sampled monthly during wet seasons of the 2015-2016 hydrological year (7 dates in total). Ultrafiltration at three pore sizes (5 kDa, 30 kDa and 0.45 μm) was combined with ICP-MS to investigate variability in colloidal P concentration and its concomitant elemental composition. Results showed that colloidal P represented on average 45% and 30% of the total P (<0.45 μm) in the soil waters and stream waters, respectively. We found that colloidal P was preferentially associated with i) organic carbon in the fine nanoparticle fraction (5-30 kDa) and ii) Fe-oxyhydroxides and organic carbon in the coarse colloidal fraction (30 kDa - 0.45 μm). The results confirmed that colloidal P is an important component of total P in both soil waters and stream waters under field conditions, suggesting that riparian wetlands are hotspot zones for the production of colloidal P at the catchment scale which have the potential to be transported to adjacent streams. We emphasize that these findings were based on limited sampling times and further longer-term monitoring and application of tracer or isotope methods would be necessary to better assess colloidal P variations and its transfer from soils to streams.

INTRODUCTION

Excess phosphorus (P) in surface water threatens the continental and coastal water quality since P constitutes, along with nitrogen, one of the two main nutrients that influence waterbody eutrophication (Elser et al., 2007; Dodds and Smith, 2016; Schindler et al., 2016; Smith and Schindler, 2009). In most western countries, improvements in sewage treatment have decreased point-source P inputs and resulted in riverine P being nowadays dominated by diffuse P losses (Dupas et al., 2018; Kronvang et al., 2007). Thus, most recent management efforts in these countries focus on reducing diffuse P losses from agricultural landscapes (Schoumans et al., 2014; Sharpley et al., 2015, and references therein).

Studies in the past ten years have demonstrated that natural colloids (1-1000 nm) are important P carriers in stream/river waters (Baken et al., 2016a, 2016b; Gottselig et al., 2014, 2017a, 2017b). Coupled with other studies demonstrating that colloids are also important P carriers in soils (Heathwaite et al., 2005; Hens and Merckx, 2001; Jiang et al., 2015, 2017; Makris et al., 2006; Regelink et al., 2013), the possibility arises that colloids could be an important component of diffuse P losses in agricultural landscapes. The ability of diffuse P to trigger eutrophication is assumed to depend on its chemical form. Free ionic orthophosphate is considered to pose the greatest risk for eutrophication because it is the most readily available form of P for living organisms. In principle, the eutrophication risk posed by colloidal P (colloidal-P) is considered to

be lower because it is considered less bioavailable due to the association of P with organic matter (OM) or various types of mineral species such as iron (Fe) or aluminum (Al)(hydr)oxides or clay minerals (Baken et al., 2014). However, this risk can be high in reality because colloidal-P may contribute to plant P uptake (Montalvo et al., 2015), and processes such as reduction of P-bearing Fe oxides and sorption-desorption can change colloidal-P into dissolved form that are ultimately released to the water column (Baken et al., 2016a). Therefore, in the context of mitigating eutrophication, it is important to assess the mobilization and transfer of colloidal-P in agricultural landscapes.

Current studies on colloidal-P in agricultural landscapes have two major shortcomings. First, most studies on soil colloids were not conducted on colloids present in natural soil waters but rather on water-dispersible colloids extracted under laboratory conditions (Gu et al., 2018; Jiang et al., 2015, 2017; Missong et al., 2017, 2018). Previous studies have reported that parameters such as ionic strength or pH of extraction waters can alter the interaction of phosphate ions and colloids (Gérard, 2016; Yan et al., 2016a). Thus, uncertainties exist about whether the extracted colloidal-P are equivalent in concentration and composition to those involved under natural field conditions. Second, few studies have attempted to compare the concentration and composition of colloidal-P in natural soil waters and stream/river waters (Haygarth et al., 1997; Pokrovsky et al., 2005), especially on soils that are hydrologically connected to streams/rivers. Yet, certain processes can result in direct production of P-bearing colloids in streams/rivers, such as oxidation of Fe^{2+} and the

subsequent scavenging of free orthophosphate by the newly formed Fe (hydr)oxides (Smolders et al., 2017), challenging the existence of a direct link between colloidal-P found in streams/ivers and soils. Current knowledge is therefore limited in both identifying catchment-scale critical source zones of colloidal-P under natural field conditions, and evaluating variations in the concentration and composition of colloidal-P in soil waters and stream/river waters in order to identify the potential linkage between them.

To meet these knowledge gaps, we studied the colloidal-P in natural soil waters from riparian wetlands (RWs) and stream waters from the adjacent streams in an intensive agricultural catchment in western France during one hydrological year. A previous three-years monitoring study in this catchment indicated that the RWs are hotspots for the release of dissolved P ($< 0.45 \mu\text{m}$) in natural soil waters which was observed to enter the adjacent streams (Dupas et al. 2015b; Gu et al. 2017). Another laboratory rewetting experiment in this catchment showed that the RW soils had great potential to release colloidal-P upon rewetting, with the proportion of colloidal-P differing with different soil properties (Gu et al., 2018). The objectives of the present study were to i) explore the variations in colloidal P concentration and elemental composition in natural soil waters and stream/river waters at the catchment scale and ii) identify potential linkage between colloidal-P in soil waters and stream/river waters to verify whether the RW soils identified as colloidal-P sources in the laboratory are relevant colloidal-P sources for the stream network under natural field conditions.

MATERIALS AND METHODS

Catchment characteristics

This field study was conducted in the Kervidy-Naizin catchment, a small (5 km²) headwater catchment in central Brittany (western France, **Fig. 1a**). The climate is temperate oceanic, with an average annual temperature of 10.5°C and rainfall of 875 mm determined (2006 - 2016) (Fovet et al., 2018). The catchment is drained by an intermittent stream of 2nd Strahler order that is usually dry in summer. The catchment lithology consists of impervious Brioverianschists capped by 2-30 m of unconsolidated weathered materials, where a shallow aquifer develops. The catchment is well-drained in the upland domain and is hydromorphic in valley bottoms where RWs develop. Groundwater levels were recorded every 15 min since 2002 by piezometers (2-8 m) installed along the two transects (**Fig. 1b**). The piezometer data of the past 15 years indicated that groundwater levels at the two RWs studied fluctuated between 2 m below the soil surface during dry seasons (summer and autumn), and close to the soil surface during wet seasons (winter and spring).

Transects A and B, and the corresponding RWs located at their foot-slope (RW_A and RW_B) differ morphologically (**Fig. 1**). Transect A is steeper than transect B (mean slope of 3.8% and 2.8%, respectively). Both RW_A and RW_B were managed as unfertilized riparian buffer zones for approximately 25 years without biomass export. Soils from RW_A and RW_B are silty loams, classified as Albeluvisol. Two soils within RW_A (WetUp-A and WetDown-A, located 13 m and 40 m downslope from the

RW-field interface, respectively) and two soils within RW_B (WetUp-B and WetDown-B, located 2 m and 9 m downslope from the RW-field interface, respectively) were sampled for analysis of the chemical and mineral compositions (**Fig. 1, Supplemental Table S1**). RW_A soil had higher P content with more of it inorganic (> 65%), while RW_B soil had lower P content with more of it organic (ca. 70%) (Gu et al., 2017). A previous 3-year field monitoring of natural soil waters in this catchment evidenced that the dissolved P (<0.45 μm) released in RW soils could be effectively transferred to the stream network, making the RW soils the main source of dissolved P output at the catchment scale (Gu et al. 2017).

Insert Figure 1 here

Water sampling and sample treatment

Wetland soil water was sampled with zero-tension lysimeters (10-15 cm deep) placed in triplicate at two sites in each RW, i.e. the same locations at which soil characteristics were analyzed. The lysimeters were designed and installed to collect free soil water without disturbing in-situ redox conditions (Dupas et al., 2015b). A previous field monitoring study in this catchment indicated that the surface soil waters (10-15 cm) have generally higher P concentrations than in deeper ones (50-55 cm) (Gu et al. 2017). Due to the limit of analytical method and cost consideration, we only selected the surface soil water in the present study.

We collected soil water monthly during the wet seasons from December 2015 to June 2016 (seven dates in total). On each sampling date, samples from the triplicate

lysimeters from each site were mixed to increase the amount of soil water available for chemical analysis. Two dates had no samples for each RW_A site, due to dry periods and the drawdown of groundwater level. We collected stream water samples at three locations: in stream reaches immediately adjacent to the two RWs (Stream-A and -B) and at the outlet of the catchment (Stream-E). Due to logistical constraints, stream water could be collected only on five of the seven soil-water sampling dates. The present study aims at evaluating the production of P-bearing colloids in soil water and the subsequent transfer of these colloids to the stream through subsurface water pathways during baseflow periods. An important condition was to check that no storm events were included in the sampling dates of the present study, as soil erosion during storm events could influence colloid production in soil waters and stream waters. This was done by examining the sampling dates of the present study using the storm-identification criteria developed for the studied catchment (Dupas et al., 2015a), which confirmed that our sampling dates included no storm events.

All samples were filtered through $<0.45 \mu\text{m}$ cellulose acetate filters within 6 h after sampling. Ultrafiltrations were then conducted immediately using 15 ml centrifugal tubes (Vivaspin, Sartorius) equipped with permeable membranes of 30kDa and 5kDa, of which the approximate diameters are 2 nm and 10 nm, respectively (Combe et al., 1999; Moon et al., 2006). Aliquots of $0.45 \mu\text{m}$ -filtered samples were transferred into the 30kDa and 5kDa cells and then centrifuged at $3000\times g$ for 15 and 25 min, respectively. Before use, ultrafiltration cells were rinsed three times with deionized water, soaked twice in deionized water for 24 h and then centrifuged with

deionized water three times to avoid potential contamination. All filtrates and ultrafiltrates were then kept in a refrigerator in the dark at 4°C until analysis within 36 h. Due to cost and labor considerations, ultrafiltration was not conducted in triplicate. A previous trial ultrafiltration experiment in triplicate on the same soil waters revealed that the standard deviations were < 10% for total P (TP, < 0.45 µm) when TP concentration is above 100 µg l⁻¹, and were < 5% for molybdate-reactive P (MRP), dissolved organic carbon (DOC), Al, Fe and silica (Si) (unpublished data).

Chemical analysis

The MRP concentrations for all filtrates and ultrafiltrates were determined colorimetrically via direct reaction with ammonium molybdate (Murphy and Riley, 1962). The same method was used for TP after digestion in acidic potassium persulfate. Detection and quantification limits for MRP and TP measurements were ±3 and ±8 µg l⁻¹, and ±4 and ±12 µg l⁻¹, respectively. Molybdate-unreactive P (MUP) was calculated as TP minus MRP. The DOC concentrations were analyzed with a total organic analyzer (Shimadzu TOC-5050A), with ± 5% precision (using potassium hydrogen phthalate as the standard solution). The element composition (Fe, Al, Si) of all filtrate and ultrafiltrate samples was measured with an inductively coupled plasma mass spectrometer (ICP-MS; Agilent 7700×, Santa Clara, USA). Calibration curves and accuracy were assessed according to Yeghicheyan et al. (2013), using the SLRS-5 river water standard (National Research Council of Canada) for trace elements with a wide compositional range. Deionized water purified with a Milli-Q (Millipore) system

was used as a blank. Total relative uncertainties of the ICP-MS measurements were $\pm 5\%$.

The Fe^{2+} concentrations were measured at the same frequency (biweekly) as that used by Gu et al. (2017), as indicators of the redox condition of the soil water. Fe^{2+} concentrations were measured by the 1,10 phenanthroline colorimetric method (AFNOR NF T90-017, 1997), with a precision of $\pm 5\%$. The Fe^{2+} reactants were mixed immediately in the field with samples filtrated by 0.2 μm filters to avoid the influence of oxidation on Fe^{2+} concentration during sample storage and transport.

Ultrafiltration data treatment

The TP in the $< 0.45 \mu\text{m}$ solution was divided into colloidal-P (difference in TP concentration between the $< 0.45 \mu\text{m}$ and $< 5 \text{ kDa}$ samples) and truly dissolved P (truly-DP, TP concentration in the $< 5 \text{ kDa}$ samples) (**Supplemental Fig. S1**). Depending on the reaction to the ammonium molybdate solution, colloidal-P and Truly-DP could be further divided as follows:

$$\text{Colloidal-MRP} = \text{MRP}_{0.45\mu\text{m}} - \text{MRP}_{5\text{kDa}} \quad (1)$$

$$\text{Colloidal-MUP} = \text{colloidal-P} - \text{colloidal-MRP} \quad (2)$$

$$\text{Truly-MRP} = \text{MRP}_{5\text{kDa}} \quad (3)$$

$$\text{Truly-MUP} = \text{MUP}_{5\text{kDa}} \quad (4)$$

where colloidal-MRP is the difference in MRP concentration between the $< 0.45 \mu\text{m}$ and $< 5 \text{ kDa}$ samples and is considered to consist of P-bearing colloids that can be easily solubilized in an acidic ammonium molybdate solution. Colloidal-MUP is the

difference between colloidal-P and colloidal-MRP and is considered to consist of P-bearing colloids from which P can be released only after digestion. Truly-MRP is the truly dissolved MRP (< 5 kDa) and Truly-MUP is the difference between truly-DP and Truly-MRP.

Depending on the cutoffs of ultrafiltration cells, the colloidal fraction was separated into coarse colloidal (30 kDa - 0.45 μm) and fine nanoparticle (5-30 kDa) fractions (**Supplemental Fig. S1**). The 30 kDa and 5 kDa cutoffs were selected because previous studies on natural soil water from the Kervidy-Naizin catchment showed that ca. 50% of DOC and metals (rare earth elements and Fe) were carried by colloids and nanoparticles in the size range of 30 kDa - 0.45 μm and 5-30 kDa (Pourret et al., 2007).

Statistical analysis

Ultrafiltration experiments in the present study were not performed in O_2 -free conditions. We could not exclude potential oxidation of Fe^{2+} during these experiments, which could have formed additional colloids and biased the true fraction of colloidal-P in the samples. Another difficulty was the low TP concentrations in certain samples, which resulted in high uncertainties in the estimation of P speciation. Thus, results were considered reliable only if they met two criteria: i) TP concentration exceeded the TP quantification limit of $12 \mu\text{g l}^{-1}$ and ii) soil water was sampled during oxic conditions (i.e. no Fe^{2+} present in the samples at the time of ultrafiltration). On this basis, two samples with TP concentration lower than $12 \mu\text{g l}^{-1}$

and two samples collected during the anoxic condition (indicated by high total Fe concentrations) were considered outliers and were not considered further. Significance of the differences in P speciation between RW_A and RW_B, and between soil waters and stream waters, were assessed using variance-analysis tests (ANOVA with $p < 0.05$), using the 7 sampling dates as pseudo-replicates. All statistical analyses were performed using the SPSS (IBM Statistics v.22) software package.

RESULTS

Spatio-temporal variations in TP fractions in soil waters and stream waters

The TP concentrations in RW_A soil waters were significantly higher than those in RW_B soil waters (mean \pm SD = $345 \pm 151 \mu\text{g l}^{-1}$ vs. $79 \pm 55 \mu\text{g l}^{-1}$, respectively, $p < 0.001$, **Figs. 2-3**). The speciation of TP in soil waters from RW_A and RW_B was also different, being dominated by MRP (i.e. truly-MRP + colloidal-MRP) at RW_A (mean \pm SD = $75 \pm 9\%$), while MRP and MUP (i.e. truly-MUP + colloidal-MUP) had similar proportions at RW_B (mean \pm SD = $55 \pm 17\%$ and $45 \pm 18\%$, respectively) (**Supplemental Fig. S2**). The proportion of colloidal-P was higher in RW_B soil water than in RW_A soil water (mean \pm SD = $51 \pm 16\%$ vs. $37 \pm 17\%$, respectively, $p = 0.086$). This difference was maintained in the corresponding stream water, since colloidal-P represented a higher average proportion in Stream-B than in Stream-A (mean \pm SD = $40 \pm 25\%$ vs. $19 \pm 22\%$, respectively, $p = 0.296$, **Figs. 4-5**).

Insert Figure 2 here

Insert Figure 3 here

In soil water of WetUp-A, TP, colloidal-P and truly-DP concentrations initially decreased and then slightly increased up to the end of the hydrological year (**Fig. 2a**). Colloidal-P represented approximately one third of TP in soil water at this site (mean \pm SD = $29 \pm 5\%$, n = 5). The groundwater level at WetUp-A fluctuated around the lysimeter depth, and the lysimeters were never submerged for more than 11 consecutive days. Consequently, Fe^{2+} concentrations remained low ($< 0.6 \text{ mg l}^{-1}$) at this site (**Fig. 2c**). In soil water of WetDown-A, concentration and speciation of TP were temporarily more variable than at WetUp-A, with large variations in the concentrations of colloidal-P and truly-DP (**Fig. 2b**). Truly-DP remained a major fraction of TP at this site, but the proportion of colloidal-P was higher than that in WetUp-A (mean \pm SD = $47 \pm 23\%$, n = 4). The groundwater level at WetDown-A remained above the lysimeter depth for approximately three consecutive months, leading to a peak in Fe^{2+} concentration (17.6 mg l^{-1}) on the 15 March 2016 sampling date (**Fig. 2d**). Therefore, we excluded this date from data analysis.

Insert Figure 4 here

Insert Figure 5 here

In soil waters of WetUp-B and WetDown-B, TP, colloidal-P and truly-DP concentrations initially decreased and then increased up to the end of the hydrological year (**Figs. 3a, b**). At both sites, colloidal-P was a major fraction of TP in the soil water (mean \pm SD = $48 \pm 17\%$ and $54 \pm 16\%$, $n = 7$ and 5 , respectively). The groundwater level remained above the lysimeter depth for > 150 consecutive days at both sites (**Figs. 3c, d**). However, Fe^{2+} concentrations remained low in the soil water of WetUp-B ($< 1.5 \text{ mg l}^{-1}$), but peaked markedly (11.7 mg l^{-1}) at WetDown-B on the 10 May 2016 sampling date. Along with the 15 March 2016 sampling date at which the TP concentration ($10.4 \text{ } \mu\text{g l}^{-1}$) was below the quantification limit, both dates at WetDown-B were identified as outliers and excluded from data analysis.

The TP concentrations were generally low in all stream waters ($< 47.4 \text{ } \mu\text{g l}^{-1}$) and were similar among the three streams (**Fig. 4**). The proportion of colloidal-P was quite variable, ranging on average from 19-40%. The 15 March 2016 sampling date for Stream-B had a TP concentration ($7.1 \text{ } \mu\text{g l}^{-1}$) below the quantification limit and was excluded from data analysis.

Elemental composition of the colloidal-P fractions in soil waters and stream waters

On average, colloidal-P represented on average $39 \pm 21\%$ ($n = 35$) of the TP ($< 0.45 \text{ } \mu\text{m}$) in all soil and stream water samples. The colloidal fraction also represented on average $89 \pm 10\%$, $65 \pm 16\%$ and $35 \pm 21\%$ of total Fe, Al and DOC in the $< 0.45 \text{ } \mu\text{m}$ solution, respectively, but only $4 \pm 5\%$ of total Si (**Table 1**). Interestingly, for all

soilwaters and stream waters from both RW_A and RW_B , the coarse colloidal fraction (30 kDa - 0.45 μm) contained most of the colloidal-P (mean = $78 \pm 21\%$, n = 32), total colloidal Fe (mean = $79 \pm 15\%$, n = 35) and total colloidal Al (mean = $72 \pm 21\%$, n = 34) but a much smaller proportion of the total colloidal DOC (mean = $37 \pm 19\%$, n = 32). In contrast, in all samples, the fine nanoparticle fraction (5-30 kDa) contained most of the total colloidal DOC (mean = $63 \pm 19\%$, n = 32) but only small proportions of the total colloidal P, Fe and Al (mean = $22 \pm 21\%$, $21 \pm 15\%$ and $28 \pm 21\%$, respectively). Thus, a fundamental difference in elemental composition was observed between coarse colloids and fine nanoparticles in all samples: the former was dominated by Fe and Al, while the latter was dominated by organic C.

Insert Table 1 here

DISCUSSION

Colloids as an important component of diffuse P losses in agricultural catchments

With the joint investigation of colloidal-P distribution in natural soil waters and streamwaters, the present study provides clear evidence that colloids are important carriers of P in both natural soil waters and stream/river waters, which further confirms conclusions of previous studies on natural stream/river colloids (Baken et al.,

2016a, 2016b; Gottselig et al., 2017a) and on laboratory-extracted soil colloids (Jiang et al., 2017; Missong et al., 2017, 2018).

The detailed elemental composition of colloidal-P fractions showed that, in both soil waters and stream waters, colloidal-P in the fine nanoparticle fraction was preferentially associated with organic C ($r^2 = 0.55$), while was preferentially associated with Fe as well as organic C in the coarse colloidal fraction ($r^2 = 0.61$ and 0.70 , respectively) (**Table 1**). Previous studies on natural and laboratory-extracted colloids have shown the important role of Fe-oxyhydroxides and organic matter as efficient sink for the adsorption of P (Baken et al., 2016a; Jiang et al., 2015; Yan et al., 2016a). Thus, the close association of P with Fe and organic C in the coarse colloids in the water samples of the present study is not surprising. We can reasonably speculate that the colloidal vectors carrying P in this coarse colloidal fraction consist principally of colloid-size Fe-oxyhydroxides complexed with organic C. On the other hand, the OM-rich composition of the fine nanoparticle fraction fits well with the composition obtained by Jiang et al. (2017) for P-bearing nanoparticles extracted from a cultivated Stagnosol. According to Jiang et al. (2017), the O_2 -limitation and reduction regime that characterized the water-saturated soils, such as Stagnosol or the Albeluvisol in the present study, explains this difference in P-bearing colloid composition, since these two characteristics would favor an increased formation of small OM-rich, P-containing nanoparticles, with a minor contribution from Fe- and Al-containing mineral phases.

In a previous study, Gu et al. (2018) explored the ability of soils collected in RW_A and RW_B to release colloids upon rewetting of the dry soils, using the same analytical protocol as in the present study. Their results, however, showed no fundamental difference in the elemental composition of the coarse colloidal and fine nanoparticle fractions (Gu et al., 2018). This difference between soil column leachates and field-collected soil waters could be related to the heterogeneous distribution of fine nanoparticles in the soil. Redox conditions are known to vary greatly in wetland soils at small scales because of the common occurrence of strong spatial variations in soil permeability (Wanzek et al., 2018). Oxidic conditions can still exist in soil macropores, while strongly reducing conditions occur in nearby micropores. In their column leaching experiments, waters percolated through columns over a short period (0.5h), indicating that it had likely circulated through soil macropores, especially during the beginning of each rewetting phase (Gu et al., 2018). In the present study, although soil water also likely circulated through soil macropores, the longer equilibrium time with the bulk soil matrix is expected to have increased diffusion of small nanoparticles, potentially formed in soil micropores, into soil macropores. This fundamental difference in the geometry of soil water circulation could explain the difference in results between the present field study and the laboratory study of Gu et al. (2018). This relative inconsistency between field and laboratory results further reinforces doubts about the ability of laboratory-extraction studies to accurately replicate the composition range of naturally generated P-bearing colloids.

The composition difference between the P-bearing coarse colloids and fine nanoparticles in soil water was also observed in the stream waters of the present study. This result differs from that of Gottselig et al. (2017a), who found that P-bearing nanoparticles (1-20 nm) from a small stream draining a forested catchment were dominated by nano-sized Fe-oxyhydroxides. In contrast, those in the present study (**Table 1**) or the study of Jiang et al. (2017) were dominated by OM-rich materials. One possible cause is the difference in land use: agricultural in the present study and Jiang et al. (2017) but forested in Gottselig et al. (2017a). As suggested later by Gottselig et al. (2017b) in their European-scale study on colloids in stream water, factors such as acidity, dominant land use and lithology are expected to affect the elemental compositions of colloidal fractions, especially the nanoparticle fraction (< 60 nm).

Riparian wetlands as potential source zones of colloidal-P

Simultaneous monitoring of colloidal-P in soil waters from RW area that are hydrologically connected to the stream network and in adjacent stream waters themselves may help to identify the potential linkage between stream water colloids and soil waters colloids (Haygarth et al., 2005). In this respect, featured by high soil OM content and hydromorphic condition which can stabilize and enhance the release of colloids from soils (Yan et al., 2016b) and because of their location at the soil-stream interface, RWs could represent hotspots of colloid production at the catchment scale.

We hypothesize that during the baseflow period, colloidal-P in stream waters of the Kervidy-Naizin catchment was originally produced in the RW soil waters and was transferred to the streams via shallow groundwater flows. Results of the present study revealed that colloidal-P represented on average 45% of the TP released in natural soil water, thus providing evidence that the RWs are potential source zones for the natural production of colloidal-P. The consistent elemental composition of colloidal fractions in soil waters and stream waters suggests that the colloidal-P in stream water could be originated from RW soils (**Table 1**). This link between soil water and stream water colloids could be reinforced by the higher colloidal-P proportions observed in RW_B soil waters than in RW_A soil waters ($p = 0.086$). This difference, if preserved in their adjacent stream waters, would provide stronger evidence that the P-bearing colloids found in stream water were transferred from adjacent RW soils. However, due to the high uncertainty resulting from the low P concentrations in stream water, the proportions of colloidal-P in Stream-B water were higher but not significantly than those in Stream-A water ($p = 0.296$, **Fig. 5**). Thus, the results of the present study cannot directly conclude that P-bearing colloids produced in RW soils are effectively transferred to adjacent streams. We can only suggest that during the baseflow period, RWs are hotspots for the production of P-bearing colloids, which have great potential to be transported to adjacent streams due to hydrological connectivity between RWs and the stream network.

The proportion of colloidal-P was higher in soil water than in stream water in the two RWs studied ($p = 0.053$, **Fig. 5**). This could indicate the existence of retention

processes during the potential transport of P-bearing colloids from soil to stream, or the dilution by deep groundwater (> 1m) in this catchment that has low dissolved P concentration ($7 \mu\text{g l}^{-1}$, unpublished data) which is mainly truly dissolved form. For example, P-bearing colloids could be re-sedimented during transport through macropores, which serve as preferential flow pathways of colloids in well-aggregated soil (Julich et al., 2016).

Groundwater dynamics as an important driver of colloidal-P spatial variations in riparian wetlands

We found that the four sites studied showed spatial variation in the colloidal-P proportions in their soil water: soil water at WetUp-A had smaller colloidal-P proportions than the three other sites (WetDown-A, WetUp-B and WetDown-B), where soils were more hydromorphic ($p = 0.012$, **Supplemental Fig. S2**). This spatial variation could be due to differences in groundwater level dynamics among the four sites. The flatter topography of RW_B and closer proximity of WetDown-A to the stream result in the groundwater level remaining near the soil surface for several months during the same hydrological year (**Figs. 2-3**). The potential development of anoxic conditions would cause the reductive dissolution of Fe-oxyhydroxides and the simultaneous release of Fe^{2+} and phosphate in soil water (Gu et al., 2019; Ponnamperna, 1972; Vidon et al., 2010). Oxidation of Fe^{2+} during groundwater level drawdown would favor amorphous Fe-oxyhydroxides, which have a high capacity to sorb P (Wang et al., 2013), to form in these RW soils. It is likely that this precipitation of Fe-oxyhydroxide in soil micro- and macropores would create a

reservoir of colloids in the soil, explaining why soils experiencing Fe-reduction events (i.e. WetDown-A, WetUp-B and WetDown-B soils) have higher proportions of colloidal-P in their soil waters. The influence of soil properties (especially soil OM content) on spatial variation of colloidal-P is less clear in the present study, since OM contents did not differ greatly between the two RWs (**Supplemental Table S1**). However, it is well known that prolonged saturation of soil tends to increase OM content of the soil and its soil water (FAO, 2005). Also, precipitation of Fe-oxyhydroxides in OM-rich water tends to produce smaller Fe-oxyhydroxides than precipitation in OM-poor water (Pédrot et al., 2015). Smaller Fe-oxyhydroxides have a larger specific surface area than larger crystals and thus greater relative capacities to bind P. It is likely that the OM-rich nature of the present RWs soils could have increased the colloidal-P proportion in those soils experiencing Fe-oxyhydroxide precipitation events (i.e. WetDown-A, WetUp-B and WetDown-B soils).

CONCLUSION

The present study investigated colloidal-P in both stream water and natural soil water from RWs that are hydrologically connected to the stream network at catchment scale. The results demonstrate that colloidal-P is an important component of TP in both soil waters and stream waters under field conditions. The fine nanoparticle fraction (5-30 kDa) is preferentially associated with organic C, while the coarse colloidal fraction (30 kDa - 0.45 μm) is preferentially associated with Fe-oxyhydroxides and organic C. The colloidal-P fraction represents, on average, 45% of the TP in natural soil water, which indicates that RWs are hotspots for the natural

production of P-bearing colloids. However, the results cannot conclude directly that P-bearing colloids in stream water originated from adjacent RW soils; the results suggest only that P-bearing colloids produced in RWs have a high potential to be transported to adjacent streams. We proposed the groundwater level dynamics as an important factor influencing spatial variations in colloidal-P in RW soil water, via the influence on soil OM content and redox reactions of Fe. We emphasize that these findings were based on limited sampling times, and that further longer-term monitoring would be required for better assessment of colloidal-P spatial-temporal variations.

ACKNOWLEDGMENTS

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SUPPLEMENTAL MATERIAL

The supplemental material provides details on soil physicochemical properties (**Supplemental Table S1**), colloidal P definition (**Supplemental Fig. S1**), and

proportional P composition of all soil waters and stream waters (**SupplementalFig. S2**).

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Table 1. Composition and size distribution of the colloidal fraction in soil waters and stream waters. “Coll-” represents colloidal, “DOC” means dissolved organic carbon. “F1” represents the fine nanoparticle fraction (5-30 kDa), “F2” represents the coarse colloidal fraction (30 kDa - 0.45 μm). Outliers were excluded from calculations. The r^2 represents the Pearson correlation coefficient between concentrations of colloidal-P and other variables within corresponding size range.

	Coll-P			Coll-Fe			Coll-Al			Coll-DOC			Coll-Si
	% TP	% Coll-P		% Tot-Fe	% Coll-Fe		% Tot-Al	% Coll-Al		% Tot-DOC	% Coll-DOC		% Tot-Si
		F1	F2		F1	F2		F1	F2		F1	F2	
All_Samples	38.9	22.2	77.8	89.1	21.3	78.7	65.3	28.4	71.6	35.3	63.2	36.8	4.0
Soil_A	36.9	15.4	84.6	94.4	15.0	85.0	78.5	22.0	78.0	54.2	61.0	39.0	6.4
Soil_B	50.5	17.4	82.6	90.9	22.2	77.8	67.4	31.2	68.8	29.5	70.1	29.9	4.3
Stream_All	30.1	33.2	66.8	84.2	24.6	75.4	54.1	30.2	69.8	28.1	58.6	41.4	2.1
r^2					0.27	0.61		0.44	0.26		0.55	0.70	

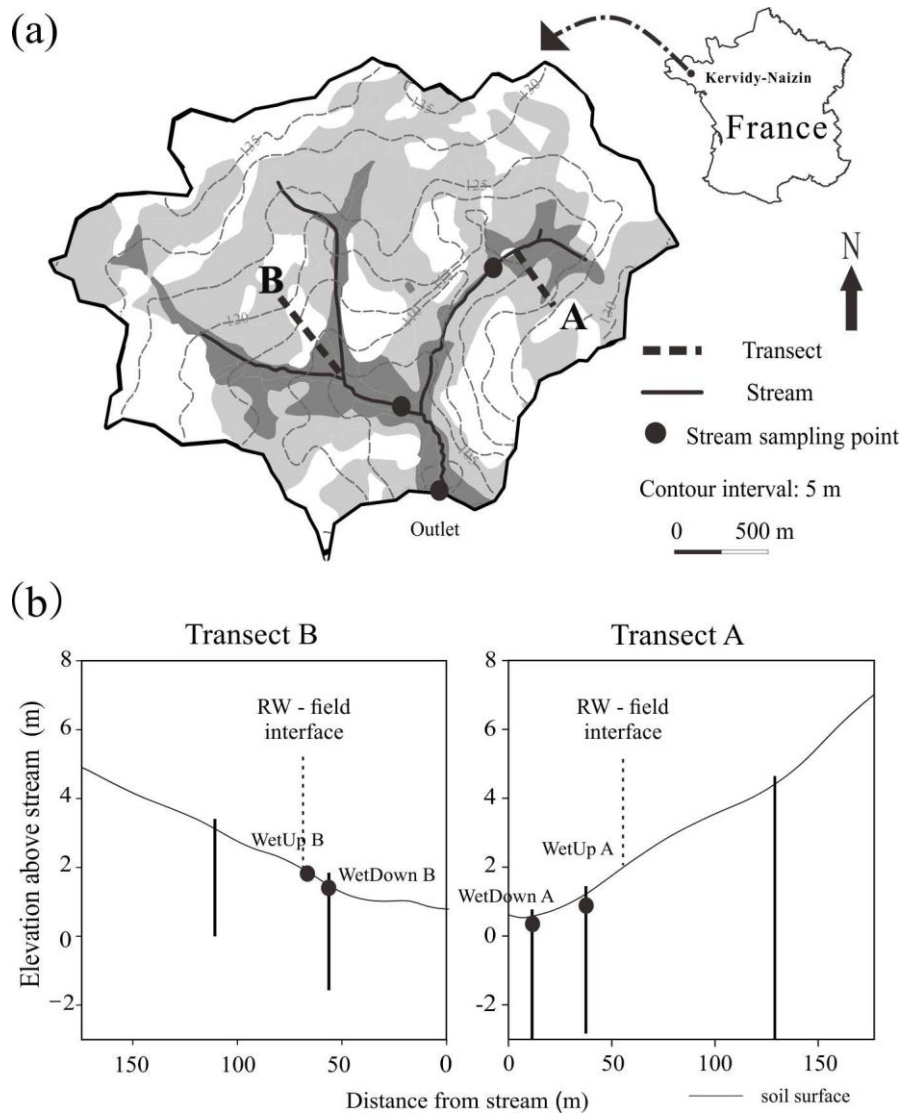


Fig. 1. (a) Map of the Kervidy-Naizin catchment; (b) location of sampling sites (black dots) and variability of groundwater level along the two transects, as established from analysis of 15 years of piezometric data. Vertical black lines represent piezometers (2-8 m deep). “RW” means riparian wetland.

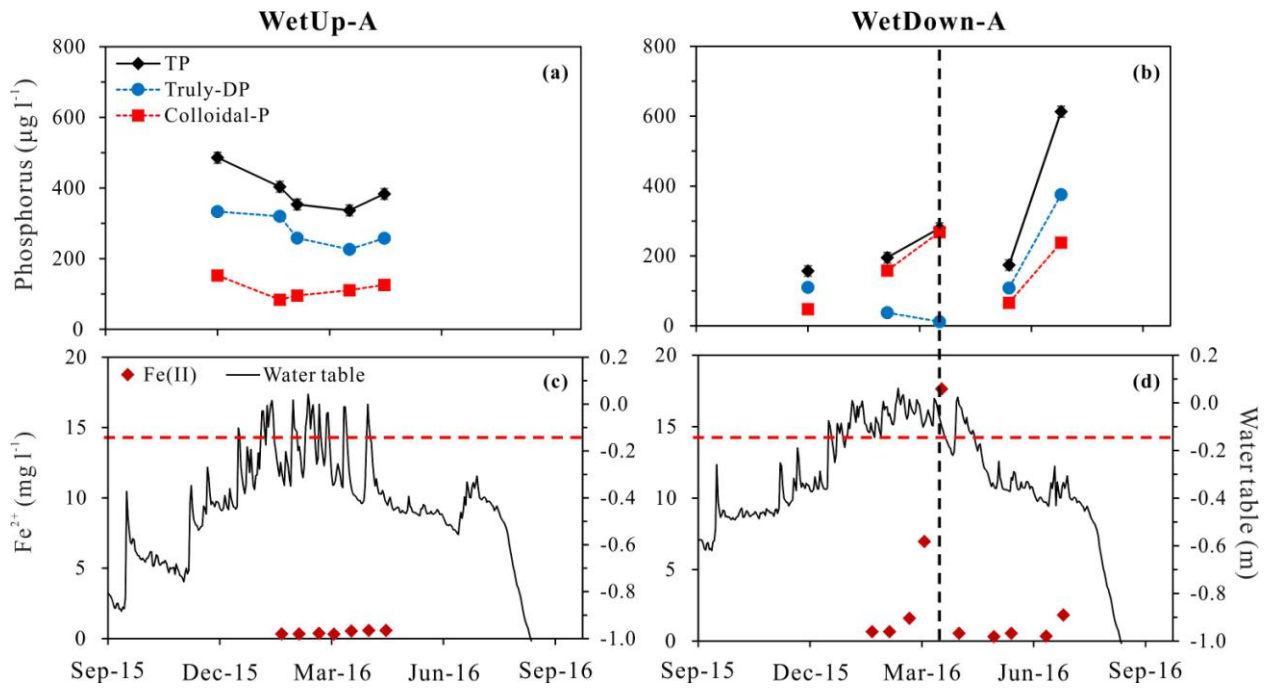


Fig.2. Concentrations of P fractions in total P (TP < 0.45 μm), groundwater level and Fe²⁺ concentrations in soil water at WetUp-A and WetDown-A. Truly-DP and Colloidal-P represent the truly dissolved P and colloidal P in TP, respectively. Horizontal red dashed lines in (c) and (d) represent the depth of sampling. The vertical black dashed line represents the outlier sampling date. Error bars represent uncertainties in TP measurements.

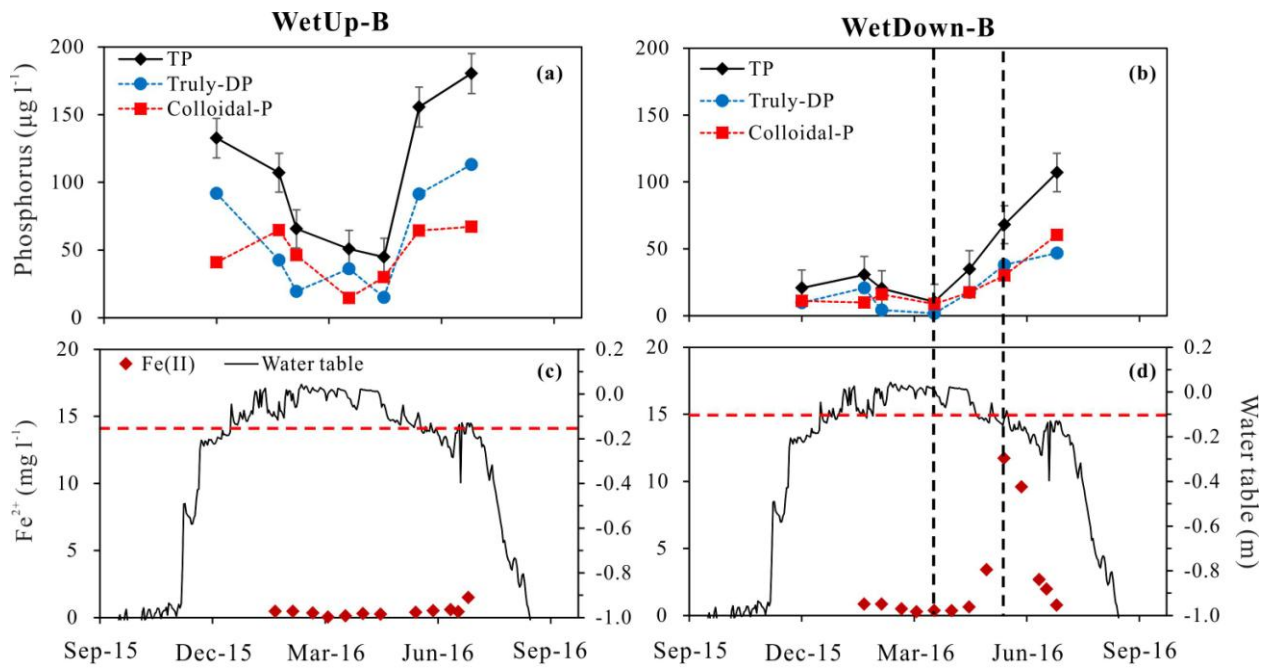


Fig.3. Concentrations of P fractions in total P (TP < 0.45 μm), groundwater level and Fe²⁺ concentrations in soil water at WetUp-B and WetDown-B. Truly-DP and Colloidal-P represent the truly dissolved P and colloidal P in TP, respectively. Horizontal red dashed lines in (c) and (d) represent the depth of sampling. The vertical black dashed lines represent the outlier sampling dates. Error bars represent uncertainties in TP measurements.

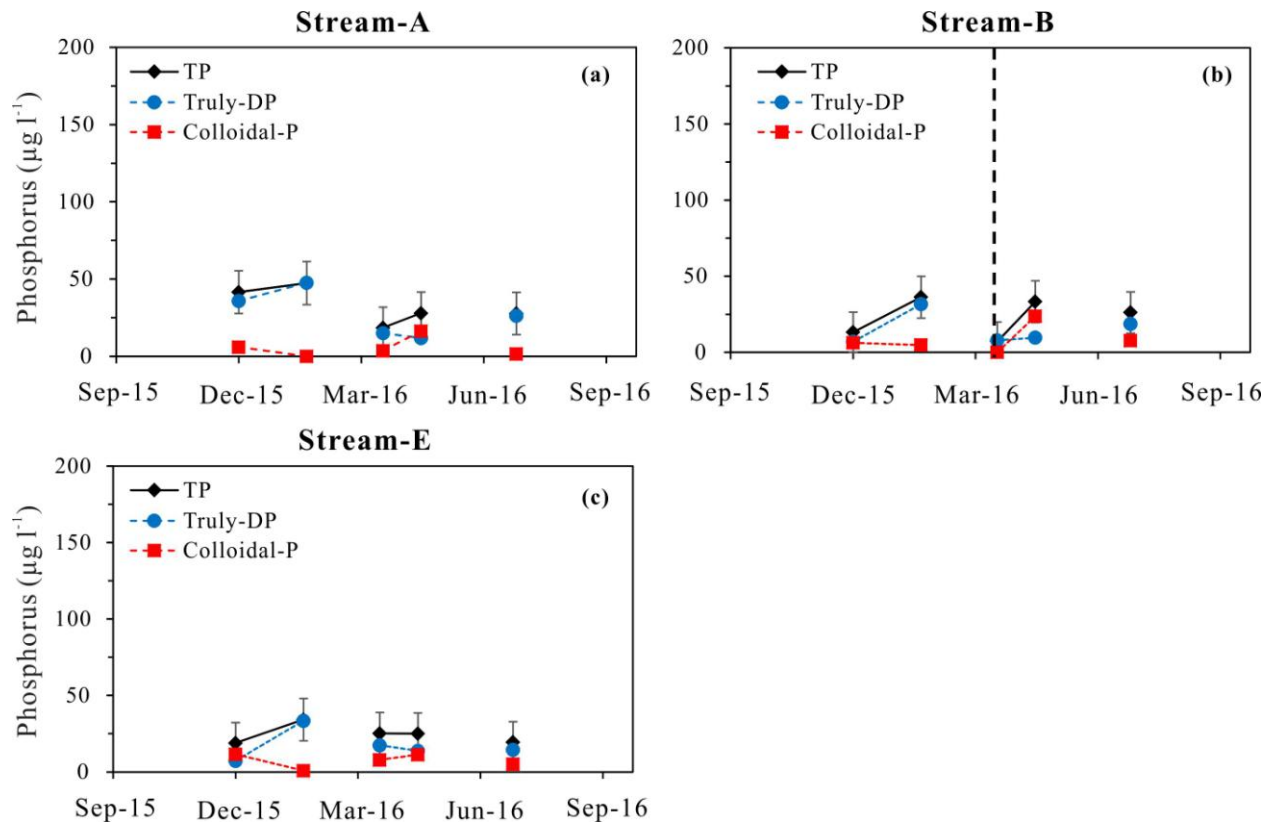


Fig.4. Concentrations of P fractions in total P (TP < 0.45 µm) in stream waters at Stream-A, -B and -E. Truly-DP and Colloidal-P represent the truly dissolved P and colloidal P in TP, respectively. The vertical black dashed line represents the outlier sampling date. Error bars represent uncertainties in TP measurements.

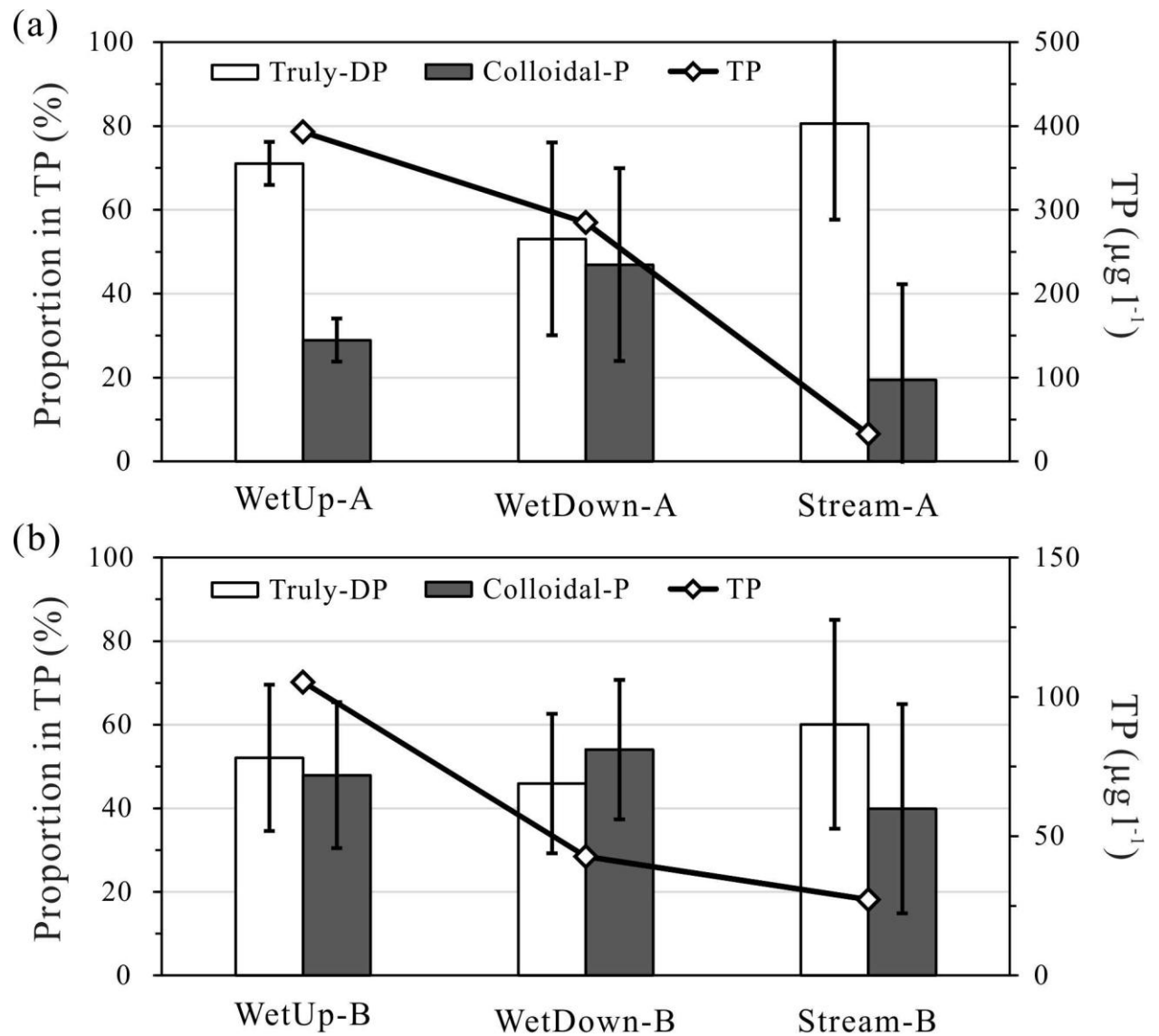


Fig.5. Mean composition and concentration of total P (TP < 0.45 μm) in soil waters and stream waters from riparian wetland (a) A and (b) B. Error bars represent the standard deviation of proportions in all samples from each site. Outliers were excluded from this calculation.

Supplemental Material

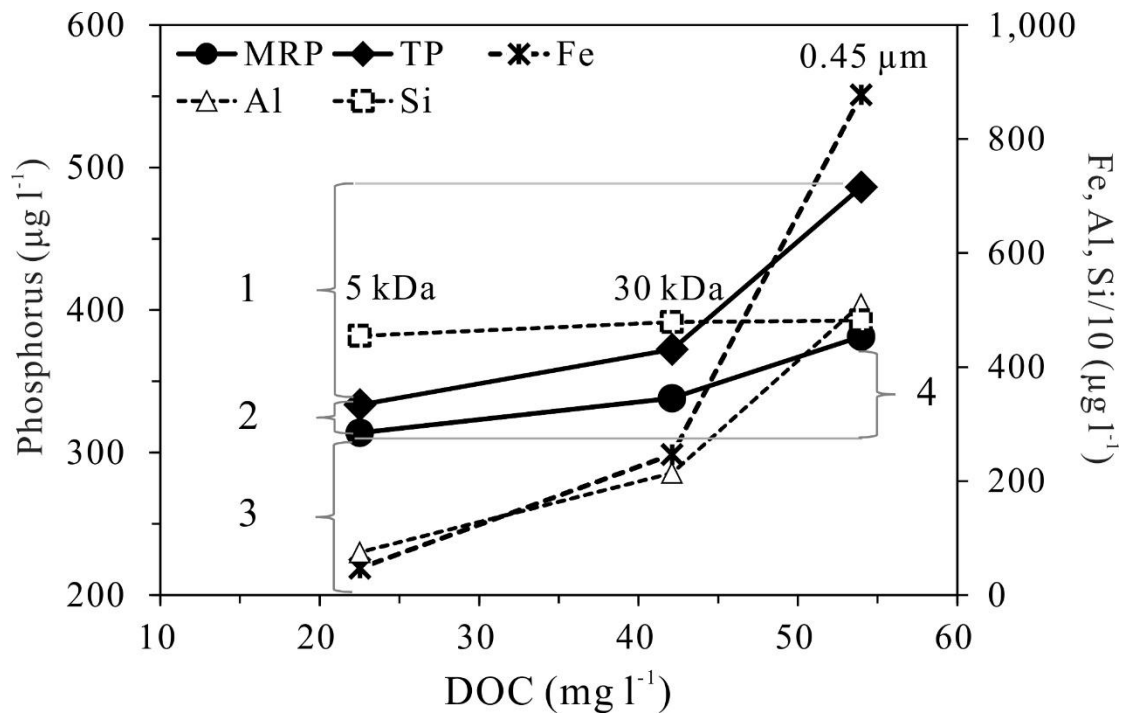
EVIDENCE OF COLLOIDS AS IMPORTANT PHOSPHORUS CARRIERS IN NATURAL SOIL/STREAM WATERS IN AN AGRICULTURAL CATCHMENT

Sen Gu, Gérard Gruau, Rémi Dupas, Laurent Jeanneau

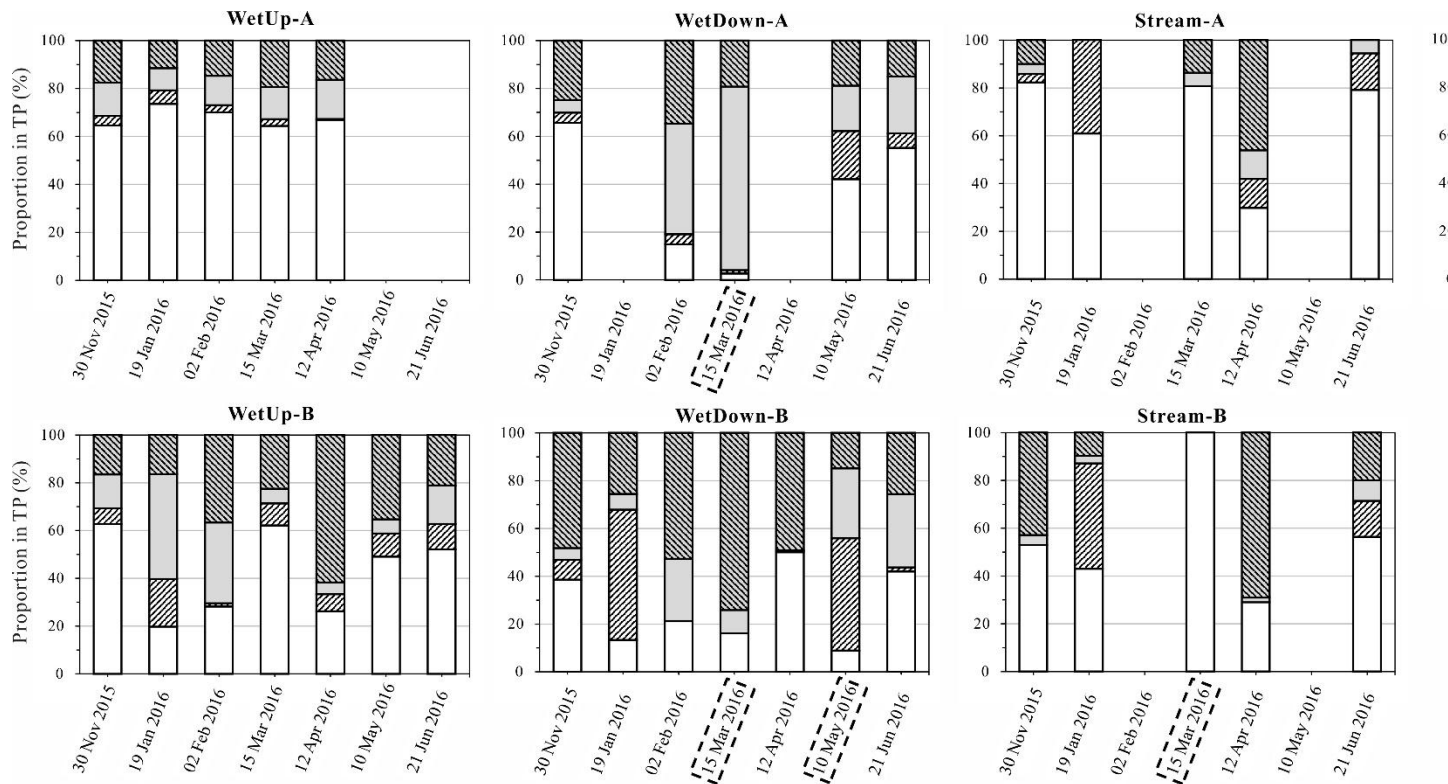
SupplementalTable S1.Soil properties (0-15 cm) in the riparian wetlands studied.

Soil property (0-15 cm)	WetUp-A	WetDown-A	WetUp-B	WetDown-B
Clay (<2 μm) (g kg^{-1})	241	233	220	288
Silt (2-50 μm) (g kg^{-1})	615	589	588	599
Sand (50-2000 μm) (g kg^{-1})	144	178	192	113
Organic carbon (g C kg^{-1})	40.9	37.1	26.1	60.2
Total nitrogen (g N kg^{-1})	3.65	3.30	2.28	4.66
C:N ratio	11.2	11.2	11.4	12.9
Organic matter (g kg^{-1})	70.7	64.2	45.1	104.0
pH	6.08	6.11	6.52	6.18
P-Oxalate (g P kg^{-1})	0.24	0.16	0.08	0.03
P-Olsen (g P kg^{-1})	0.08	0.05	0.04	0.01
Si-Oxalate (g Si kg^{-1})	0.29	0.34	0.33	0.31
Al-Oxalate (g Al kg^{-1})	1.69	1.41	2.13	1.71
Fe-Oxalate (g Fe kg^{-1})	4.25	6.00	6.81	7.71
Total P (g P kg^{-1})	1.21	1.05	0.93	0.68
[§] Soilwater MRP (mean \pm sd) $\mu\text{g l}^{-1}$	290 \pm 28	154 \pm 59	96 \pm 56	19 \pm 22
[§] SoilwaterTP (mean \pm sd) $\mu\text{g l}^{-1}$	363 \pm 35	228 \pm 75	148 \pm 79	36 \pm 23

[§]Soilwater MRP and TP data from Gu et al. (2017) during the biweekly sampling in the 2015-2016 hydrological year.



Supplemental Fig.S1.Diagram describing how ultrafiltration data were used to estimate molybdate-reactive phosphorus (MRP), totalP (TP<0.45µm), dissolved organic carbon (DOC), Fe, Al and Si speciation in soil waters and stream waters studied. Labels “0.45 µm”, “30 kDa”, and “5 kDa” indicate the pore sizes used for ultrafiltration. ‘1’: colloidal-P = $TP_{0.45\mu m} - TP_{5kDa}$; ‘2’: trulydissolvedMUP = MUP_{5kDa} ; ‘3’: trulydissolvedMRP = MRP_{5kDa} ; ‘4’: colloidal-MRP= $MRP_{0.45\mu m} - MRP_{5kDa}$. The example sample comes from WetUp-A on 30 Nov 2015.



1
 2 **Supplemental Fig.S2.** Proportional composition of total P (TP < 0.45 μm) in soil water from riparian
 3 wetland A and B and in stream water from Stream-A, -B and -E. Truly-MRP, Truly-MUP, Colloidal-
 4 MRP and Colloidal-MUP represent, respectively, the truly dissolved molybdate-reactive/unreactive P and
 5 the colloidal molybdate-reactive/unreactive P in TP. Dashed sampling dates are outliers.

6
 7