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1	Conservation practice modify soil phosphorus sorption properties
2	and the composition of dissolved phosphorus losses during runoff
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16	Abstract
17	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

- 19 conventional tillage (CT). However, there is still lack of quantitative descriptors of
- 20 how variations in tillage practices influence soil P sorption properties and how these
- 21 properties in turn control the dissolved P release. Moreover, the control of tillage

practices on the form of dissolved P, particularly molybdate unreactive dissolved 22 phosphorus (MUDP), is still poorly assessed. Thus, we conducted the runoff 23 24 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 25 to bind P, with Olsen-P, Dyer-P, equilibrium phosphorus concentration (EPC₀), water 26 soluble phosphorus (WSP), and degree of phosphorus saturation (DPS_{OX}) increased 27 obviously. The runoff simulation experiment confirmed that the switching from CT to 28 ST and NT could increase the P loss in the event of runoff. The increase was evident 29 30 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 31 MUDP, again with an exacerbated effect in the case of the poultry manure modality, 32 33 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, 34 positive linear correlations were indeed obtained in the five cases, but the results of 35 36 DPS_{OX} was opposite to that of WSP, EPC_0 and available P, suggesting DPS_{OX} was not 37 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 38 release during change to ST and NT, considering that MUDP are bioavailable and 39 therefore also capable of contributing to the eutrophication of surface waters. 40

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

43 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.

48 **1. Introduction**

49 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 50 (Jarvie et al., 2017). Phosphorus losses from cultivated fields to aquatic ecosystems 51 52 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 53 various P forms, dissolved inorganic and organic P are major concerns as they are 54 highly reactive and readily bioavailable for algae growth (Li and Brett, 2013; Van 55 Moorleghem et al., 2013; Jarvie et al., 2017). Thus, reducing the loss of dissolved P 56 from cultivated soils is an essential challenge in the fight against eutrophication of 57 58 surface water (Pizzeghello et al., 2016; Jarvie et al., 2017; Bol et al., 2018; Ulén et al., 2019; Messiga et al., 2021). 59

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.,

64	2020). However, although efficient in reducing particulate P loss, ST and NT may
65	increase the loads of dissolved P in surface soil and thus increase the loss of dissolved
66	P in case of runoff development (Ulén et al., 2010; Pizzeghello et al., 2016; Daryanto
67	et al., 2017). Two mechanisms are commonly invoked to account for this increase: i)
68	enhancing organic P mineralization from crop residues left at the soil surface leading
69	to higher concentration of dissolved P in the topmost soil layers (Deubel et al., 2011);
70	ii) general enrichment in P (and thus also in potentially soluble P) of the soil topmost
71	layers due to the lack of downward transfer and mixing of the P brought to the soil for
72	crop growth (Baker et al., 2017; Daryanto et al., 2017; Jarvie et al., 2017; Duncan et
73	al., 2019). Two emblematic examples, the first one in Erie Lake Basin, the other in
74	Chesapeake Bay basin, reveal an increase in dissolved P loss associated with areas of
75	increased implementation of conservation tillage practices (Ulén et al., 2010; Dodd
76	and Sharpley, 2016; Jarvie et al., 2017; Ni et al., 2020). These results demonstrate that
77	the implementation of ST and NT practices could lead to a shift from particulate P to
78	dissolved P diffusion in rural catchments, with a potentially highly negative impact on
79	freshwater ecosystems, given that dissolved P is more bioavailable than particulate P
80	(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

86	dissolved P diffusion in case of adoption ST and NT practices. Some existing soil P
87	tests originally developed for agronomic purposes work reasonably well to assess soil
88	dissolved P loss risk, such as total phosphorus (TP), Olsen-P, and Dyer-P (Sims, 2000)
89	and could be suitable for that purpose. Recently, other indicators more directly related
90	to the soil properties engaged in P sorption such as the degree of phosphorus
91	saturation (DPS $_{\text{OX}}$) have received interest as a possible indicator of dissolved P
92	release risk in soils (Pöthig et al., 2010; Wang et al., 2016; Fischer et al., 2017). The
93	determination of adsorption isotherms makes it possible to determine the value of
94	equilibrium phosphorus concentration (EPC ₀) in soils, which has been shown to
95	predict well dissolved P concentrations in runoff (Hughes et al., 2000; Munira et al.,
96	2018), and to be also well correlated with DPS_{OX} values (Sims, 2000; Pöthig et al,
97	2010; Fischer et al., 2017). Another parameter which can be determined from
98	adsorption isotherms is the phosphorus sorption maximum (Q_{max}), which quantify the
99	maximum amount of P that a soil can bind. In addition, the amount of water-soluble
100	phosphorus (WSP) is also viewed has a potential efficient indicator for the dissolved P
101	release risk by soils (Pöthig et al., 2010; Xue et al., 2014; Fischer et al., 2017).

102 Although all these four indicators (DPS_{OX} , EPC_0 , Q_{max} , and WSP) are generally 103 accepted for the assessment of dissolved P release risk of soils, their use has not yet 104 been tested as a mean of predicting the increase in dissolved P release risk in case of 105 shifting a plot from conventional tillage (CT) to ST and NT. A key question in this 106 context, with possible important implication for the deployment of ST and NT 107 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), 113 given that these horizons are the layers that ST and NT practices are likely to modify 114 the most with respect to their P sorption properties and P concentrations. The 115 116 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 117 complexes between OM, metal cations such as Fe, Al, Ca and phosphate oxyanions 118 119 (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, 120 the enrichment in OM of the soil surface horizon induced by ST and NT practices 121 122 (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 123 proportion evolve according to the evolution of tillage practices? This question has 124 not yet been addressed to our knowledge. 125

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

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2 **2. Materials and methods**

133 2.1. Site description

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

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

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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).

The B plots comprise three plots (12×25 m, Fig. S1). The fertilization management is receiving poultry manure with three tillage practices (CT, ST, and NT). Cropping system on B plots consists of a corn-wheat rotation. The average annual P input is 156 kg ha⁻¹ (chicken manure = 17.2 g of P per kg). The amount of fertilizer supplied to soils is adjusted annually to ensure the balance between the input and 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.

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2.2. Soil sampling and preparation

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

Soils from six plots were selected for the rainfall simulation experiments. Three plots (A (Pig)-CT, A-ST, and A-NT) were from the A trial, and three plots from B trial (B (Poultry)-CT, B-ST, and B-NT). The surface (0-5cm) soil samples from each excavation were combined to form a composite sample of each studied plot, each composite sample being then air-dried, thoroughly mixed, and sieved (20 mm). Note that the crop was harvested approximately one week prior to the sampling, and that allcrop residues were removed out of soil samples either manually or by sieving.

175 2.3. Rainfall experiment design

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

192

Fig. 1. Rainfall simulation device.

All soil samples used in rainfall experiments were analyzed at the soil analysis 194 laboratory of INRAE in Arras, France, on soil aliquots of about 2 kg sieved at < 2 mm. 195 The soil particle size was classified into three categories: clay (<0.002 mm), silt 196 (0.002-0.05 mm), and sand (0.05-2 mm) (Day, 1965). The organic matter (OM) was 197 measured as loss on ignition (Jensen et al., 1992). The dissolved organic carbon (DOC) 198 concentrations in runoff samples were analyzed with a total organic analyzer 199 (Shimadzu TOC-5050A) (using potassium hydrogen phthalate as the standard solution) 200 (Gu et al., 2018). Soil pH was determined with a pH electrode in a soil to water ratio 201 of 1:5 (NF ISO 10390). The Si-ox/Al-ox/Fe-ox concentrations were determined with 202 ICP-AES after extraction with ammonium oxalate and oxalic acid (Ross and Wang, 203 1993). The TP content was also measured (ICP-AES) after total solubilization with 204 hydrofluoric and perchloric acid (NF X 31-147). Dyer-P was extracted with 20 g L⁻¹ 205 monohydrate citric acid solution (NF X 31-160) and Olsen-P was extracted with 42 g 206 L^{-1} NaHCO₃ (pH = 8.5) (Sims, 2000). 207

The WSP concentrations was determined following the standard method developed by Murphy and Riley (1962). The Q_{max} and EPC₀ were determined based on Langmuir P sorption isotherms obtained using the method proposed by Pöthig et al., (2010). Briefly, the air-dried and sieved soil (< 2 mm) of 1.0 g was suspended in 50 mL of 0.01 M CaCl₂ solution containing various initial P concentrations: 0, 0.5, 1, 5, 10, 25, 50, 75 mg L⁻¹, and centrifuged at 1500 rpm for 10 min, suspensions were 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:

221
$$Q = (c * K * Q_{max}) / (l + K * c)$$
(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 EPC₀ represents the solution P concentration at which no net sorption or desorption of P would occur between soil and solution. To calculate EPC₀ 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 EPC₀ 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):

$$231 DPS_{OX} = P_{OX} / \alpha (Al + Fe)_{OX} (2)$$

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).

236 Molybdate reactive dissolved phosphorus (MRDP) runoff filtrates were 237 determined colorimetrically by direct reaction with ammonium molybdate (Murphy 11 and Riley, 1962). The same method was used for total dissolved phosphorus (TDP), but after digestion of filtrates in acidic potassium persulfate. The precision of MRDP and TDP measurements was ± 4 and $\pm 13 \ \mu g \ L^{-1}$, respectively. The difference between TDP and MRDP was defined as the molybdate unreactive dissolved phosphorus (MUDP), which includes truly dissolved organic P as well as both organic and inorganic P associated with colloidal particles (Haygarth and Sharpley, 2000).

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

247 2.5. Statistical analyses

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

254 **3. Results**

255 *3.1. Soil physicochemical properties*

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

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

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

271 *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 276 with CT, the dissolved P indexes (EPC $_0$ and WSP) that equilibrated with the solid 277 phase P were increased due to the long-term implementation of NT and ST. The 278 average EPC₀ and WSP of soils in CT were 0.60 and 3.10 mg L^{-1} , but they were 279 increased to 1.73 and 4.85 mg L^{-1} after converted to NT and ST, respectively. The 280 potential of soils to bind P exhibited similar characteristics with Q_{max} and DPS_{OX} 281 increased by different extents after converted to NT and ST. The average magnitudes 282 of Q_{max} and DPS_{OX} were increased by 10.3% and 19.7%, respectively. 283

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 EPC₀ and WSP, compared with those in ST. For example, the average values of EPC₀, 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

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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<sub>0</sub> of soils in B-NT increased by 517% compared with A-NT.
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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 299 four steps (Fig. 3). The first step, which lasted between 20 and 50 minutes, started 300 from the onset of rainfall and went on until the first drops of runoff water could be 301 collected in the pipe at the downstream edge of the experimental plate. During this 302 step, water-saturated areas were observed at the soil surface but the lack of connection 303 304 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 305 water saturated surface areas each other and with the runoff collecting pipe device, 306 but runoff flux was low and constant. The third step corresponded to the sudden 307 connection of all water saturated surface area and was marked by a sudden increase of 308 the runoff flux. Finally, the fourth step corresponded to the installation of a 309 steady-state regime during which runoff volumes were high and temporally constant. 310

311 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 MRDP, TDP, MUDP, and DOC concentrations and total fluxes for each of the six 314 rainfall simulation experiments. The volumes of collected runoff water were quite 315 similar for all experiments (between 9400 and 11950 mL), except that soil B-NT, 316 which yielded to a much lower runoff volume (6150 mL). The average TDP, MRDP, 317 MUDP and DOC in runoff waters were in an order NT > ST > CT. Thus, ST and NT 318 markedly increased dissolved P in runoff waters, compared with CT. However, a 319 notable exception was the B-NT experiment, whose highest concentrations were not 320 passed on to the level of total P losses/fluxes due to the delay in the onset of step 4 of 321 the runoff episode recorded and the much lower collected volume of runoff water. 322 In MRDP concentrations increased by 143% and 104% for plot A and B soils, 323

respectively (Table 3). The increase was even greater for MUDP, which was increased by 165 and 434%, respectively. The impact of tillage methods on DOC in runoff was similar to that of dissolved P, with NT yielding higher DOC than other modalities. However, the amplitude of the variations was much lower (increase <10%) than that observed for dissolved P. Clearly, the application of poultry manure increased the concentration of all dissolved P forms in runoff as compared to pig manure, especially MUDP.

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

333	conventional tillage; ST = shallow tillage; NT = no-tillage; MRDP = molybdate reactive dissolved
334	phosphorus; MUDP = molybdate unreactive dissolved phosphorus; TDP = total dissolved
335	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 342 same positive correlations between the relative decrease amplitude and the initial 343 levels as observed for MRDP. A major difference, however, was that the decrease 344 rates of TDP and MUDP were not constant over time. In fact, the decay amplitudes 345 were very strong during the stage 2 of runoff development, and declined then 346 stabilized at very low levels. This dynamic was particularly well expressed by the 347 treatments of A-NT, B-NT, and B-ST, which had highest initial concentrations of TDP 348 and MUDP. 349

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 353

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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 355 topmost soil layers (0-5 cm), indeed, consistent with those reported (Ulén et al., 2010; 356 Baker et al., 2017; Daryanto et al., 2017; Jarvie et al., 2017; Duncan et al., 2019). It is 357 also true that the enrichment of TP in the topmost soil layers in NT and ST increases P 358 agronomical availability (indicated by Olsen-P and Dyer-P) (Table 1), which have 359 been observed in loamy soils (Sokolowski et al., 2020). Compared with soils under 360 CT, soils under ST and NT treatment usually contained high crop residues, which 361 upon degradation by soil organisms are expected to release significant proportions of 362 P (Sokolowski et al., 2020; Ni et al., 2020; Daryanto et al., 2017), which will tend to 363 stay on the soil surface due to lack of mixing imposed by the ST and NT management 364 practices, thus leading to an accumulation of the released P into the topmost soil 365 layers (Zhang et al., 2017). 366

Many previous studies on P sorption characteristics of agricultural soils 367 emphasizes the dominant role of mineral (Al, Fe, Ca), OM content and other soil 368 properties, all of which can increase the capacity of soils to fix newly applied P and 369 thus reduce P loss from soil through (Messiga et al., 2021; Pradhan et al., 2021; 370 371 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 and Al)_{OX} 372 increased or decreased, thus (Fe and Al)_{OX} may not be the key factor affecting soil 373 374 DPS_{OX}.

Increasing soil OM can improve the crop availability of soil P, but it can also 375 increase the risk of P loss. The main mechanism is that OM can reduce the sorption 376 377 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 378 calcium carbonate. The OM will compete with P for binding sites on the surface of 379 these substances. Moreover, OM may bind to the sorption sites thereby increasing the 380 negative charges of the mineral surface, which results in a reduction in the 381 electrostatic attraction between phosphate and soil surface. The reduction of bonding 382 383 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. 384 (2018) as well as this study (Table 3 and Fig. 4). 385

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.

392 *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. 396 The P loss in MUDP accounts for 11-27% of TDP flux with the highest loss occurring 397 398 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 399 quantified in the role of conservation agriculture practices on the risks of dissolved P 400 transfer (Daryanto et al., 2017), and ii) like MRDP, MUDP compartments (organic P 401 and colloidal P) also contains some bioavailable P forms to aquatic organisms (Li and 402 Brett, 2013; Van Moorleghem et al., 2013; Li et al., 2015). Thus, the loss of MUDP is 403 404 of great concern as regards eutrophication risks in cultivated landscapes, and should be taken into account during implementation of conservation agriculture. 405

As shown in Fig. 5, the formation and rapid exhaustion of a MUDP peak 406 407 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 408 Fe(Al)oxide-rich colloids, which is a well-established feature (Liu et al., 2014). It is 409 also well established that drying of the soil matrix generates soil colloids, which can 410 be mobilized and flushed out of the soil matrix during rewetting (Mohanty et al., 411 2015). Runoff development as simulated here is similar to the rewetting of dried soils, 412 so we can reasonably speculate that it is the rewetting processes that results in the loss 413 of P bound to organic-rich colloids as observed by Gu et al. (2018). Based on this 414 origin of MUDP, it is not difficult to explain the observed transient peaks of MUDP at 415 416 the onset of runoff development.

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

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

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

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

Both the results of soil sorption properties and simulation experiments showed that 430 NT and ST aggravated the loss of dissolved P in the topmost soil layers. To explore 431 432 the possibility using soil sorption indicators to predict the dissolved P loss, the relationship between EPC₀, WSP, Q_{max} and DPS_{OX} indicators and the concentration 433 and fluxes of TDP, MRDP, MUDP are analyzed. The results shows that EPC₀, WSP, 434 and DPS_{OX} are positively and significantly correlated with the concentration and 435 fluxes of TDP, MRDP, MUDP in runoff, suggesting that these three indicators could 436 be used to assess P loss risks (Fig. 6; Table S1 in Supplementary Data). The Q_{max} has 437 no correlation with P concentrations and fluxes in runoff (Fig. 6; Table S1 in 438

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.

However, the soil DPS_{OX} was always lower than 25%, indicating that the risk of 446 soil P release was not large (van der Zee et al., 1987), which is contrast to the results 447 of WSP, EPC₀, available P as well as simulated rainfall experiments. Furthermore, 448 DPS_{OX} is also not a good indicator to evaluate the marked increases in dissolved P 449 loss caused by the change in tillage, because this switch not being accompanied by a 450 significant change in DPS, whether in the poultry or pig fertilization modality. 451 Compared with DPS_{OX} , the calculation of EPC_0 and WSP are convenient and simpler 452 soil P release risk assessment indicators. Therefore, EPC₀ and WSP are more suitable 453 for assessing changes in P release risk when shifting soil management from CT to ST 454 and NT. 455

The EPC₀ values show the most significantly positive correlation with MRDP, TDP, and MUDP concentrations and fluxes in runoff ($R^2 = 0.910-0.997$, P < 0.01). The EPC₀ values > 0.03 mg L⁻¹ such as observed in all investigated plots, especially those fertilized with poultry manure, are indicative of a high potential risk of eutrophication due to the capacity of these soils to easily exchange large quantities of

dissolved P with runoff waters (US EPA, 1988). Indiati and Sharpley (1998) and 461 Munira et al. (2018) have found that there is generally a threshold of EPC_0 in soils, the 462 position of which depends on the physicochemical properties of soils (Indiati and 463 Sharpley, 1998; Hughes et al., 2000; Munira et al., 2018). Given that soil EPC₀ is 464 above the threshold, it strongly increases as a function of Olsen-P concentrations. We 465 also find that there are significantly linear correlations between EPC₀ values and 466 bioavailable P contents (Dyer-P and Olsen-P) (Fig. 7a, b). The slopes of the 467 correlations are quite high, indicating that the bioavailable P contents in these soils 468 469 may have exceeded the threshold.

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

483	Finally, soil Olsen-P and Dyer-P contents are also significantly positively
484	correlated with TDP, MRDP and MUDP concentrations and fluxes in runoff (Fig. 6;
485	Table S1 in Supplementary Data). Many published studies have reported such positive
486	correlations between Olsen-P and Dyer-P concentrations in soils and P loss from
487	runoff (Mcdowell et al., 2003; Hopkins and Ellsworth, 2005; Pizzeghello et al., 2016).
488	This means that agronomic soil tests for P can be also used as indicators to assess
489	dissolved P loss risk in soils, since these tests are widespread and not very expensive
490	(Pizzeghello et al., 2016). Some authors have reported a threshold of ca. 60 mg
491	Olsen-P kg ⁻¹ , above which the dissolved P loss risk increases sharply (Heckrath et al.,
492	1995; Johnston and Poulton, 1997). In this study, only for the soils amended with
493	poultry manure had Olsen-P concentrations $> 60 \text{ mg kg}^{-1}$, suggesting the application
494	of poultry manure increases the loss risk of dissolved P in the topmost soil layers.
495	It can also be seen that the four tested indicators (EPC ₀ , WSP, Olsen-P, Dyer-P)
496	define linear correlations of very good quality when they are plotted against each
497	other, with no evidence of a break in the correlations. It can be concluded that in the
498	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 499 surplus of dissolved P loss risk caused by changing soil management from CT to ST 500 and NT. Obviously, one will favor the use of Olsen-P and Dyer-P concentrations for 501 reasons of ease of measurement and lower cost. 502

503 4.4. Implication for management

504

Results from this study confirm that if beneficial for limiting soil erosion and 24

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

In light of these findings, we may recommend to combine NT with other land management techniques (e.g., injection instead of broadcast application of P fertilizer, inclusion of cover crops to scavenge residual P) to limit the risk of dissolved P losses. 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.

531 **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 539 manure)-NT > B-ST > B-CT > A (pig manure)-NT > A-ST > A-CT. Clearly, the 540 application of poultry manure increased the concentration and flux of all dissolved P 541 in runoff waters as compared to pig manure, especially as regards MUDP. Special 542 543 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 544 the early stages of rainfall. The EPC₀, WSP, agronomically Olsen-P and Dyer-P 545 546 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 547

and Dyer-P are also commonly measured by farmers to control crops and aretechnically 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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730 Figure









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

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



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.



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.



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.



751

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



757

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

Table

Table 1

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

	Clay	Silt	Sand	pН	TOC	ОМ	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

765 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.

767 **Table 2**

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

	A-CT (Pig)	A-ST (Pig)	A-NT	B-CT	B-ST	B-NT
			(Pig)	(Poultry)	(Poultry)	(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

769 measurements.

770 $CT = conventional tillage; ST = shallow tillage; NT = no-tillage; EPC_0 = equilibrium phosphorus$

concentrations; Q_{max} = phosphorus sorption maximum; WSP = water soluble phosphorus; DPS_{OX}

772 = degree of phosphorus saturation.

773 **Table 3**

	Runoff	Average	P concen	tration (mg	L ⁻¹)	Total	flux (mg)		
	volume (mL)	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

Average concentrations of runoff waters and total P and DOC losses measured during simulatedrainfall.

The average P concentration in the runoff is the weighted average value of the P concentration in

the runoff in each time period; total flux is the sum of P flux in each time period. CT =

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

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

780 phosphorus; DOC = dissolved organic carbon.

782 Supplementary materials

783 Table S1

785

784 Pearson's correlation analysis between P loss flux and concentration in runoff and P release risk

assessment parameters $(n = 6)$.											
	Concentrat	ion		Flux	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 =

787 molybdate reactive soluble phosphorus; MUDP = molybdate unreactive dissolved phosphorus;

788 EPC₀ = equilibrium phosphorus concentrations; Q_{max} = phosphorus sorption maximum; WSP =

789 water-soluble phosphorus; DPS_{OX} = degree of phosphorus saturation.



792 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.



Fig. S2. Influences of tillage (a, c, e, g) and fertilization (b, d, f, h) on flux of TDP, MRDP, MUDP
and DOC in runoff during simulated rainfall. TDP = total dissolved phosphorus; MRDP =
molybdate reactive dissolved phosphorus; MUDP = molybdate unreactive dissolved phosphorus;
DOC = dissolved organic carbon; CT = conventional tillage; ST = shallow tillage; NT = no-tillage.