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Conservation practice modify soil phosphorus sorption properties and the composition of dissolved phosphorus losses during runoff

Xuemei Chen[a, d], Wen Zhang[a, *], Gérard Gruau[b], Ewan Couic[b], Patrice Cotinet[c], Qingman Li[d]

[a]*State Key Laboratory of Geohazard Prevention and Geoenvironment Protection, Chengdu University of Technology, Chengdu 610059, China*

[b]*OSUR, Géosciences Rennes, CNRS, UMR 6118, Campus de Beaulieu, 35042 Rennes, France*

[c]*Chambres d'Agriculture de Bretagne, Station expérimentale de Kerguehennec, 56500 Bignan, France*

[d] *Key Laboratory of Algal Biology, Institute of Hydrobiology, Chinese Academy of Sciences, 430072 Wuhan, China*

* Corresponding authors.

E-mail addresses: zhangwen2014@cdut.edu.cn (W. Zhang).

Tel: +86 15008491570 (W. Zhang).

Abstract

It is now well established that shallow tillage (ST) and no-tillage (NT) of cultivated soils can increase the risk of dissolved phosphorus (P) loss during runoff compared to conventional tillage (CT). However, there is still lack of quantitative descriptors of how variations in tillage practices influence soil P sorption properties and how these properties in turn control the dissolved P release. Moreover, the control of tillage

practices on the form of dissolved P, particularly molybdate unreactive dissolved phosphorus (MUDP), is still poorly assessed. Thus, we conducted the runoff simulation with the pilot soils benefited from different tillage practices for 20 years. The results showed that shifting from CT to ST and NT changed the capacity of soils to bind P, with Olsen-P, Dyer-P, equilibrium phosphorus concentration (EPC_0), water soluble phosphorus (WSP), and degree of phosphorus saturation (DPS_{OX}) increased obviously. The runoff simulation experiment confirmed that the switching from CT to ST and NT could increase the P loss in the event of runoff. The increase was evident for the two fertilizations (pig manure and poultry manure) with an amplified effect for the poultry manure modality. Switching from CT to ST and NT favored the loss of MUDP, again with an exacerbated effect in the case of the poultry manure modality, for which the proportion of MUDP went up to represent more than 40% of the TDP. Regarding on indication of the risk of dissolved P loss with P sorption property, positive linear correlations were indeed obtained in the five cases, but the results of DPS_{OX} was opposite to that of WSP, EPC_0 and available P, suggesting DPS_{OX} was not suitable as the risk predictor of dissolved P loss. Our results from this study propose that the MUDP should be taken into account in assessing the risk of dissolved P release during change to ST and NT, considering that MUDP are bioavailable and therefore also capable of contributing to the eutrophication of surface waters.

Keywords: Tillage practices; Soil phosphorus sorption capacity; Dissolved phosphorus loss; Organic and colloidal phosphorus; Risk assessment indicators.

Highlights

- No-tillage increase the three forms of dissolved P loss risk.
- No-tillage exacerbates the proportion of molybdate unreactive dissolved P.
- High organic matter is the key to exacerbate molybdate unreactive dissolved P loss.

1. Introduction

Long-term addition of phosphorus (P) can significantly increase the content of P in cultivated soils, resulting in P loss risks through soil erosion, leaching, or runoff (Jarvie et al., 2017). Phosphorus losses from cultivated fields to aquatic ecosystems can lead to cyanobacterial blooms, which can make water toxic to wildlife and human (Ma et al., 2009; Messiga et al., 2010; Perrotet al., 2014; Bol et al., 2018). Among various P forms, dissolved inorganic and organic P are major concerns as they are highly reactive and readily bioavailable for algae growth (Li and Brett, 2013; Van Moorleghem et al., 2013; Jarvie et al., 2017). Thus, reducing the loss of dissolved P from cultivated soils is an essential challenge in the fight against eutrophication of surface water (Pizzeghello et al., 2016; Jarvie et al., 2017; Bol et al., 2018; Ulén et al., 2019; Messiga et al., 2021).

In the past decades, mitigation of agricultural P loss is mainly addressed by agricultural conservation practices, notably shallow tillage (ST) or no-tillage (NT), which have been shown to reduce soil erosion and soil P losses (Schoumans et al., 2014; Sharpley et al., 2015; Dodd and Sharpley, 2016; Zhang et al., 2017; Ni et al.,

2020). However, although efficient in reducing particulate P loss, ST and NT may increase the loads of dissolved P in surface soil and thus increase the loss of dissolved P in case of runoff development (Ulén et al., 2010; Pizzeghello et al., 2016; Daryanto et al., 2017). Two mechanisms are commonly invoked to account for this increase: i) enhancing organic P mineralization from crop residues left at the soil surface leading to higher concentration of dissolved P in the topmost soil layers (Deubel et al., 2011); ii) general enrichment in P (and thus also in potentially soluble P) of the soil topmost layers due to the lack of downward transfer and mixing of the P brought to the soil for crop growth (Baker et al., 2017; Daryanto et al., 2017; Jarvie et al., 2017; Duncan et al., 2019). Two emblematic examples, the first one in Erie Lake Basin, the other in Chesapeake Bay basin, reveal an increase in dissolved P loss associated with areas of increased implementation of conservation tillage practices (Ulén et al., 2010; Dodd and Sharpley, 2016; Jarvie et al., 2017; Ni et al., 2020). These results demonstrate that the implementation of ST and NT practices could lead to a shift from particulate P to dissolved P diffusion in rural catchments, with a potentially highly negative impact on freshwater ecosystems, given that dissolved P is more bioavailable than particulate P (Duncan et al., 2019).

Given the growing success of ST and NT practices among farmers and soil health advocates, it is important to develop knowledge to predict the loss risk of dissolved P that adoption of these practices could engage. One option is to determine whether the P tests conventionally used to evaluate the capacity of soils to release dissolved P have the capacity to be good predictors of the potential increase of

dissolved P diffusion in case of adoption ST and NT practices. Some existing soil P tests originally developed for agronomic purposes work reasonably well to assess soil dissolved P loss risk, such as total phosphorus (TP), Olsen-P, and Dyer-P (Sims, 2000) and could be suitable for that purpose. Recently, other indicators more directly related to the soil properties engaged in P sorption such as the degree of phosphorus saturation (DPS_{OX}) have received interest as a possible indicator of dissolved P release risk in soils (Pöthig et al., 2010; Wang et al., 2016; Fischer et al., 2017). The determination of adsorption isotherms makes it possible to determine the value of equilibrium phosphorus concentration (EPC_0) in soils, which has been shown to predict well dissolved P concentrations in runoff (Hughes et al., 2000; Munira et al., 2018), and to be also well correlated with DPS_{OX} values (Sims, 2000; Pöthig et al, 2010; Fischer et al., 2017). Another parameter which can be determined from adsorption isotherms is the phosphorus sorption maximum (Q_{max}), which quantify the maximum amount of P that a soil can bind. In addition, the amount of water-soluble phosphorus (WSP) is also viewed has a potential efficient indicator for the dissolved P release risk by soils (Pöthig et al., 2010; Xue et al., 2014; Fischer et al., 2017).

Although all these four indicators (DPS_{OX}, EPC_0, Q_{max}, and WSP) are generally accepted for the assessment of dissolved P release risk of soils, their use has not yet been tested as a mean of predicting the increase in dissolved P release risk in case of shifting a plot from conventional tillage (CT) to ST and NT. A key question in this context, with possible important implication for the deployment of ST and NT practices, is to know which of these four indicators, if any, provides the best

prediction of this increase. At the same time, there is the question of the amplitude of the variations that the change from CT to ST and NT is able to induce on soil P sorption properties, all cultivation practices (type and dose of fertilizer applied, in particular) being moreover kept constant, and of the consequences of these changes on the use of these indicators.

Of particular interest in this context is the case of soil surface horizons (0-5 cm), given that these horizons are the layers that ST and NT practices are likely to modify the most with respect to their P sorption properties and P concentrations. The enrichment in organic matter (OM) caused by the cessation of plowing is, in particular, expected to increase the capacity of P sorption of surface soils, by creating ternary complexes between OM, metal cations such as Fe, Al, Ca and phosphate oxyanions (Gerke and Hermann, 1992; Messiga et al., 2011). How does this increase, if it exists, affect the release of dissolved P by ST and NT soils compared to CT soils? Likewise, the enrichment in OM of the soil surface horizon induced by ST and NT practices (Daryanto et al., 2017; Duncan et al., 2019) raises the question of the proportion of organic form of dissolved P likely to be released in the event of runoff. How does this proportion evolve according to the evolution of tillage practices? This question has not yet been addressed to our knowledge.

The objectives of this study are to i) evaluate how the different tested ploughing modalities affect the P sorption properties of soils and how this affect in turn the potential dissolved P loss risk of soils; ii) screen out which soil indicator(s) can be used to predict the best P loss magnitude in case of runoff development, and how the

130 organic/inorganic dissolved P ratio vary depending on whether the soil is
131 conventionally tilled or benefit from conservation tillage practices.

132 2. Materials and methods

133 *2.1. Site description*

134 The study site was established in 2000 at the Kerguéhennec Agricultural
135 Experimental Station in Brittany, western France (48º N, 3º W; Fig. S1). Brittany is a
136 major agricultural region in France, with agriculture occupying approximately 66% of
137 the region, which also is a hot spot region of eutrophication of surface waters at the
138 scale of France and Europe (Bol et al., 2018). The highest soil P budget was observed
139 in Brittany where the P budget was 17 kg P ha^{-1} in 2006 (national average was 4.4 kg
140 P ha^{-1}) (Senthilkumar et al., 2012). In Brittany, almost 76,000 t of nitrogen was
141 discharged into the sea in 2008 (Perrotet al., 2014). Climate is temperate oceanic, with
142 20-years average of annual precipitation and temperature of 1000 mm and 10.6 °C at
143 the station, respectively. Soils at the Kerguéhennec station are well-drained silty
144 loamy Luvisols.

145 The studied soils were sampled from two distinct series of plots separated from
146 each other by ca. 50 m (Fig. S1). The A plots comprise nine contiguous plots (6×50
147 m), with three plots being continuously maintained in CT (tillage depth 0-25 cm),
148 three maintained in ST (tillage depth 0-15 cm), and three maintained in NT (tillage
149 depth 0 cm). This “tillage comparison” experiment is a long-term trial which started
150 in 2000, and still continue today. Crop rotations on these plots consist of

151 corn-wheat-rapeseed succession. The A plots are fertilized annually with pig manure.
152 The average annual P input is 122 kg ha^{-1} (pig manure = 4.8 g of P per kg).

153 The B plots comprise three plots (12×25 m, Fig. S1). The fertilization
154 management is receiving poultry manure with three tillage practices (CT, ST, and NT).
155 Cropping system on B plots consists of a corn-wheat rotation. The average annual P
156 input is 156 kg ha^{-1} (chicken manure = 17.2 g of P per kg). The amount of fertilizer
157 supplied to soils is adjusted annually to ensure the balance between the input and
158 output of nitrogen, P and carbon, and to provide ideal nutrient amounts for the crop.

159 Crop residues are left on the soil surface of A and B plots managed with NT,
160 while being incorporated in the surface soils by chisel plough for soils of the other
161 two tillage modalities. The average annual coverage rates of crop residues returned to
162 the soil CT, ST and NT is 0.5%, 8.5%, and 26.5%, respectively.

163 *2.2. Soil sampling and preparation*

164 Sampling 100 different surface soils (0-5cm) from 5 different sampling sites in
165 each plot. The composite soil samples were air-dried, thoroughly mixed, and passed
166 through a sieve (2 mm) and analyzed for physicochemical properties, isothermal
167 adsorption experiment and WSP determination.

168 Soils from six plots were selected for the rainfall simulation experiments. Three
169 plots (A (Pig)-CT, A-ST, and A-NT) were from the A trial, and three plots from B trial
170 (B (Poultry)-CT, B-ST, and B-NT). The surface (0-5cm) soil samples from each
171 excavation were combined to form a composite sample of each studied plot, each
172 composite sample being then air-dried, thoroughly mixed, and sieved (20 mm). Note

173 that the crop was harvested approximately one week prior to the sampling, and that all
174 crop residues were removed out of soil samples either manually or by sieving.

175 *2.3. Rainfall experiment design*

176 Rainfall experiments were performed at the Kerguéhennec station as follows (Fig.
177 1). Samples from each plot were tiled in a metal frame of 1 m × 1 m with a slope of 5%
178 and a thickness of 3 cm. An impermeable membrane was laid at the bottom of the
179 sample to facilitate the collection of runoff water. Rainfall was simulated by means of
180 an oscillating nozzle set at about 3 m height, and by using tap water. Due to time
181 constraints, no pre-rain wetting of the sample was performed. Artificial rainfall was
182 applied at a rate of 25 mm h^{-1}, which represented common storm characteristics in
183 Brittany. Each experiment was lasted about 90 minutes. Runoff was collected
184 continuously by mean of a pipe set on the downstream edge of the plate and water
185 stored in pre-cleaned 500 mL to 1000 mL polypropylene bottles. One on two water
186 samples were used to determine the suspended matter content of runoff. The
187 measurement was made by weight difference of the bottles, after evaporation of the
188 water to the oven. All other water samples were used to monitor the evolution of
189 water chemistry. Samples used for monitoring of runoff water composition were
190 stored in the dark at 4 °C and filtered through pre-cleaned 0.45 µm filters (cellulose
191 acetate) within less than 24 h before chemical analysis at Rennes University.

192 **Fig. 1.** Rainfall simulation device.

193 *2.4. Laboratory analyses*

194 All soil samples used in rainfall experiments were analyzed at the soil analysis
195 laboratory of INRAE in Arras, France, on soil aliquots of about 2 kg sieved at < 2 mm.
196 The soil particle size was classified into three categories: clay (<0.002 mm), silt
197 (0.002-0.05 mm), and sand (0.05-2 mm) (Day, 1965). The organic matter (OM) was
198 measured as loss on ignition (Jensen et al., 1992). The dissolved organic carbon (DOC)
199 concentrations in runoff samples were analyzed with a total organic analyzer
200 (Shimadzu TOC-5050A) (using potassium hydrogen phthalate as the standard solution)
201 (Gu et al., 2018). Soil pH was determined with a pH electrode in a soil to water ratio
202 of 1:5 (NF ISO 10390). The Si-ox/Al-ox/Fe-ox concentrations were determined with
203 ICP-AES after extraction with ammonium oxalate and oxalic acid (Ross and Wang,
204 1993). The TP content was also measured (ICP-AES) after total solubilization with
205 hydrofluoric and perchloric acid (NF X 31-147). Dyer-P was extracted with 20 g L^{-1}
206 monohydrate citric acid solution (NF X 31-160) and Olsen-P was extracted with 42 g
207 L^{-1} $NaHCO_3$ (pH = 8.5) (Sims, 2000).

208 The WSP concentrations was determined following the standard method
209 developed by Murphy and Riley (1962). The Q_{max} and EPC_0 were determined based
210 on Langmuir P sorption isotherms obtained using the method proposed by Pöthig et
211 al., (2010). Briefly, the air-dried and sieved soil (< 2 mm) of 1.0 g was suspended in
212 50 mL of 0.01 M $CaCl_2$ solution containing various initial P concentrations: 0, 0.5, 1,
213 5, 10, 25, 50, 75 mg L^{-1}, and centrifuged at 1500 rpm for 10 min, suspensions were
214 filtered (<0.45 μm), and soluble reactive P concentration of the supernatant was

measured colorimetrically. The sorbed P (SP) was calculated from the difference between the measured P concentration of the filtrate (EPC) and the initial P concentration of the solution before equilibrium with the soil. The P sorption isotherms are obtained by plotting SP against EPC (Pöthig et al., 2010). The Q_{max} was determined by fitting a Langmuir equation to the last three points (25, 50, 75 mg P L^{-1}), as follows:

$$Q = (c * K * Q_{max}) / (1 + K * c) \quad (1)$$

where Q is the total amount of P sorbed (mg mg^{-1}), c is the concentration of P in the equilibrium solution, which is also EPC (mg L^{-1}) and K is a constant parameter (L mg^{-1}). The EPC_0 represents the solution P concentration at which no net sorption or desorption of P would occur between soil and solution. To calculate EPC_0 values, the data points corresponding to the first three concentrations (0, 0.5, 1 mg P L^{-1}) of the isotherms were plotted as a straight line, and the EPC_0 value calcultaed as the intersection of this straigth line with the X axis (SP = 0) (Pöthig et al., 2010).

The DPS_{OX} was calculated as the molar ratio of acid ammonium oxalate extracts as follows (van der Zee et al., 1987):

$$DPS_{OX} = P_{OX} / \alpha\,(Al + Fe)_{OX} \quad (2)$$

where P_{OX}, Al_{OX}, and Fe_{OX} are quantified in acid ammonium oxalate extracts (mmol kg^{-1}). The sum of Al_{Ox} and Fe_{OX} is termed P sorption capacity (PSC, mmol kg^{-1}). We used an average α value of 0.5 to calculate DPS_{OX} (van der Zee et al., 1987; Messiga et al., 2021).

Molybdate reactive dissolved phosphorus (MRDP) runoff filtrates were determined colorimetrically by direct reaction with ammonium molybdate (Murphy

238 and Riley, 1962). The same method was used for total dissolved phosphorus (TDP),
239 but after digestion of filtrates in acidic potassium persulfate. The precision of MRDP
240 and TDP measurements was ± 4 and ± 13 μg L^{-1}, respectively. The difference
241 between TDP and MRDP was defined as the molybdate unreactive dissolved
242 phosphorus (MUDP), which includes truly dissolved organic P as well as both organic
243 and inorganic P associated with colloidal particles (Haygarth and Sharpley, 2000).

244 The DOC concentrations were analyzed with a total organic analyzer (Shimadzu
245 TOC-5050A), with a precision of ± 5% (using potassium hydrogen phthalate as the
246 standard solution) (Gu et al., 2018).

247 *2.5. Statistical analyses*

248 Pearson correlation analysis was carried out to identify relationships among the
249 various soil parameters (P content, DPS_{OX}, WSP, EPC_0, Q_{max}) and the amount of
250 dissolved P in runoff waters. All statistical analyses were conducted using the SPSS
251 22.0 (IBM, USA) software package. Figures were created using the Origin 8.0
252 (OriginLab, USA) software package. Measurements in triplicate of each sample were
253 conducted, and their arithmetic mean values were reported.

254 ## 3. Results

255 *3.1. Soil physicochemical properties*

256 Comparison of soil physicochemical properties showed that tillage management
257 had no regular effect on soil particle size, metal oxide contents, and pH values (Table
258 1). Conversely, ST and NT obviously increased TOC, OM, TP, Dyer-P, Olsen-P, and

259 P_{OX} contents of soils compared to CT. For TOC, the increase was 23-42% for plot A
260 soils (pig manure), and 34-50% for plot B soils (poultry manure). The TP increases
261 were also obvious, ranging from 6-9% for plot A soils and 18-20% for plot B soils,
262 respectively. The highest increases were found for Dyer-P and Olsen-P, with increases
263 in between 36-64% and 28-79%, respectively, for plot A soils, and in between 57%
264 and 25-59%, respectively, for plot B soils. Thus, the switch from conventional tillage
265 to conservation tillage led to a strong enrichment of soils in OM, TP, Olsen-P and
266 Dyer-P in the topmost layers (0-5cm). It was noteworthy that the addition of poultry
267 manure yielded to the highest increases of OM, TP, Dyer-P and Olsen-P at comparable
268 tillage modality.

269 **Table 1** Basic surface soil (0-5 cm) characteristics of each field experiment site. The data
270 represent the mean ± standard deviation.

3.2. Soil sorption properties

Fig. 2. Plot A (pig manure applied) (a) and plot B (poultry manure applied) (b) soil adsorption isotherm fitting curves. CT = conventional tillage; ST = shallow tillage; NT = no-tillage.

Table 2 Phosphorus sorption parameters of the studied soils. Each value is the mean of three separate measurements.

The NT and ST changed the parameters of soils to bind P (Table 2). Compared with CT, the dissolved P indexes (EPC_0 and WSP) that equilibrated with the solid phase P were increased due to the long-term implementation of NT and ST. The average EPC_0 and WSP of soils in CT were 0.60 and 3.10 mg L^{-1}, but they were increased to 1.73 and 4.85 mg L^{-1} after converted to NT and ST, respectively. The potential of soils to bind P exhibited similar characteristics with Q_{max} and DPS_{OX} increased by different extents after converted to NT and ST. The average magnitudes of Q_{max} and DPS_{OX} were increased by 10.3% and 19.7%, respectively.

The change of soils in sorption property highly depended on the type of conservation tillage practices. Soils in NT had a high Q_{max} and DPS_{OX}, also a large EPC_0 and WSP, compared with those in ST. For example, the average values of EPC_0, Q_{max}, WPS and DPS_{OX} of soils in ST were merely 1.60 mg L^{-1}, 1249 mg kg^{-1}, 4.33 mg L^{-1} and 15.13% respectively, but the corresponding values of soils in NT were as high as 1.87 mg L^{-1}, 1326 mg kg^{-1}, 5.36 mg L^{-1} and 16.54%, respectively.

The change of soils in sorption property was also related to the type of manures. The application of poultry manure had a greater impact on soil sorption properties

than pig manure. Except for Q_{max}, all the indicators of soils P sorption in plot B (poultry manure applied) were higher than those in plot A (pig manure). For example, EPC_0 of soils in B-NT increased by 517% compared with A-NT.

3.3. Runoff P concentration and flux

Fig. 3. Hydropgraphs of rainfall simulation experiments for plot A (pig manure applied) (a) and plot B (poultry manure applied) (b) soils. CT = conventional tillage; ST = shallow tillage; NT = no-tillage.

Runoff development in the rainfall simulation experiments could be divided into four steps (Fig. 3). The first step, which lasted between 20 and 50 minutes, started from the onset of rainfall and went on until the first drops of runoff water could be collected in the pipe at the downstream edge of the experimental plate. During this step, water-saturated areas were observed at the soil surface but the lack of connection between these areas prevented the collection and downward transfer of the surface accumulated water. The second step corresponded to the onset of the connection of water saturated surface areas each other and with the runoff collecting pipe device, but runoff flux was low and constant. The third step corresponded to the sudden connection of all water saturated surface area and was marked by a sudden increase of the runoff flux. Finally, the fourth step corresponded to the installation of a steady-state regime during which runoff volumes were high and temporally constant.

Table 3 Average concentrations and total fluxes of different P forms and DOC in rainfall water

312 during simulated rainfall.

313 Table 3 showed the total amount of collected runoff water, as well as average
314 MRDP, TDP, MUDP, and DOC concentrations and total fluxes for each of the six
315 rainfall simulation experiments. The volumes of collected runoff water were quite
316 similar for all experiments (between 9400 and 11950 mL), except that soil B-NT,
317 which yielded to a much lower runoff volume (6150 mL). The average TDP, MRDP,
318 MUDP and DOC in runoff waters were in an order NT > ST > CT. Thus, ST and NT
319 markedly increased dissolved P in runoff waters, compared with CT. However, a
320 notable exception was the B-NT experiment, whose highest concentrations were not
321 passed on to the level of total P losses/fluxes due to the delay in the onset of step 4 of
322 the runoff episode recorded and the much lower collected volume of runoff water.

323 In MRDP concentrations increased by 143% and 104% for plot A and B soils,
324 respectively (Table 3). The increase was even greater for MUDP, which was increased
325 by 165 and 434%, respectively. The impact of tillage methods on DOC in runoff was
326 similar to that of dissolved P, with NT yielding higher DOC than other modalities.
327 However, the amplitude of the variations was much lower (increase <10%) than that
328 observed for dissolved P. Clearly, the application of poultry manure increased the
329 concentration of all dissolved P forms in runoff as compared to pig manure, especially
330 MUDP.

331 **Fig. 4.** Influences of tillage (a, b, c, d) and fertilization (e, f, g, h) practices on concentrations of
332 TDP, MRDP, MUDP and DOC in runoff waters during simulated rainfall experiments. CT =

conventional tillage; ST = shallow tillage; NT = no-tillage; MRDP = molybdate reactive dissolved phosphorus; MUDP = molybdate unreactive dissolved phosphorus; TDP = total dissolved phosphorus; DOC = dissolved organic carbon.

The change of MRDP in runoff showed a tendency to decrease during the experiment (Fig. 4). The magnitude of the decreases clearly increased with the level of initial MRDP in runoff, with decreases in the range 20-30% for the high initial concentrations, as against <5% for the lowest initial concentrations. As the MRDP concentrations increased in the experiments in the CT < ST < NT direction, the amplitudes of decrease of concentrations are also CT < ST < NT.

Temporal decreases were also observed for TDP and MUDP (Fig. 4), with the same positive correlations between the relative decrease amplitude and the initial levels as observed for MRDP. A major difference, however, was that the decrease rates of TDP and MUDP were not constant over time. In fact, the decay amplitudes were very strong during the stage 2 of runoff development, and declined then stabilized at very low levels. This dynamic was particularly well expressed by the treatments of A-NT, B-NT, and B-ST, which had highest initial concentrations of TDP and MUDP.

To conclude, compared to CT, the conversion of soil management to ST and NT led to more export of MUDP (along with more export of reactive P), a large part of these MUDP being solubilized and exported quickly during the early stages of runoff.

4. Discussion

4.1. Impact of soil management on soil P sorption property and dissolved P loss

Our results show that NT and ST significantly increase total P content of the topmost soil layers (0-5 cm), indeed, consistent with those reported (Ulén et al., 2010; Baker et al., 2017; Daryanto et al., 2017; Jarvie et al., 2017; Duncan et al., 2019). It is also true that the enrichment of TP in the topmost soil layers in NT and ST increases P agronomical availability (indicated by Olsen-P and Dyer-P) (Table 1), which have been observed in loamy soils (Sokolowski et al., 2020). Compared with soils under CT, soils under ST and NT treatment usually contained high crop residues, which upon degradation by soil organisms are expected to release significant proportions of P (Sokolowski et al., 2020; Ni et al., 2020; Daryanto et al., 2017), which will tend to stay on the soil surface due to lack of mixing imposed by the ST and NT management practices, thus leading to an accumulation of the released P into the topmost soil layers (Zhang et al., 2017).

Many previous studies on P sorption characteristics of agricultural soils emphasizes the dominant role of mineral (Al, Fe, Ca), OM content and other soil properties, all of which can increase the capacity of soils to fix newly applied P and thus reduce P loss from soil through (Messiga et al., 2021; Pradhan et al., 2021; Messiga et al., 2011). In this study, compared with conventional tillage, the DPS_{OX} of conservative tillage always increased, regardless of the content of $(Fe \text{ and } Al)_{OX}$ increased or decreased, thus $(Fe \text{ and } Al)_{OX}$ may not be the key factor affecting soil DPS_{OX}.

Increasing soil OM can improve the crop availability of soil P, but it can also increase the risk of P loss. The main mechanism is that OM can reduce the sorption strength of soils to bind P. The substances in soils that directly bind P through chemical bonds mainly include Fe, Al and Mn oxides, secondary clay minerals, and calcium carbonate. The OM will compete with P for binding sites on the surface of these substances. Moreover, OM may bind to the sorption sites thereby increasing the negative charges of the mineral surface, which results in a reduction in the electrostatic attraction between phosphate and soil surface. The reduction of bonding energy with conservative tillage and poultry manure application, could increase dissolved P loss through runoff as suggested by Pradhan et al. 2021 and Abboud et al. (2018) as well as this study (Table 3 and Fig. 4).

It should be noted that the soil would have a different structure in situ (the porosity of the soil and the straw coverage, etc.), which will affect water infiltration, runoff, as well as P losses (Daryanto et al., 2017; Baker et al., 2018). In this study, we are only concerned with the impact of tillage and fertilization on soil physicochemical properties and thus on dissolved P loss. Therefore, the soil samples were screened before simulating rainfall, soil structures in situ are not considered.

4.2. Significance and origin of the MUDP compartment

Fig. 5. Proportion of MUDP flux to TDP flux for plot A (pig manure applied) (a) and plot B (poultry manure applied) (b) soils during simulated rainfall experiments. CT = conventional tillage; ST = shallow tillage; NT = no-tillage; MUDP = molybdate unreactive dissolved phosphorus.

The tillage practice change from CT to ST and NT stimulates the loss of MUDP. The P loss in MUDP accounts for 11-27% of TDP flux with the highest loss occurring at the onset of runoff development, reaching to 50% of total TDP flux in ST and NT (Fig. 5). This result is very important insofar as i) this compartment is rarely quantified in the role of conservation agriculture practices on the risks of dissolved P transfer (Daryanto et al., 2017), and ii) like MRDP, MUDP compartments (organic P and colloidal P) also contains some bioavailable P forms to aquatic organisms (Li and Brett, 2013; Van Moorleghem et al., 2013; Li et al., 2015). Thus, the loss of MUDP is of great concern as regards eutrophication risks in cultivated landscapes, and should be taken into account during implementation of conservation agriculture.

As shown in Fig. 5, the formation and rapid exhaustion of a MUDP peak resemble very closely to the flush of MUDP observed by Gu et al. (2018) demonstrated that MUDP consists in P bound to a mixture of OM and Fe(Al)oxide-rich colloids, which is a well-established feature (Liu et al., 2014). It is also well established that drying of the soil matrix generates soil colloids, which can be mobilized and flushed out of the soil matrix during rewetting (Mohanty et al., 2015). Runoff development as simulated here is similar to the rewetting of dried soils, so we can reasonably speculate that it is the rewetting processes that results in the loss of P bound to organic-rich colloids as observed by Gu et al. (2018). Based on this origin of MUDP, it is not difficult to explain the observed transient peaks of MUDP at the onset of runoff development.

The hypothesis of a colloidal origin of MUDP compartment does not rule out the

418 possibility that it also contains a part of truly dissolved organic P. In the soil solution,
419 indeed, there exist a part of dissolved organic P molecules from microbial cell lysis
420 due to osmotic shock upon soil rewetting (Blackwell et al., 2013). This part of organic
421 P is not directly reaction with ammonium molybdate, but truly available to aquatic
422 organism.

423 *4.3. Prediction of P loss from soil indicators*

424 **Fig. 6.** Relationships between the concentration of TDP (a), MRDP (b) and MUDP (c) in runoff
425 and the different indicators tested here to predict the risk of dissolved P release. EPC_0 =
426 equilibrium phosphorus concentrations; Q_{max} = phosphorus sorption maximum; WSP =
427 water-soluble phosphorus; MRDP = molybdate reactive dissolved phosphorus; MUDP =
428 molybdate unreactive dissolved phosphorus; TDP = total dissolved phosphorus; DOC = dissolved
429 organic carbon.

430 Both the results of soil sorption properties and simulation experiments showed that
431 NT and ST aggravated the loss of dissolved P in the topmost soil layers. To explore
432 the possibility using soil sorption indicators to predict the dissolved P loss, the
433 relationship between EPC_0, WSP, Q_{max} and DPS_{OX} indicators and the concentration
434 and fluxes of TDP, MRDP, MUDP are analyzed. The results shows that EPC_0, WSP,
435 and DPS_{OX} are positively and significantly correlated with the concentration and
436 fluxes of TDP, MRDP, MUDP in runoff, suggesting that these three indicators could
437 be used to assess P loss risks (Fig. 6; Table S1 in Supplementary Data). The Q_{max} has
438 no correlation with P concentrations and fluxes in runoff (Fig. 6; Table S1 in

439 Supplementary Data). This indicates that Q_{max} is not a suitable indicator for assessing
440 the risk of P release. Because Q_{max} is related to the number P sorbing sites in the soil,
441 and not to the strength of these sites, which is the key parameter to consider when
442 dealing with the dissolved P loss risk (Ma 2014; Schoumans and Chardon, 2015).

443 **Fig. 7.** Relationships between concentrations of available P (Dyer-P (a, b) and Olsen-P (c, d))
444 in soils and soil EPC_0 and WSP values. EPC_0 = equilibrium phosphorus concentrations; WSP =
445 water-soluble phosphorus.

446 However, the soil DPS_{OX} was always lower than 25%, indicating that the risk of
447 soil P release was not large (van der Zee et al., 1987), which is contrast to the results
448 of WSP, EPC_0, available P as well as simulated rainfall experiments. Furthermore,
449 DPS_{OX} is also not a good indicator to evaluate the marked increases in dissolved P
450 loss caused by the change in tillage, because this switch not being accompanied by a
451 significant change in DPS, whether in the poultry or pig fertilization modality.
452 Compared with DPS_{OX}, the calculation of EPC_0 and WSP are convenient and simpler
453 soil P release risk assessment indicators. Therefore, EPC_0 and WSP are more suitable
454 for assessing changes in P release risk when shifting soil management from CT to ST
455 and NT.

456 The EPC_0 values show the most significantly positive correlation with MRDP,
457 TDP, and MUDP concentrations and fluxes in runoff (R^2 = 0.910-0.997, $P < 0.01$).
458 The EPC_0 values > 0.03 mg L^{-1} such as observed in all investigated plots, especially
459 those fertilized with poultry manure, are indicative of a high potential risk of
460 eutrophication due to the capacity of these soils to easily exchange large quantities of

461 dissolved P with runoff waters (US EPA, 1988). Indiati and Sharpley (1998) and
462 Munira et al. (2018) have found that there is generally a threshold of EPC_0 in soils, the
463 position of which depends on the physicochemical properties of soils (Indiati and
464 Sharpley, 1998; Hughes et al., 2000; Munira et al., 2018). Given that soil EPC_0 is
465 above the threshold, it strongly increases as a function of Olsen-P concentrations. We
466 also find that there are significantly linear correlations between EPC_0 values and
467 bioavailable P contents (Dyer-P and Olsen-P) (Fig. 7a, b). The slopes of the
468 correlations are quite high, indicating that the bioavailable P contents in these soils
469 may have exceeded the threshold.

470 Positive correlations are also obtained between WPS values and dissolved P and
471 fluxes in runoff (Fig. 6; Table S1 in Supplementary Data). This feature has been
472 already observed in several previous studies (Pöthig et al., 2010; Xue et al., 2014;
473 Fischer et al., 2017). Furthermore, the very significant positive correlation between
474 WSP and DPS_{OX} with r^2 of 0.9995 is found. van der Zee et al. (1987) report that the
475 risk of soil P loss can be predicted with the single quadratic regression and a critical
476 DPS_{OX}. When soil DPS_{OX} is more than 25%, the loss of dissolved P by runoff water is
477 high (Messiga et al., 2021). However, the linear positive correlation between WSP
478 and DPS_{OX} in this study illustrated that the critical value of DPS_{OX} is smaller than 25%
479 or insufficient amount of data. In a recent study, Messiga et al. (2021) have shown
480 that the concentration of WSP was 3.7 mg L^{-1} with critical DPS_{OX} value.
481 Comparatively, the same DPS_{OX} has a higher WSP value, indicating that the P in the
482 this studied soil is easier to lost.

Finally, soil Olsen-P and Dyer-P contents are also significantly positively correlated with TDP, MRDP and MUDP concentrations and fluxes in runoff (Fig. 6; Table S1 in Supplementary Data). Many published studies have reported such positive correlations between Olsen-P and Dyer-P concentrations in soils and P loss from runoff (Mcdowell et al., 2003; Hopkins and Ellsworth, 2005; Pizzeghello et al., 2016). This means that agronomic soil tests for P can be also used as indicators to assess dissolved P loss risk in soils, since these tests are widespread and not very expensive (Pizzeghello et al., 2016). Some authors have reported a threshold of ca. 60 mg Olsen-P kg^{-1}, above which the dissolved P loss risk increases sharply (Heckrath et al., 1995; Johnston and Poulton, 1997). In this study, only for the soils amended with poultry manure had Olsen-P concentrations > 60 mg kg^{-1}, suggesting the application of poultry manure increases the loss risk of dissolved P in the topmost soil layers.

It can also be seen that the four tested indicators (EPC_0, WSP, Olsen-P, Dyer-P) define linear correlations of very good quality when they are plotted against each other, with no evidence of a break in the correlations. It can be concluded that in the range of the P content values encountered in the soils of this study, EPC_0, WSP, Olsen-P and Dyer-P values can be used indifferently as soil indicators to assess the surplus of dissolved P loss risk caused by changing soil management from CT to ST and NT. Obviously, one will favor the use of Olsen-P and Dyer-P concentrations for reasons of ease of measurement and lower cost.

4.4. Implication for management

Results from this study confirm that if beneficial for limiting soil erosion and

505 export of particulate P, conservation practice can have the pervese effect of
506 exacerbated dissolved P losses in case of intense runoff development. Here, the
507 potential rise in dissolved P losses induced by switching soil managment from CT to
508 NT is of a factor of 2 to 3 times (Table 3), and appears independent of the type of
509 fertilizer used. As indicated in the introduction, Brittany, the region in which the
510 Kerguehenenc station is located, is a region of intensive agriculture suffering from a
511 recurring problem of eutrophication of these surface waters, with a clear role of P as
512 the limiting nutrient causing these blooms (Senthilkumar et al., 2012; Perrotet al.,
513 2014; Bol et al., 2018). In a recent study, Guillemot et al. (2021) revealed that ca. 50%
514 of the cachtments have median dissolved P concentrations already higher than the
515 eutrophication threshold of 0.03 mg L^{-1} (Yang et al., 2019), the other 50% catchments
516 having median concentration in the range 0.08-0.026 mg L^{-1}. In Brittany, the relative
517 surface area of soils conducted using NT techniques is only 25% of the total
518 cultivated area, and there is therefore room for progress to develop these techniques.
519 Taking into account the results of our study and those obtained by Guillemot et al.
520 (2021) we anticipate that the risk is great and a generalization of these techniques will
521 amplify the eutrophication problem that suffers Brittany given the already high P
522 contents of most of fresh water.

523 In light of these findings, we may recommend to combine NT with other land
524 management techniques (e.g., injection instead of broadcast application of P fertilizer,
525 inclusion of cover crops to scavenge residual P) to limit the risk of dissolved P losses.
526 Occasional soil harrowing as suggested by Daryanto et al. (2017) may be also a

solution to overcome the surface P accumulation problem. Above all, it seems that Brittany farmers should be primarily recommended to limit soil fertilization in the case of guaranteed crop yield crop yield, so as to reduce the overall P content of Brittany soils.

5. Conclusion

Our experimental results confirm that conservation agriculture may increase the risk of all dissolved P loss during runoff. The prime effect causing this risk is clearly the P enrichment of the topmost soil layers caused by ST and NT. Moreover, conservation agriculture contributes to release MUDP into the runoff, thereby increasing the total flux of dissolved P emitted out of the plots. The main species is most probably colloidal P, followed in lesser proportion by dissolved organic P. These species are also bioavailable for aquatic organisms, and in particular algae.

The concentration and flux of TDP, MRDP, and MUDP in runoff were B (poultry manure)-NT > B-ST > B-CT > A (pig manure)-NT > A-ST > A-CT. Clearly, the application of poultry manure increased the concentration and flux of all dissolved P in runoff waters as compared to pig manure, especially as regards MUDP. Special attention is required to MUDP that accounts for 11-27% of TDP fluxes, the highest value can reach 50%, which suggests that MUDP should not be ignored, especially in the early stages of rainfall. The EPC_0, WSP, agronomically Olsen-P and Dyer-P content can be used as indicators of the risk of P loss, since they had a significantly positive correlation with dissolved P concentration and fluxes in runoff. The Olsen-P

548 and Dyer-P are also commonly measured by farmers to control crops and are
549 technically easy.

550 Considering the fairly high dissolved P concentrations of most fresh water in
551 Brittany, local authorities in charge of water quality protection and farmers must be
552 aware of the risk involved in systematizing the development of conservation
553 agriculture. It is recommendation that decrease in the amounts of P brought to soil and
554 development of complementary practices specifically dedicated at maintaining low
555 runoff such as permanent cover crops.

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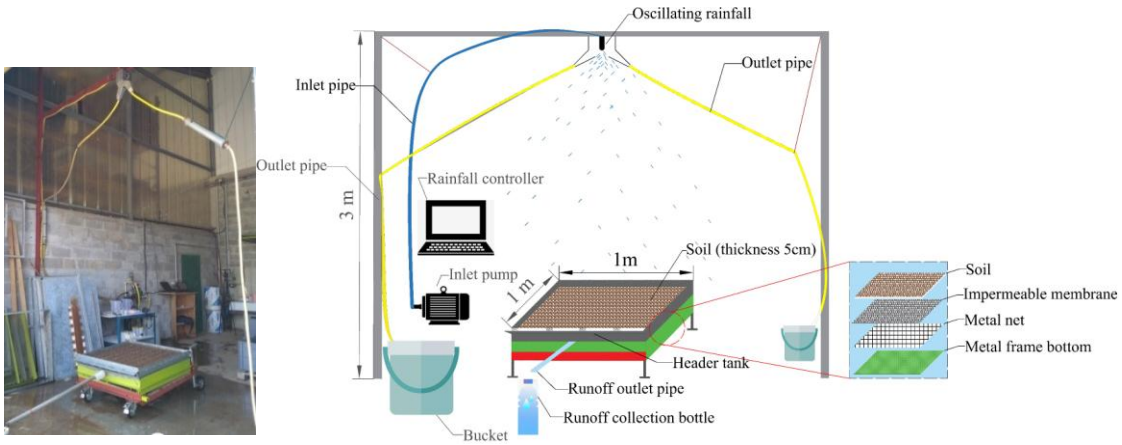
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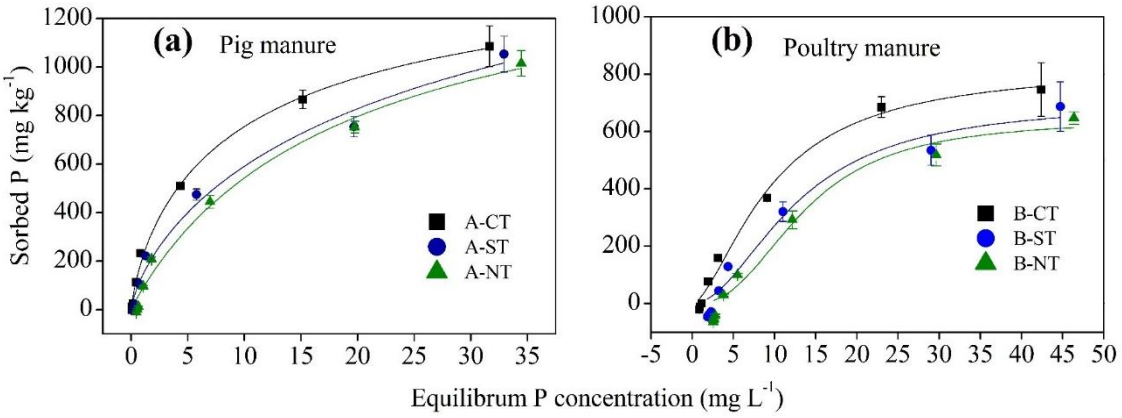
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729

730 **Figure**

731 

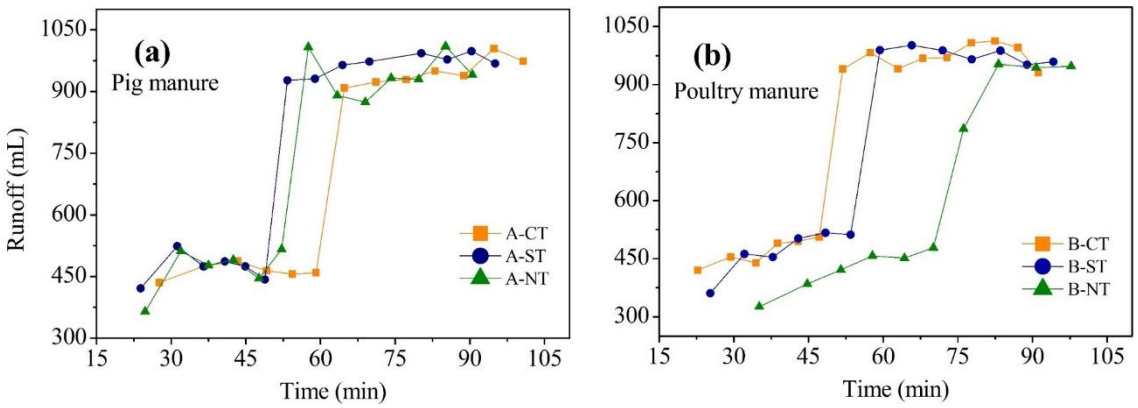
732 **Fig. 1.** Rainfall simulation device.



733

734 **Fig. 2.** Plot A (pig manure applied) (a) and plot B (poultry manure applied) (b) soil adsorption

735 isotherm fitting curve. CT = conventional tillage; ST = shallow tillage; NT = no-tillage.



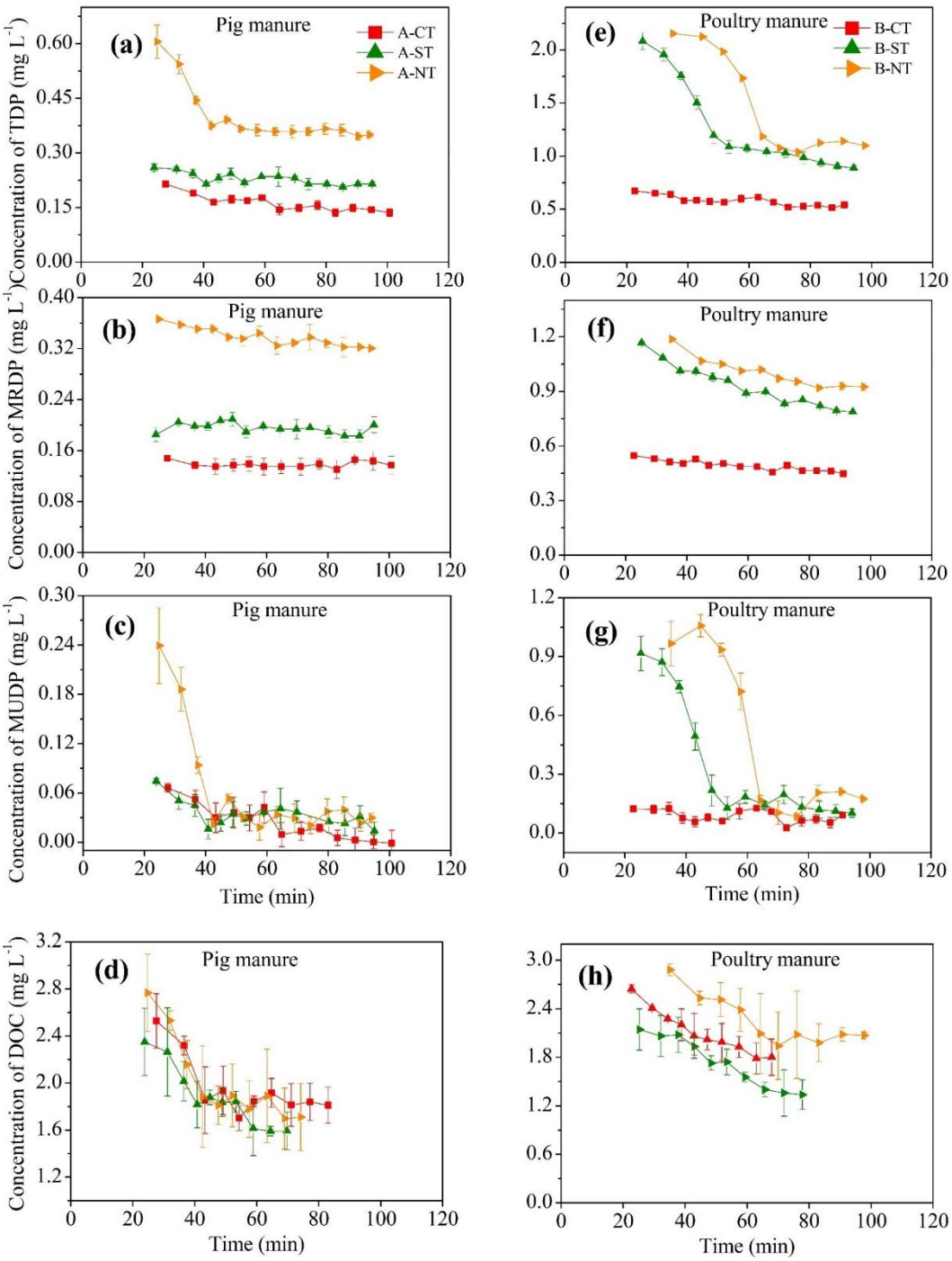
736

737 **Fig. 3.** Hydropgraphs of rainfall simulation experiments for plot A (pig manure applied) (a) and

738 plot B (poultry manure applied) (b) soils. CT = conventional tillage; ST = shallow tillage; NT =

739 no-tillage.

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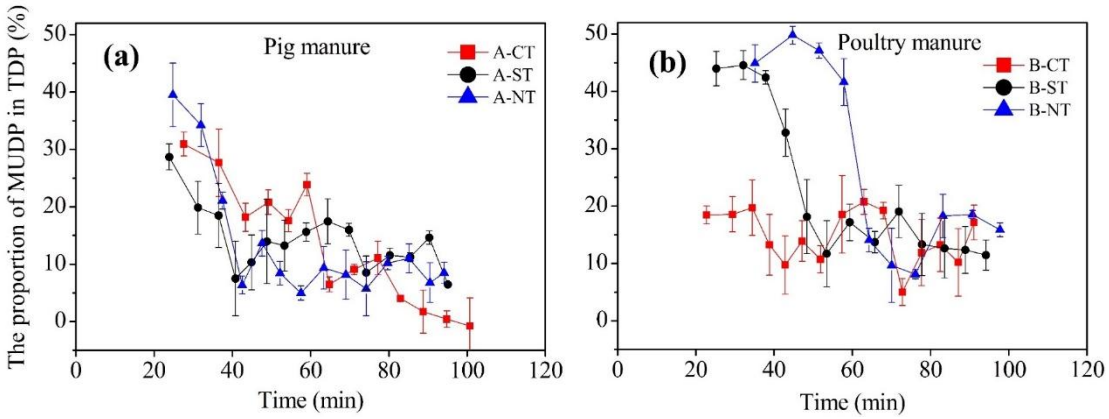
742 **Fig. 4.** Influences of tillage (a, b, c, d) and fertilization (e, f, g, h) practices on concentrations of

743 TDP, MRDP, MUDP and DOC in runoff waters during simulated rainfall experiments. CT =

744 conventional tillage; ST = shallow tillage; NT = no-tillage; MRDP = molybdate reactive dissolved

745 phosphorus; MUDP = molybdate unreactive dissolved phosphorus; TDP = total dissolved

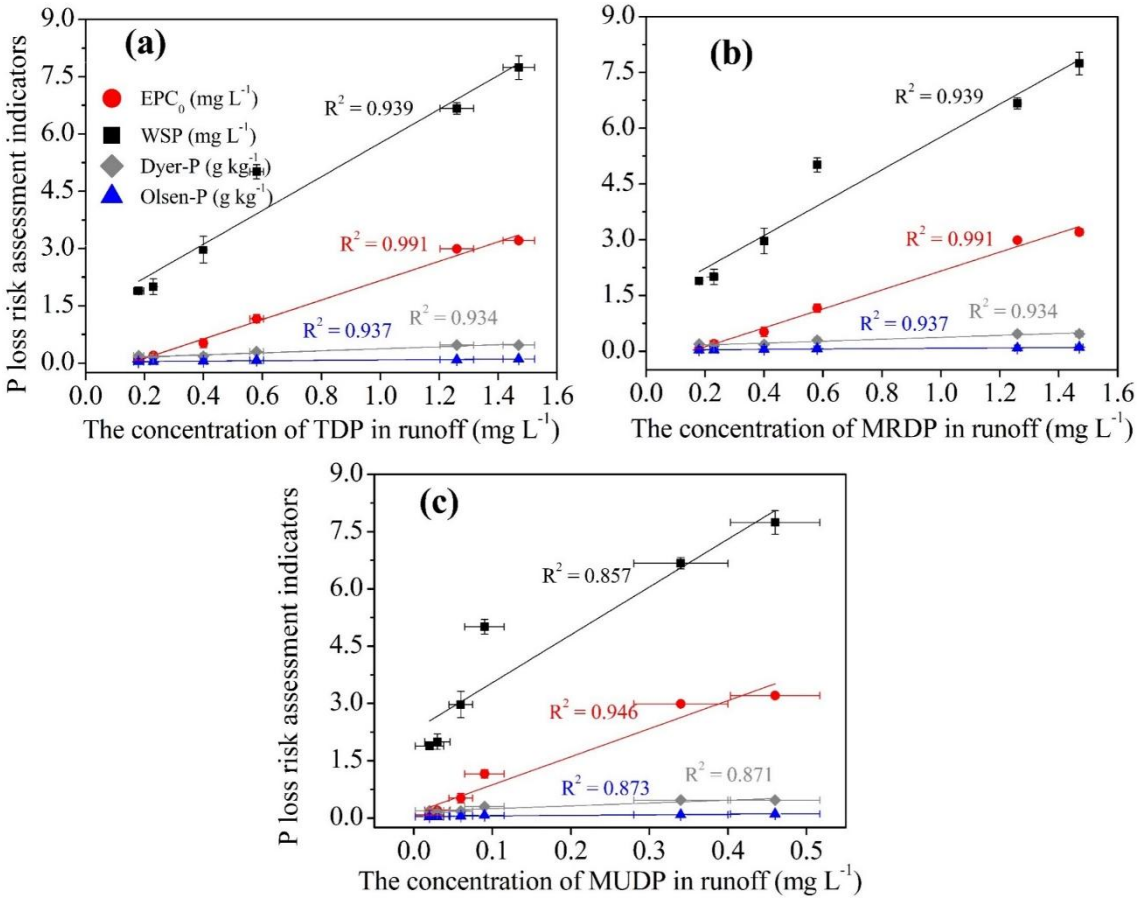
746 phosphorus; DOC = dissolved organic carbon.

747 

748 **Fig. 5.** Proportion of MUDP flux to TDP flux for plot A (pig manure applied) (a) and plot B

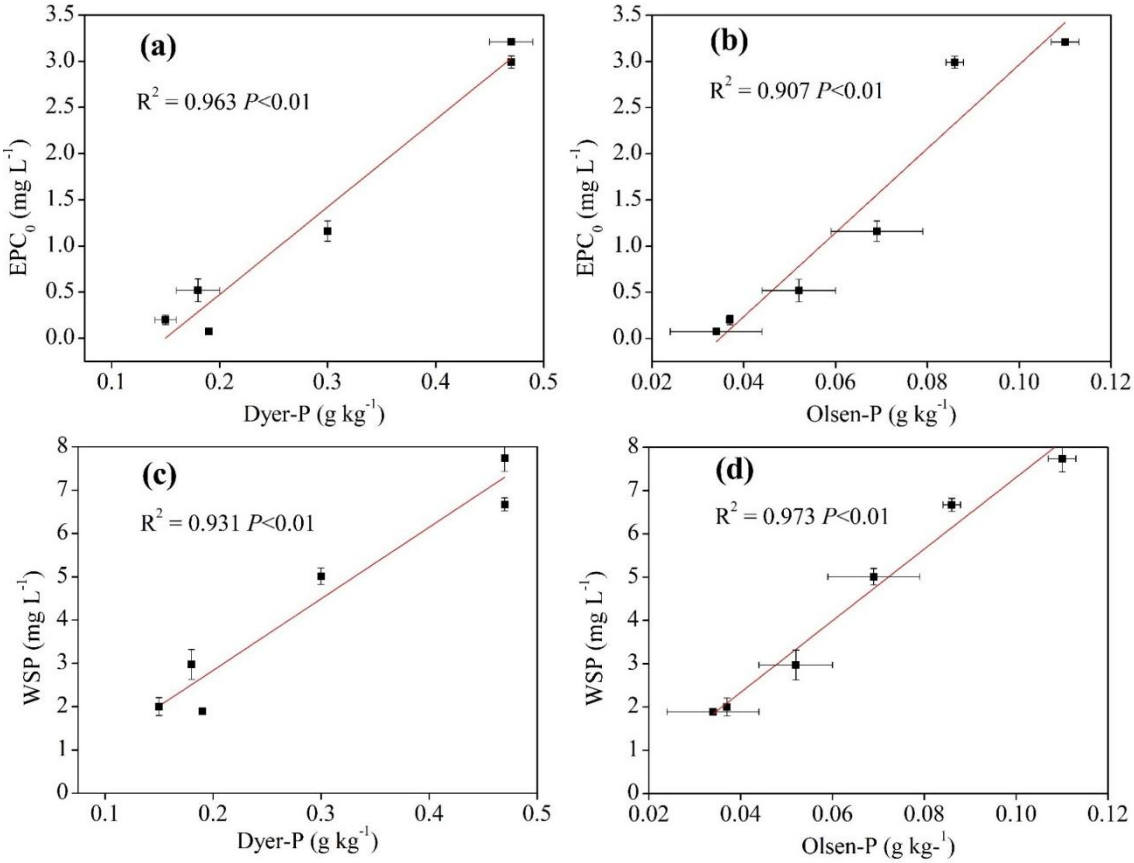
749 (poultry manure applied) (b) soils during simulated rainfall experiments. CT = conventional tillage;

750 ST = shallow tillage; NT = no-tillage; MUDP = molybdate unreactive dissolved phosphorus.



751

752 **Fig. 6.** Relationships between the concentration of TDP (a), MRDP (b) and MUDP (c) in runoff
753 and the different indicators tested here to predict the risk of dissolved P release. EPC_0 =
754 equilibrium phosphorus concentrations; WSP = water-soluble phosphorus; MRDP = molybdate
755 reactive dissolved phosphorus; MUDP = molybdate unreactive dissolved phosphorus; TDP = total
756 dissolved phosphorus.



757

758 **Fig. 7.** Relationships between concentrations of available P (Dyer-P (a, c) and Olsen-P (b, d)) in

759 soils and soil EPC_0 and WSP values. EPC_0 = equilibrium phosphorus concentrations; WSP =

760 water-soluble phosphorus.

761

Table

Table 1

Basic surface soil (0-5 cm) characteristics of each field experiment site. The data represent the mean ±standard deviation.

	Clay	Silt	Sand	pH	TOC	OM	Al-ox	Fe-ox	Si-ox	TP	Dyer-P	Olsen-P	P_{OX}
	%				g kg^{-1}								
A-CT (Pig)	15.5	47.4	37.0	6.29	18.7	32.4	2.26	5.35	0.31	1.16	0.11	0.029	0.29
	±0.6	±0.5	±1.2	±0.04	±0.5	±0.9	±0.21	±0.16	±0.03	±0.03	±0.01	±0.00	±0.01
A-ST (Pig)	15.7	47.4	36.9	6.35	23.0	39.7	2.23	5.20	0.31	1.23	0.15	0.037	0.32
	±0.8	±0.5	±0.5	±0.04	±0.7	±1.2	±0. 15	±0.27	±0.02	±0.06	±0.02	±0.02	±0.01
A-NT (Pig)	15.3	50.5	34.2	6.45	26.5	45.9	2.25	5.04	0.31	1.26	0.18	0.052	0.35
	±0.4	±0.8	±0.8	±0.05	±0.9	±1.5	±0.05	±0.24	±0.01	±0.06	±0.00	±0.01	±0.02
B-CT (Poultry)	15.2	43.0	41.8	6.10	21.8	37.6	2.05	6.14	0.31	1.74	0.30	0.069	0.46
	±0.0	±0.7	±0.1	±0.09	±0.2	±0.6	±0.03	±0.17	±0.00	±0.01	± 0.02	±0.02	±0.02
B-ST (Poultry)	15.6	43.2	41.2	6.37	29.3	50.7	2.27	6.35	0.33	2.05	0.47	0.086	0.57
	±0.4	±0.3	±0.8	±0.09	±0.2	±0.5	±0.06	±0.07	±0.00	±0.01	±0.00	±0.01	±0.01
B-NT (Poultry)	15.8	45.2	39.0	5.90	32.7	56.7	2.37	6.28	0.31	2.09	0.47	0.11	0.63
	±0.3	±0.5	±0.8	±0.02	±0.2	±0.6	±0.00	±0.11	±0.01	±0.00	±0.02	±0.02	±0.01

TOC = total organic carbon; OM = organic matter; Oxalate-Al = Al-ox; Oxalate-Fe = Fe-ox; Oxalate-Si = Si-ox; TP = total phosphorus; CT = conventional tillage; ST = shallow tillage; NT = no-tillage.

Table 2

Phosphorus sorption parameters of the studied soils. Each value is the mean of three separate measurements.

	A-CT (Pig)	A-ST (Pig)	A-NT (Pig)	B-CT (Poultry)	B-ST (Poultry)	B-NT (Poultry)
EPC_0 (mg L^{-1})	0.039	0.20	0.52	1.16	2.99	3.21
Q_{max} (mg kg^{-1})	1315	1404	1515	1020	1094	1137
WSP (mg L^{-1})	1.19	2.00	2.97	5.01	6.67	7.74
DPS_{OX} (%)	10.27	11.64	12.83	16.12	18.62	20.25

CT = conventional tillage; ST = shallow tillage; NT = no-tillage; EPC_0 = equilibrium phosphorus concentrations; Q_{max} = phosphorus sorption maximum; WSP = water soluble phosphorus; DPS_{OX} = degree of phosphorus saturation.

773 **Table 3**

774 Average concentrations of runoff waters and total P and DOC losses measured during simulated
775 rainfall.

	Runoff volume (mL)	Average P concentration (mg L^{-1})				Total flux (mg)			
		MRDP	TDP	MUDP	DOC	MRDP	TDP	MUDP	DOC
A-CT(Pig)	9405	0.14	0.16	0.023	1.96	1.30	1.46	0.16	12.5
A-ST(Pig)	11945	0.20	0.23	0.033	1.88	2.32	2.68	0.37	12.0
A-NT(Pig)	9506	0.34	0.40	0.061	2.01	3.19	3.66	0.47	12.6
B-CT(Poultry)	11554	0.49	0.58	0.086	2.11	5.60	6.55	0.96	13.5
B-ST(Poultry)	9652	0.93	1.26	0.335	1.73	8.64	11.10	2.46	11.0
B-NT(Poultry)	6149	1.00	1.47	0.460	2.26	6.00	8.20	2.20	13.4

776 The average P concentration in the runoff is the weighted average value of the P concentration in
777 the runoff in each time period; total flux is the sum of P flux in each time period. CT =
778 conventional tillage; ST = shallow tillage; NT = no-tillage, MRDP = molybdate reactive dissolved
779 phosphorus; MUDP = molybdate unreactive dissolved phosphorus; TDP = total dissolved
780 phosphorus; DOC = dissolved organic carbon.

781

Supplementary materials

Table S1

Pearson's correlation analysis between P loss flux and concentration in runoff and P release risk assessment parameters (n = 6).

	Concentration			Flux		
	TDP	MRDP	MUDP	TDP	MRDP	MUDP
EPC_0	0.991**	0.991**	0.976**	0.932**	0.892*	0.990**
Q_{max}	-0.625	-0.653	-0.560	-0.732	-0.740	-0.672
WSP	0.939**	0.959**	0.857**	0.928**	0.903**	0.948**
DPS_{OX}	0.969**	0.980*	0.923**	0.928**	0.903*	0.949**
Dyer-P	0.934**	0.934**	0.871**	0.943**	0.910**	0.981**
Olsen-P	0.937**	0.937**	0.873**	0.881*	0.847*	0.928**

* significant at $P < 0.05$, ** significant at $P < 0.01$; TDP = total dissolved phosphorus; MRDP = molybdate reactive soluble phosphorus; MUDP = molybdate unreactive dissolved phosphorus; EPC_0 = equilibrium phosphorus concentrations; Q_{max} = phosphorus sorption maximum; WSP = water-soluble phosphorus; DPS_{OX} = degree of phosphorus saturation.

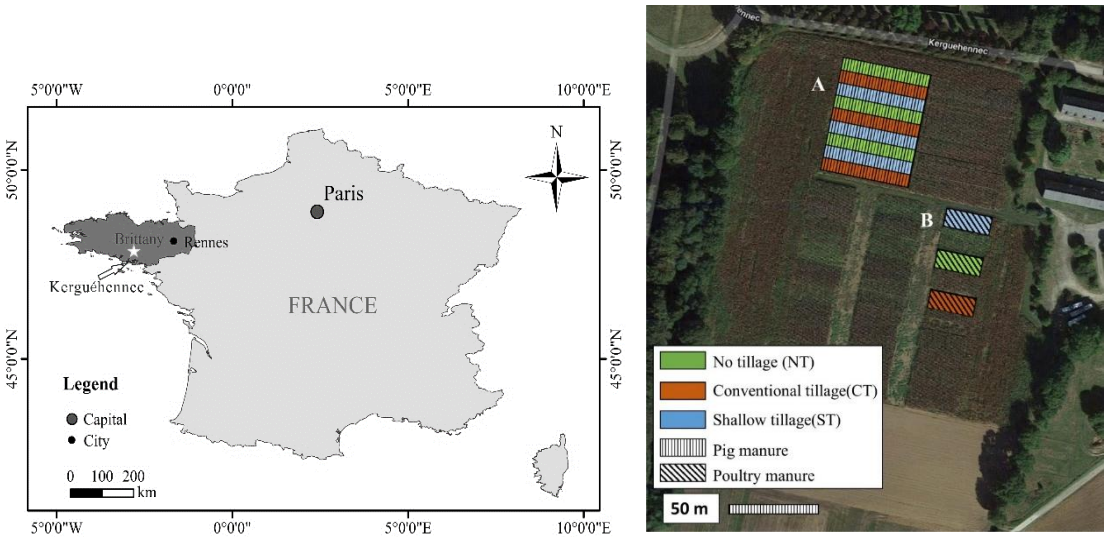
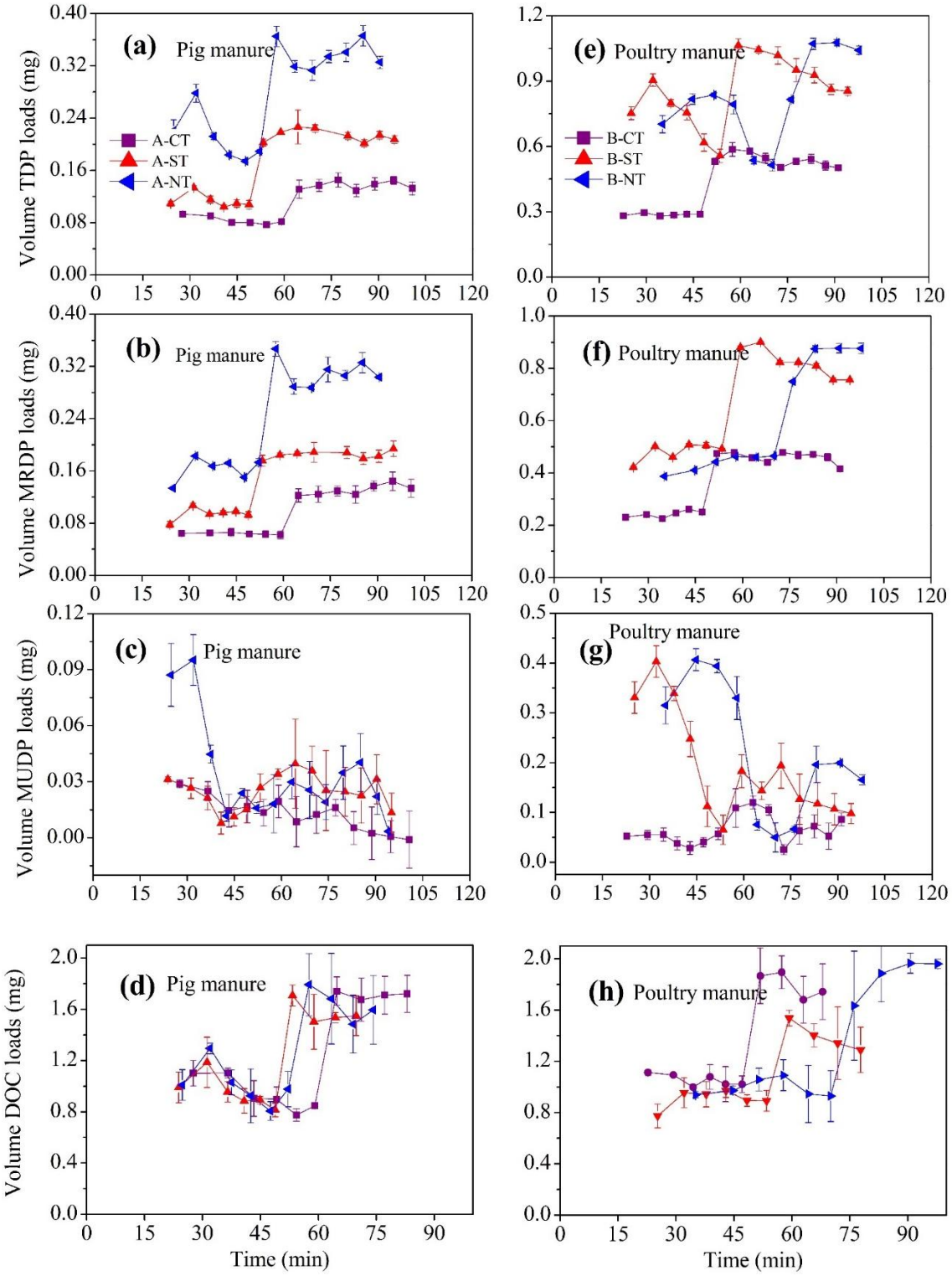


Fig. S1. Location map (left) and aerial photograph (right) of the Kerguéhennec experimental station. Plot A represents the fertilization management with pig manure. Plot B represents the fertilization management with poultry manure.



796

797

798 **Fig. S2.** Influences of tillage (a, c, e, g) and fertilization (b, d, f, h) on flux of TDP, MRDP, MUDP

799 and DOC in runoff during simulated rainfall. TDP = total dissolved phosphorus; MRDP =

800 molybdate reactive dissolved phosphorus; MUDP = molybdate unreactive dissolved phosphorus;

801 DOC = dissolved organic carbon; CT = conventional tillage; ST = shallow tillage; NT = no-tillage.