Anaerobic respiration in the unsaturated zone of agricultural soil mobilises phosphorus and manganese

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1 ABSTRACT

2 Anaerobic conditions mobilise phosphorus (P) in soils and sediments. The role of anaerobic
3 microsites in well-drained soil on P migration is unknown. This study aimed to identify
4 mechanisms that control field-scale vertical P mobility as affected by organic fertilisers that may
5 trigger variable redox conditions. Soils were sampled at different depths in a well-drained Luvisol
6 after 19-years of application of organic fertilisers. The concentrations of P and manganese (Mn)
7 in 0.45- μm -filtered extracts (10^{-3} M CaCl_2) of field-moist soil samples were strongly correlated (r
8 = + 0.95) and both peaked in and below the compacted plough pan; suggesting that reductive
9 processes mobilise P. Waterlogged soil incubations confirmed that anaerobic respiration co-
10 mobilises Mn and P and that this leads to the release of colloidal P and iron (Fe). The long-term
11 applications of farmyard manure and immature compost enhanced the concentrations of Mn, Fe,
12 and aluminium (Al) in the soil solution of subsurface samples, whereas less such effect was found
13 under the application of more stable organic fertilisers. Farmyard manure application significantly
14 enhanced soil P stocks below the plough layer despite a small P input. Overall, multiple lines of
15 evidence confirm that anaerobic respiration, sparked by labile organic matter, mobilises P in this
16 seemingly well-drained soil.

17 TOC ART

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20 1 INTRODUCTION

21 The legacy excess phosphorus (P) in agricultural soil is a chronic threat for surface water quality.¹
22 Vertical leaching is considered slow and less critical than erosion.¹ The slow migration in soil is
23 due to the large retardation of the orthophosphate anion (PO_4) by sorption on iron (Fe) and
24 aluminium (Al) oxyhydroxides and/or precipitation with calcium (Ca) as Ca-phosphates at high
25 pH values.² The theoretical PO_4 retardation factor in an agricultural soil of the temperate climate
26 is about 2000 (i.e. the time to travel a certain distance relative to that of a non-sorbing compound),
27 which leads to theoretical half-lives of P in topsoil of more than 500 years at a typical annual
28 drainage in temperate regions of 200 mm year^{-1} .^{3,4} However, several field observations do not
29 confirm that theoretical retardation and show marked P migration. For example, two surveys, of
30 Danish and Flemish soil cores, confirmed strong subsurface accumulation of P, down to 60-90 cm
31 depth.^{5,6}

32 The PO_4 mobility can be accelerated in a soil profile by various processes such as colloid-mediated
33 transport and redox-related release of PO_4 . Different column and field studies have confirmed that
34 mobile colloids, i.e. particles with a diameter $< 1 \text{ }\mu\text{m}$, bind PO_4 and facilitate P transport, up to a
35 factor of 50.^{3,7-11} The factors controlling colloid-fluxes are, however, not well known. Increasing
36 Ca^{2+} concentrations decrease organic-matter-(OM)-stabilized Fe and Al oxyhydroxide colloid
37 concentrations in freshwater by enhancing flocculation.^{12,13} This trend is also observed in soil
38 leachates, Fe and Al colloid concentrations sharply rise when solution Ca^{2+} drops below 1 mM .³
39 In addition, decreasing pH in streams is associated with increasing concentration of Fe-rich
40 colloids, likely because acid waters are associated with high dissolved organic carbon (DOC)
41 concentrations and organic anion sorption stabilizes Fe colloids.^{12,14}

Reducing conditions dissolve Fe oxyhydroxides and release sorbed PO_4 , thereby dissolved PO_4 concentrations can increase by several orders of magnitude.^{15,16} This process is well demonstrated in soils submerged for rice culture.¹⁷ Interestingly, Henderson et al. showed that waterlogging soils, incubated in laboratory conditions with the addition of a carbon (C) source, released P-bearing colloids into solution.¹⁸ Ferric Fe, Fe(III), was suggested to act as cement in soil aggregates and its dissolution releases mineral P-bearing colloids. Similarly, drying/rewetting and anoxic/oxic cycles are often found to release P and colloids.^{19,20} It is unclear if that is related to biological processes, such as microbial cell lysis or organic matter disruption, or due to reductive P release.²¹ Manganese (Mn) is an even more redox-sensitive element than Fe, exists in three oxidation states (+II, +III and +IV) in the environment, and its reductive dissolution precedes that of Fe upon waterlogging.²² Manganese (+II) is present as a dissolved cation, Mn(+III) can be both dissolved or form particulate oxyhydroxides and Mn(IV) is present as particulate Mn oxyhydroxides.²³ Rapid Mn redox cycling can control respiration at oxic-anoxic interfaces and in forest floors.^{24,25} In soil, Mn oxyhydroxides form strong associations with Fe oxyhydroxides, especially in redoximorphic soils.^{26,27} Pure Mn oxyhydroxides have a pH-dependent charge with a point-of-zero-charge ranging from 1.5 to 4.6; resulting in a negative charge at near-neutral pH values.²⁶

The role of redox cycling on P migration is generally studied in wetlands, not in well-drained agricultural soils.²¹ However, well-drained soils can have anoxic microsites,²⁸ in which OM decomposition slows down,²⁸ denitrification takes place²⁹ and nitrous oxide (N_2O) and methane (CH_4) are produced.³⁰ Potentially, such microsites may be hot spots for release of P and, as far as known, this process is yet unverified at field-scale. Anoxic microsites form in soil aggregates when oxygen gas (O_2) diffusion into the aggregate is insufficient to compensate for O_2 consumption by micro-organisms.³¹ Large water-filled pore space (WFP) of the aggregates, large content of labile

soil OM and high temperature (T) enhance the anoxic microsite formation.^{29,31} Traditionally, N₂O fluxes have been related to soil physical parameters (large bulk density, T and clay content) and architecture.²⁹ For example, soil compaction and zero-tillage were found to trigger N₂O fluxes as compared to tilled and well-structured soil, especially in warm and wet conditions.²⁹ More recently, a planar optode imaging system showed that microsities (i.e. spaces with less than 5 % oxygen saturation) constituted 14-85 % of the total pore volume, while bulk oxygen concentrations were 40-100 % of saturation.³² This anoxic volume increased with increasing soil clay content.³² In a Retisol, reductive Fe(III) and Mn(IV) dissolution were observed.¹¹ Reduction of Fe(III) minerals in riparian soils can increase P mobility by an order of magnitude¹⁶ and we expect that this can occur within anoxic microsities of well-drained soils.

The objective of this study was to unravel the mechanisms controlling P mobility at field scale and the effect of OM management on these. The Qualiagro long-term field trial, in Feucherolles (France), offers a unique opportunity for this because of the long-term treatments with different organic amendments and because wick samplers are installed that monitor *in situ* leaching from 2013 until present.³³ Soils from this trial had been sampled before for measuring P leaching in disturbed columns.³ That study showed that the leachate P concentrations were in general determined by PO₄ sorption on bulk soil Fe and Al oxyhydroxides and that colloidal forms of these oxyhydroxides accelerated P transport.³ The controlling factors at field scale remain poorly resolved. Therefore, the strategy here was to analyse element associations and seasonality in long-term wick leachates, to analyse P solubility (through CaCl₂ extracts with fresh soil) and speciation (through P K-edge X-ray absorption near edge structure (XANES) spectroscopy) at various depths under various treatments. Finally, to underpin the causality behind the observations, P release and fractionation (“colloidal” versus “truly dissolved”) was experimentally analysed in a waterlogged

88 soil incubation and dialysis experiment. Throughout this work, size classes of the elements are
89 operationally defined. Elements that do pass the 0.45- μm -pore-size-filters but not the dialysis
90 membranes (with a molecular weight cut-off of 10-12 kDa or about 3 nm³⁴) are called “colloids”.
91 “Truly dissolved” elements are those entities that pass the dialysis membranes and are thus smaller
92 than ca. 3 nm.³⁴ Filterable (0.45 μm) elements are referred to as “total ‘dissolved’” and thus include
93 both “colloidal” as “truly dissolved” entities.

94 2 MATERIAL AND METHODS

95 **2.1 Observational part: soil core characterisation, CaCl₂ extracts and wick leachate data**

96 In a long-term field experiment, observations on the solubility of phosphorus (P) in soil were made
97 by analysis of leachate that was collected by wick samplers and by analysis of 0.45- μ m-filtered
98 calcium chloride (CaCl₂) extracts of field-moist soil samples of various depths and treatments (105
99 samples). On all samples, the content of poorly crystalline Fe, Al and Mn oxyhydroxides, the
100 organic carbon content and the nitrogen content were determined. The solid phase P speciation
101 was investigated by P K-edge XANES spectroscopy on a subset of samples.

102 *2.1.1 Field experiment and wick sampler data*

103 The experiment started in 1998 in Feucherolles (Yvelines, France) on a silt loam Glossic Luvisol,
104 a typical arable soil for the Paris Basin (description of soil horizons is given in Figure S1 of the
105 supporting information, SI). The experiment evaluates the agronomic value and environmental
106 impact of different organic amendments. Apart from the mineral N treatment (MIN N), four
107 different organic fertiliser have been applied every two years on an equal carbon (C) basis: an
108 immature municipal solid waste compost (MSW), dairy farmyard manure (FYM) and two more
109 stable, less biodegradable composts, one is a mixture of green waste and the source-separated
110 organic fraction of municipal waste, BIO, and another is compost of green waste, wood chips and
111 sewage sludge, GWS.³⁵ Four glass fibre wick samplers are installed in one field plot per treatment,
112 two at 45 and two 100 cm depth, to collect percolating water (Figure S1).³³ From the autumn of
113 2012 until summer 2018, leachates were pumped out about twice a month, depending on the
114 precipitation and analysed for pH, dissolved organic carbon, DOC; inorganic carbon, IC; nitrate,
115 NO₃⁻; sulphate, SO₄²⁻; chloride, Cl⁻; P; silicon, Si and the major cations; the full list is in Table S1.

Temperature and volumetric moisture content (θ_v) were measured at various depths. More details have been published previously^{33,36} and are provided in SI, section S1.

2.1.2 Soil core sampling and analyses

On the 1st of March 2018, 15 soil cores (three for each plot) were sampled next to the location of the wick samplers, down to a depth of 140 cm. The outside temperature was -2 °C. Each of the soil cores is considered as an independent sampling replicate of a treatment. Sampling was done using a motorized sampler with a hydraulic impact system (Geonor, Norway; 2 cm core diameter). These soil cores were divided into seven layers: 0–28 cm (plough layer with an average bulk density, ρ_b , of 1320 kg m⁻³)³⁷; 28–35 cm (compacted plough pan; ρ_b = 1490 kg m⁻³)³⁷; 35–45 cm; 50–70 cm; 70–90 cm; 90–100 cm and 130–140 cm depth. Each layer was transferred to a closed plastic bag, stored in a cooling box, before being stored at 4° C. The upper soil layer was frozen at the time of sampling while subsurface soil temperature increased with depth: from 2 °C at 40 cm depth to 7 °C at 160 cm (data from 26th of February). The gravimetric moisture content (θ_g) and the calcium chloride (CaCl₂) extractions were performed within two weeks after sampling.

Calcium chloride extractions (1 mM CaCl₂, solid-liquid ratio = 0.25 kg L⁻¹; 24 hours) were performed on duplicate subsamples of each fresh soil sample, but duplicate analytical data were averaged because the statistical tests on treatments only used the mean data of each of three independent sampling replicates. Ten gram of field moist soil was added to a polyethene tube (volume = 50 ml) and 1 mM CaCl₂ solution was added until the tubes were completely filled (i.e. no headspace). These were shaken in an end-over-end shaker (0.42 s⁻¹; T = 20 +/- 2 °C) for 24 hours, centrifuged at 2500 g for ten minutes, filtered over 0.45 µm (Chromafil® Xtra PET-45/25; Macherey-Nagel, Germany), thereby discarding the first droplets, and acidified using concentrated

nitric acid (65 % HNO₃; ultra-pure; Chem-Lab NV, Belgium) to a volume percentage of 1 %; prior to analysis of the concentrations of P, Fe, Al, Mn and Ca by ICP-MS and ferrous Fe, Fe(II), by the ferrozine method.³⁸ The Limit of Quantification (LOQ) for P was 0.15 µM and for Fe(II) 0.52 µM. The pH was measured in the supernatants after centrifugation. A test was performed assessing potential artificial oxidation of soil samples during handling and extraction (section S2). That test showed that the 24-hours CaCl₂ extraction of fresh soil in ambient conditions yielded less total ‘dissolved’ P and Fe (< 0.45 µm) than a comparable extraction inside an anoxic glove box and thus confirms that some oxidation reactions occur at ambient conditions. Hence, our findings based on extractions under ambient conditions underestimate the reduced state of the *in situ* soil. Moreover, several lines of evidence are also given in section S2 that it does not overestimate that reduced state.

Oxalate extractions were performed on air-dried, 2 mm sieved and ground soil samples to determine the concentration of poorly crystalline Fe, Al and Mn oxyhydroxides and associated P.³⁹ The concentrations in that extract were measured by ICP-OES (Inductively Coupled Plasma-Optical Emission Spectroscopy; Thermo Scientific, ICAP 7000 series). Organic carbon (OC) and total nitrogen (N) content were determined in oven-dried (70 °C) subsamples by an elemental analyser (EA1108 Carlo Erba, Val de Reuil, France). The P speciation was investigated by use of P K-edge XANES spectroscopy, which was carried out at BL-8 at the Synchrotron Light Research Institute (SLRI), Nakhon Ratchasima, Thailand (details in section S3).

2.2 Experimental part: waterlogged soil incubations and anoxic dialysis experiment

Waterlogged soil incubations were performed to analyse the possible causality behind the association of P and Mn mobility in the field data. Air-dried soil was incubated for one month

160 under waterlogged conditions and respiration was monitored along with mobilisation of elements,
161 thereby fractionating the solution by sequential filtration (0.45 μm) and dialysis ($< 10\text{-}12\text{ kDa}$).
162 This allowed calculation of operationally defined size classes: “colloidal” ($< 0.45\text{ }\mu\text{m}$; $> 10\text{-}12$
163 kDa or ca. 3 nm^{34}) and “truly dissolved” ($< 10\text{-}12\text{ kDa}$) entities of elements.

164 Additionally to the soil that was sampled on 01/03/2018 (section 2.1.2), extra soil was sampled in
165 the plots amended with farmyard manure (FYM), bio-compost (BIO) and mineral N fertilisers
166 (MIN N). On two lines at 1.0 and 1.5 m distance from the wick samplers, ten cores were sampled
167 (20 in total). Only the soil from the 28-45 and 103-120 cm was retained and all cores per plot were
168 homogenised to yield six samples in total (two depths for the three treatments) and air-dried.
169 Subsamples from these were incubated (in duplicate), while saturated with water, for up to one
170 month, yielding 12 incubations in total.

171 Air-tight glass vials (300 ml) were filled with 50 g air-dried, 2 mm sieved and crushed soil. To
172 this, 250 ml 1 mM CaCl_2 solution was added, yielding a total volume that was slightly below 300
173 ml and an insignificant headspace. The selected Ca^{2+} concentration of 1 mM was considered
174 relevant for *in situ* conditions, wick leachate Ca concentrations ranged 1-4 mM ($\text{P}_{10}\text{-P}_{90}$, see Table
175 S1), higher concentrations could decrease colloidal Fe and Al as Ca^{2+} is a prime colloidal
176 flocculating cation in these conditions. The suspensions were placed on an end-over-end shaker
177 (0.42 s^{-1}) in darkness at $20 \pm 1\text{ }^\circ\text{C}$. At seven moments in time (between one day and one month),
178 the vials were opened inside a glove box with N_2/H_2 (95/5) atmosphere and with platinum
179 catalysers converting any trace O_2 to H_2O (Coy Laboratory Products, Grass Lake, United States)
180 and 18 ml suspension was sampled with a syringe and $0.45\text{-}\mu\text{m}$ -filtered. A 5 mL subsample was
181 dialysed (see below), another subsample was acidified pending ICP-MS analysis, another was used
182 to determine inorganic carbon (IC) in a TOC analyser (Shimadzu, TOC-L), and a final one to

183 determine nitrate via the hydrazanium sulfate reduction method in a continuous flow analyser
184 (Skalar). After sampling, the pH of the suspension was measured and 18 ml of deoxygenated 1
185 mM CaCl₂ was added to maintain a constant volume throughout the experiment. The release of
186 elements was corrected for the removal by sampling (section S4, equation 1). Respiration was
187 calculated from the cumulative release of IC, also corrected for removal by periodic sampling. The
188 inorganic C is ca. 95% in the liquid phase and not in a conservative high estimated headspace
189 volume of 10 mL vial⁻¹. The dialysis of the 5 ml filtered suspension was performed in the glovebox
190 with dialysis bags (molecular weight cut off = 10 – 12 kDa; Spectra/Por® 4 Dialysis Membrane
191 Standard RC Tubing; Spectrum Laboratories, Inc. Rancho Dominguez, United States) against 45
192 mL deoxygenated 1 mM CaCl₂ solution for 24 h on a benchtop end-over-end shaker (0.19 s⁻¹).
193 Preliminary experiments showed that equilibrium was reached within 24 h. The outer solution
194 (dialysate) was sampled, acidified and analysed using ICP-MS to obtain the concentrations of truly
195 dissolved elements.

197 **3.1 Subsoil enrichment with P and speciation as analysed by P K-edge XANES**

198 Nineteen years of excess P input via organic matter application has enriched the subsoil (depth >
199 28 cm) with P (Table S4). Table 1 provides the net P balances (P input through fertilisation minus
200 P export via grains and residues). The composted sludge application (GWS) yielded the highest
201 net P balance ($85.0 \text{ kg P ha}^{-1} \text{ year}^{-1}$) because the annual P application (113 kg P ha^{-1}) was almost
202 fivefold the annual export (28 kg P ha^{-1}). Both the municipal solid waste compost (MSW) and the
203 mineral N treatment (MIN N) yielded a negative P balance, due to their low P content. A significant
204 subsoil enrichment of the oxalate extractable P (P_{Ox}) and the degree of phosphate saturation (DPS,
205 i.e. $P_{\text{Ox}}/0.5(\text{Fe}_{\text{Ox}}+\text{Al}_{\text{Ox}})$), relative to MIN N, was found for GWS down to 50-70 cm, down to 28-
206 35 cm for the farmyard manure application (FYM; p-value is 0.07 for enrichment in 35-45 cm
207 layer, Table S4) and down to 28-35 cm for the bio-compost application (BIO; Table S4).

208 Qualiagro's topsoil (0-28 cm) contains about 20 mmol kg^{-1} poorly crystalline Al (Al_{Ox}); 50 mmol
209 kg^{-1} poorly crystalline Fe (Fe_{Ox}) and 7 mmol kg^{-1} poorly crystalline Mn (Mn_{Ox}); apart from the
210 GWS topsoil that contains $29 \text{ mmol Al kg}^{-1}$ and $60 \text{ mmol Fe kg}^{-1}$ (Table S4). On average, 9 % of
211 the oxalate extractable oxyhydroxide fraction in the topsoil consists of Mn and this fraction does
212 not change with depth in the deeper soil layers (Table S4). The organic carbon (OC) and nitrogen
213 (N) content decrease significantly with depth for all treatments (i.e. the slope of a linear relation is
214 sign. negative $p < 0.0001$).

215 A summary of the P K-edge XANES results is shown in Table S4. Linear combination fitting was
216 used to differentiate between P adsorbed on Al oxyhydroxides, P adsorbed on Fe oxyhydroxides,
217 iron phosphate precipitates (FePO_4 ; not detected in any sample), aluminium phosphate precipitates

(AlPO₄; detected in one sample), calcium phosphates (Ca-P) and organic phosphorus. In all samples, at least 60 % (and up to 70 %) of the P is adsorbed on Fe and Al oxyhydroxides. This is in line with the previously reported finding that leachate P concentrations from columns with these soils were controlled by the sorption of orthophosphate on Fe and Al oxyhydroxides.³ Calcium phosphates were present in all samples, varying between 16 and 36 % of the P, but these are generally considered not-readily exchangeable.⁴⁰ Organic P was present as a minor fraction, generally around 10 %, which is consistent with the relatively low organic C content (~10 g C kg⁻¹) of these soils.

3.2 Observations suggest that anaerobic respiration mobilises colloids and P in the field

A weight of evidence suggests that anaerobic conditions occur in this seemingly well-drained soil and that these conditions mobilise colloids and P, as has been reported previously in wetlands and controlled laboratory redox experiments.^{18,20,41} This evidence is supported by the soil horizon description, trends and element associations in wick leachates and soil extracts and the combination of elemental composition in soil extracts in relation to soil properties, water-filled pore space, soil depth and treatments.

Mottling in the B_{tg} horizon (Figure S1) provides a first clue for redox processes taking place and may be explained by temporal stagnant water since the clay content of the 50-90 cm layer is highest in this zone (30 % vs. 15 % in topsoil).³³

Table S1 shows the summary statistics of all measured variables in the leachates collected by the wicks at 45 cm and 100 cm depth. Forty-seven per cent of the P concentration data are below the limit of quantification (LOQ). A correlation analysis (Table S5) shows that the P concentration is most strongly and positively associated with those of Fe and Mn. In the last drainage season, the

Al concentration was measured and correlates positively with that of Fe ($r = + 0.83$; log-log scale; $p < 0.0001$) and P (Table S5). Moreover, both the concentrations of Mn and Fe decrease with increasing concentration of SO_4^{2-} and NO_3^- (Figure S5). In addition, in June 2016, a Mn and P peak in the leachates coincides with a period of large volumetric moisture content and high temperatures (T) (Figure S6). Birnessite (MnO_2) and Fe(III) and Al oxyhydroxides are insoluble in oxic conditions at neutral pH.^{42,43} Therefore, the positive correlations between the concentrations of Mn, Fe, P and Al suggest that reductive dissolution of Mn(III,IV) and/or Fe(III) occurs and that thereby colloidal $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$ and associated P are released, which is similar to previous findings under experimentally varied redox conditions.^{18,20} Nitrate, and even sulphate, may act as electron acceptor in subsoil in anaerobic conditions and that may explain the negative correlation with the concentrations of Mn and Fe. Furthermore, a seasonal trend is detected: leaching starts usually in December, typically with high P concentrations, the P concentrations are lowest in the months January-March and increase again from March-June, until no more water is leached into the wicks (example in Figure S6). This trend follows the observed temperatures and is similar to the seasonality observed in CaCl_2 extracts from another soil.³⁶ Microbial respiration of organic matter increases with temperature and supplies electrons that may trigger anaerobic reductions once O_2 is depleted.²² This might explain the observed seasonality. Overall, the wick leachates suggest that P release is triggered by reducing conditions.

The soil core sampling and analysis campaign corroborates that anaerobic respiration occurs *in situ*. Table S6 and Table S7 provide soil properties and the correlation table. The elements present in the 0.45- μm -filtered 1 mM CaCl_2 extracts of soil are defined here as “total ‘dissolved’ elements”, these include both truly dissolved and colloidal elements as defined above (section 2.2). The total ‘dissolved’ Mn concentrations ($< 0.45 \mu\text{m}$) range 0.007-5 μM and generally peak in soil

263 samples of the plough pan, the same is true for corresponding P concentrations (Figure 1). Overall,
264 little Fe(II) is detected in the extracts: the 90th percentile is 1.1 µM and only 15 samples (n = 105)
265 have an Fe(II) concentration above the LOQ, i.e. 0.52 µM (8 of these 15 correspond to the farmyard
266 manure treatment, see section 3.4). Anaerobic respiration is expected at a large water-filled pore
267 space (WFP), large organic carbon (OC) content and at low pH. At soil sampling, the average WFP
268 (estimated from the measured gravimetric water content, average bulk densities and the volumetric
269 water contents at saturation for each depth layer^{37,44}) was 80 % in the plough layer while that was
270 95 % in the plough pan (28-35 cm), 87 % in the 35-45 cm layer and 88 - 100 % in the other layers.
271 Hence, soil compaction significantly increased the WFP in the plough pan as compared to the
272 plough layer (Tukey HSD, $p < 0.05$). The type of organic amendment had no significant effect on
273 the estimated WFP (Tukey HSD, $p > 0.05$). For all treatments, the OC content decreases with depth
274 and ranges from 1 to 18 g C kg⁻¹. A multivariate model, using OC content and WFP as input,
275 largely explains total ‘dissolved’ Mn (< 0.45 µM) concentrations ($\text{Log}_{10}(\text{Mn}, \mu\text{M}) = -2.7 +$
276 $1.9\text{log}_{10}(\text{OC}, \text{gC kg}^{-1}) + 0.8\text{WFP}$; $R^2 = 0.82$) and both OC and WFP have a significant effect ($p <$
277 0.05) The pH had no significant effect, likely as there is little pH variation among the samples
278 (Table S6). Large OC content and large WFP co-occur in, and below the plough pan, giving rise
279 to the peak in total ‘dissolved’ Mn (< 0.45 µM) concentrations in those layers (Table 1, Figure 1).
280 The good model fit, the significant effect of both OC content and WFP and the location of Mn
281 solubilisation in the profile suggest that reductive dissolution of Mn oxyhydroxides occurs. The
282 total ‘dissolved’ P concentrations (< 0.45 µM) exhibit a remarkably strong correlation with those
283 of Mn among all depths and treatments (Figure 2). Moreover high total ‘dissolved’ Fe(III) and Al
284 concentrations (< 0.45 µM) are present where high total ‘dissolved’ Mn concentrations (< 0.45
285 µM) are found and Fe(III) and Al are highly positively correlated (Figure S7). At pH values

between 6.4 and 7.6, Fe(III) and Al are likely present as mineral Fe and Al colloids because of the low true solubility of Fe^{3+} and Al^{3+} and their inorganic complexes in natural waters and the low Fe^{3+} and Al^{3+} complexation capacity by dissolved organic matter at neutral pH.^{3,10,42} The high Fe(III)-Al correlation also suggests that Fe(III) is released as colloids rather than as dissolved Fe^{2+} through reductive dissolution.^{7,10,18} Total ‘dissolved’ P ($< 0.45 \mu\text{m}$) logically rises as the degree of phosphate saturation of the soil rises (Figure 2) i.e. as $\text{P}_{\text{Ox}}/0.5(\text{Fe}_{\text{Ox}}+\text{Al}_{\text{Ox}})$ increases with subscript Ox referring to oxalate extraction. The soil extract data hence suggests that not only Mn, but also P, Fe(III) and Al are mobilised where anaerobic conditions occur.

3.3 Waterlogged incubations confirm that anaerobic respiration mobilises phosphorus and manganese

During the waterlogged soil incubations, the concentrations of inorganic carbon (IC) increased and indicate soil respiration. The respiration rate increased with increasing OC content of the sample. After one month of incubation, this resulted in an average cumulative microbial respiration of $19 \pm 8 \text{ mmol C kg}^{-1}$ (mean $\pm$ standard deviation) for the 28-45 cm depth layers and $2.6 \pm 1.6 \text{ mmol C kg}^{-1}$ for the deeper layers with little OC. Due to waterlogging of the 28-45 cm depth layers, denitrification started and reductive Mn dissolution occurred (Figure 3). Total ‘dissolved’ Mn ($< 0.45 \mu\text{m}$) was released up to concentrations of more than $100 \mu\text{M}$, about factor 60 above what was found in fresh soil extracts from corresponding samples of the field (contrast Figure 3 and Table 1). Total ‘dissolved’ Mn ($< 0.45 \mu\text{m}$) was generally present as truly dissolved Mn ($< 10\text{-}12 \text{ kDa}$; Figures 4 and S8), i.e. confirming reduction of Mn(IV) oxyhydroxides to ionic $\text{Mn}^{2/3+}$. Figure 3 shows that reductive dissolution of Mn increases with increasing cumulative respiration and with decreasing pH (i.e. faster Mn release for Min N treatment with initial pH of 6.5 vs. 7.0 for FYM

and BIO) as expected from redox theory. Total ‘dissolved’ Fe ($< 0.45 \mu\text{m}$) but not truly dissolved Fe ($< 12 \text{ kDa}$) increases with increased respiration unless after prolonged respiration (final samples; Figure 4). Anaerobic respiration triggered a P ($< 0.45 \mu\text{m}$) release but only for the soils with sufficient OC to boost respiration and with a sufficient P status (i.e. ‘FYM 28-45 cm’, ‘BIO 28-45 cm’, Figure 3) and the P release linearly related to the Mn release ($p < 0.0001$). A detailed view on the P release and its size fraction shows that mostly colloidal P (i.e. $< 0.45 \mu\text{m}$ and $> 12 \text{ kDa}$) was released and this coincides with the release of colloidal Fe ($\text{Log}_{10}([\text{P}]_{0.45} - [\text{P}]_{12\text{kDa}}) = -0.2 + 0.8\text{Log}_{10}([\text{Fe}]_{0.45} - [\text{Fe}]_{12\text{kDa}})$; $p < 0.0001$). The release of truly dissolved P ($< 12 \text{ kDa}$), likely ionic P or small dissolved organic P, was only found at the final stage of the incubation after prolonged respiration. The incubations of deeper soil layers, with little OC (in contrast to the topsoil samples), showed no reductive release of Mn nor Fe: total ‘dissolved’ Mn ($< 0.45 \mu\text{m}$) remained below $1 \mu\text{M}$ and total ‘dissolved’ Fe was $13 \pm 10 \mu\text{M}$ (standard deviation) and did not increase with respiration (data not shown).

3.4 Application of labile organic matter favours reductive P mobilisation

Table 1 shows how total ‘dissolved’ P, Mn, Fe(II), Fe(III) and Al ($< 0.45 \mu\text{m}$) in the CaCl_2 extracts of the soil relate to the different organic fertiliser applications. The 19 years applications of farmyard manure (FYM) and of municipal solid waste compost (MSW) enhanced total ‘dissolved’ Mn, Fe(III) and Al ($< 0.45 \mu\text{m}$) in the subsoil compared to corresponding elements at corresponding depths in the mineral N treatment (MIN N) treatment. The different organic fertilisers were added on an equal C basis, thus the OM quality may matter. The composting process of the MSW involved a short or sometimes lacking maturation phase, in contrast to the

BIO and GWS composts, leading to a larger biodegradability for the first.³⁵ Compost is a more decomposed and stable product than farmyard manure. Thus, farmyard manure likely introduces more labile OM that can leach and spark reductive processes in the subsoil. Therefore, the MSW and FYM likely enhanced more Fe(III) and Mn(III,IV) reducing reactions in the subsoil than the more stable composts (BIO and GWS). This coincides with higher total ‘dissolved’ P ($< 0.45 \mu\text{m}$) as well. Colloid-mediated P leaching was previously suggested to explain the higher P concentrations in column leachates for FYM than that for BIO, despite the two times larger net P balance for the latter.³ The Mn and Fe(III) concentrations in the 90-100 cm depth layers are significantly higher for FYM as compared to that for BIO. The data of GWS with high total ‘dissolved’ P concentrations ($< 0.45 \mu\text{m}$) obviously deviate from the trend because of the excess P that was added in the GWS treatment (Table 1).

3.5 Discrepancy between wicks and extracts: artificial oxidation

The concentrations of P, Fe, Al and Mn in the 1 mM CaCl_2 extracts of field-moist soils, sampled from the 35-45 cm layers (near the wick sampler depth), are orders of magnitude larger than those measured in the wick samplers of corresponding treatments and sampling time at 45 cm depth (Table S8). The leachates are stored in tanks and pumped out twice a month and colloid aggregation and/or sedimentation on the tank bottom may occur. Other wick samplers had been removed in 2010 and were clearly loaded with colloids after about 6 years of use (as shown by a reddish colour on the wicks). The Ca concentration in the CaCl_2 extracts of field-moist soil ranged 0.97-1.3 mM (measured after extraction; $\text{P}_{10}\text{-P}_{90}$) while wick leachates Ca^{2+} ranged 1-4. This difference in Ca^{2+} concentration is not fully explaining the difference in Fe and Al between wicks and extracts. For the MIN N treatment, for example, there is no difference in the Ca concentration between the soil extracts and the wick samples, but still a factor six difference in that of P, 23 in

that of Fe, 38 in that of Al and 14 in that of Mn. Most likely, wick samplers introduce sampling artefacts and do not reflect the *in situ* (redox) state. Artificial oxidation of Fe^{2+} and $\text{Mn}^{2/3+}$ and retention of colloids/particles might occur in the wicks. This does, however, not imply that the CaCl_2 extracts offer a single true representation of the soil solution that is free from artefacts (see also section SI S2).

3.6 Environmental significance

Taken together, this study provides multiple lines of evidence for anaerobic respiration and reduction of Mn(IV) oxyhydroxides, even in a relatively well-drained unsaturated soil, and that this enhances the mobilisation of P. This P mobilisation is likely as colloidal P as demonstrated in the laboratory conditions. We have additionally calculated the speciation of P in the soil extracts of the field (details not shown) using methods and assumption that we previously described.³ This calculation showed that P is mainly colloidal-bound on the Fe(III) and Al mineral colloids. Hence, the data suggest that Mn reduction triggers the release of colloidal Al and Fe(III) that, in turn, is able to act as a mobile P-vector. Reductive dissolution of Fe(III), releasing ionic P, might also be involved as shown by (1) a limited number of enhanced Fe(II) concentrations, e.g. under FYM (Table 1) and (2) the incubation experiment at prolonged respiration (Figure 4). In addition, Fe(III) reduction in the microsites (inside aggregates) might release Fe(II) that is subsequently oxidised in larger, oxygen-rich pores (between aggregates), forming colloidal Fe(III). Moreover, it cannot be excluded that oxidation of Fe(II) to Fe(III) upon sampling and soil extraction under ambient conditions occurs. Long-term application of labile and mobile organic matter stimulates reductive P release where the WFP is larger, e.g. in the compacted plough pan. Modelling P transport in soil is now required to identify to what extent reductive P mobilisation contributes to accelerated leaching beyond what is to be expected based on the local sorption equilibrium assumption with

377 no redox related processes. The link between redox cycling and P solubility should be considered
378 to fully understand the dynamics of P in saturated *and* unsaturated agricultural soil and its vertical
379 P migration towards groundwater.

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383

384 **Author Contributions**

385 The manuscript was written through the contributions of all authors. All authors have given
386 approval of the final version of the manuscript.

387 **Funding**

388 FWO (Research Foundation Flanders): strategic basic research grant.

389 **Notes**

390 The authors declare no competing financial interest.

391 ACKNOWLEDGMENTS

392 Thanks to J.-C. Gueudet, the ECOSYS team, all colleagues (especially S. Ysabee) of the Division
393 of Soil and Water Management (KU Leuven). Thanks to Wantana Klysubun and her team at BL-
394 8, SLRI, Thailand for professional help with P K-edge XANES analysis. The QualiAgro field
395 experiment is part of the SOERE-PRO (network of long-term experiments dedicated to the study
396 of impacts of OM recycling), integrated as a service of the “Investment in the Future” infrastructure
397 AnaEE-France, overseen by the French National Research Agency (ANR-11-INBS-0001). It has
398 been founded and is still supported by INRA and Veolia R&I. Thanks to T. Driessens.

399

400 **Supporting Information.**

401 **Section S1** The Qualiagro field experiment and wick samplers (Figure S1, Table S1)

402 **Section S2** Test for potential oxidation during soil handling and CaCl₂ extraction on field-moist
403 soil. (Table S2, Figure S2)

404 **Section S3** P K-edge XANES spectroscopy. (Figure S3, Figure S4, Table S3)

405 **Section S4** Correction factor waterlogged soil incubations

406 **Table S4** Selected average soil properties.

407 **Table S5** Correlation analyses wick data.

408 **Figure S5** Correlations between Fe and Mn versus nitrate and sulphate in the wick samples.

409 **Figure S6** Mn and P concentrations peak in wick leachates in June 2016 at high temperature and
410 moisture content.

411 **Table S6** Summary statistics of the soil properties (all depths & treatments).

412 **Table S7** Correlation analyses soil properties.

413 **Figure S7** Total 'dissolved' Fe(III) vs. Al and Fe(III)+Al vs. Mn

414 **Figure S8** Total 'dissolved' Mn (< 0.45 µm) vs. Truly dissolved Mn (< 12 kDa).

415 **Table S8** Comparison between solutes measured in wicks and CaCl₂ extracts.

416 This information is available free of charge via the internet at <http://pubs.acs.org>.

417

419
420 **Figure 1** Soil depth profiles of Mn and P concentrations in field-moist soil extracts (1 mM CaCl₂, 0.45-μm-filtered) show that both are
421 mobilised in and below the compacted plough pan (28-35 cm), where large organic carbon (OC) content and large water-filled pore
422 space co-occur. The shown profiles are those of field plots amended with mineral N and farmyard manure for 19 years, the other
423 treatments yield similar trends. Trend lines are shown to guide the eye.

424

425 **Figure 2** The correlations among P, Mn, and Fe(III) + Al concentrations in field-moist soil extracts (1 mM CaCl_2 , 0.45- μm -filtered) of
 426 all samples, i.e. all depths and soil treatments. High Mn concentrations indicate anaerobic conditions, Fe(III) and Al likely occur as
 427 colloids that bind P (see text). The P mobilisation also depends on the internal loading of the soil, i.e. the degree of phosphate saturation,
 428 i.e. $P_{\text{Ox}}/0.5(\text{Fe}_{\text{Ox}} + \text{Al}_{\text{Ox}})$ with $_{\text{ox}}$ referring to oxalate extraction. Note that molar P concentrations are about one order of magnitude larger
 429 than those of Mn, excluding the possibility for P being bound to colloidal Mn mineral particles.

430

431 **Figure 3** Sequential redox reactions and phosphorus release during anoxic incubation of the 28-45 cm depth layers (1 to 30 days) in
 432 waterlogged conditions (1 to 30 days; 5 L kg⁻¹; 1 mM CaCl₂ that was not deoxygenated) at 20 °C. Once all oxygen and nitrate (NO₃) is
 433 consumed, total ‘dissolved’ Mn, Fe and P concentrations (< 0.45 μm) are released but only for the soils with large P loading
 434 ($P_{Ox}/0.5(Fe_{Ox}+Al_{Ox})$) and large respiration. Trend lines are shown to guide the eye.

Figure 4 The release and size fractionation of Mn, Fe, and P upon anaerobic respiration of the ‘FYM 28-45 cm’ and ‘BIO 28-45 cm’ samples. During the initial phases of Mn and Fe release, mostly colloidal P (< 0.45 μm ; > 10-12 kDa) is released. Black points are total ‘dissolved’ concentrations (< 0.45 μm), grey points are 10-12 kDa dialysed concentrations and the difference is indicated by the green double arrow, i.e. colloidal concentrations. Trend lines are shown to guide the eye. For the first time point for ‘FYM 28-45 cm’ and for the first, fifth and sixth time point for ‘BIO 28-45 cm’, dialyzable P could not be determined due to a P contamination in the dialysates.

Table 1 Treatment effects on the total ‘dissolved’ (< 0.45 μm) concentrations of P, Mn, Fe(II), Fe(III) and Al in the 1 mM CaCl_2 extracts of field-moist soils. Means and standard errors (SE) are presented (n = 3). Significant differences between treatments are indicated with capital letters (Tukey HSD test, $p < 0.05$) when tested at corresponding depths. Bold values denote concentrations exceeding the corresponding control (MIN N). Logically, a large degree of phosphate saturation (DPS, Table S4) results in elevated P concentrations, e.g. GWS treatment with the largest P balance*.

		Treatment									
		MIN N		MSW		FYM		BIO		GWS	
P balance* (kg P ha ⁻¹ year ⁻¹)		-23		-2.8		11		20		85	
Element	depth (cm)	mean	SE	mean	SE	mean	SE	mean	SE	mean	SE
[P] (μM)	0-28	4.6 ^D	1.2	6.5 ^{C,D}	0.57	18^{A,B}	2.2	11^{B,C}	0.71	28^A	4.1
	28-35	5.8 ^C	0.82	6.4 ^C	0.75	24^{A,B}	3.4	14^B	1.8	31^A	5.8
	35-45	4.5 ^A	0.82	6.7 ^A	0.63	29 ^A	5.8	13 ^A	3.6	26 ^A	11
	50-70	0.60 ^B	0.14	1.9 ^{A,B}	0.19	4.9^A	0.40	1.3 ^{A,B}	0.16	4.4^A	2.2
	70-90	0.23 ^B	0.05	0.92^A	0.13	0.69^A	0.10	0.51 ^{A,B}	0.14	0.62 ^{A,B}	0.14
	90-100	0.16 ^C	0.04	0.64^A	0.04	0.55^{A,B}	0.11	0.27 ^{A,B,C}	0.04	0.26 ^{B,C}	0.03
	130-140	0.20	0.07	0.35	0.03	0.34	0.08	0.29	0.05	0.23	0.02
[Fe(II)] (μM)	0-28	0.60	0.34	< 0.52	-	< 0.52	-	< 0.52	-	< 0.52	-
	28-35	< 0.52	-	1.4	1.1	1.1	0.86	< 0.52	-	0.70	0.44
	35-45	< 0.52	-	1.2	0.73	2.2	1.91	< 0.52	-	0.40	0.14
	50-70	< 0.52	-	< 0.52	-	5.4	4.4	< 0.52	-	< 0.52	-
	70-90	< 0.52	-	< 0.52	-	0.46	0.20	< 0.52	-	< 0.52	-
	90-100	< 0.52	-	< 0.52	-	0.46	0.20	< 0.52	-	< 0.52	-
	130-140	< 0.52	-	< 0.52	-	0.82	0.28	< 0.52	-	< 0.52	-
[Mn] (μM)	0-28	0.37	0.12	0.65	0.15	0.71	0.09	0.65	0.19	0.58	0.13
	28-35	0.60	0.19	0.86	0.22	1.7	0.31	2.0	0.76	2.0	1.4
	35-45	0.43	0.11	1.1	0.15	3.0	1.2	2.0	1.0	1.5	0.67
	50-70	0.09 ^B	0.02	0.36 ^{A,B}	0.03	0.83^A	0.26	0.21 ^{A,B}	0.03	0.49 ^{A,B}	0.21
	70-90	0.03 ^B	0.01	0.11^A	0.02	0.10^A	0.01	0.06 ^{A,B}	0.02	0.07 ^{A,B}	0.02
	90-100	0.02 ^B	0.002	0.06^A	0.003	0.06^A	0.01	0.03 ^B	0.01	0.02 ^B	0.002
	130-140	0.02 ^{A,B}	0.003	0.04 ^A	0.01	0.05 ^A	0.01	0.04 ^A	0.01	0.01 ^B	0.002
[Fe(III)] (μM)	0-28	13	3.2	23	4.7	23	3.4	14	2.2	17	1.7
	28-35	16 ^B	0.48	21 ^{A,B}	1.2	35^A	1.7	20 ^{A,B}	2.2	27 ^{A,B}	3.7
	35-45	15	4.1	25	3.7	53	17	28	7.0	37	14
	50-70	10	3.7	16	1.1	32	7.5	12	2.1	22	7.1
	70-90	4.4	2.5	24	5.1	17	3.1	9.3	5.5	11	2.8
	90-100	3.1 ^B	1.7	16^A	1.7	13^A	3.4	4.5 ^B	1.1	2.7 ^B	0.59
	130-140	2.9 ^{A,B}	1.0	8.2 ^A	0.50	7.2 ^A	2.0	5.8 ^A	1.5	1.6 ^B	0.48
[Al] (μM)	0-28	46	10	48	6.1	60	8.0	44	6.4	37	1.3
	28-35	57	12	48	1.8	82	14	68	5.4	51	4.2
	35-45	69	12	52	3.0	13 10 ¹	60	11 10 ¹	23	57	12
	50-70	37	8.8	46	1.1	11 10 ¹	42	53	6.0	46	11
	70-90	16	5.3	42	5.6	43	2.7	31	15	26	5.5
	90-100	11 ^B	2.9	36^A	3.0	37^A	11	15 ^{A,B}	3.0	8.5 ^B	1.3
	130-140	10 ^{A,B}	1.0	22 ^A	1.2	21 ^A	5.6	19 ^A	4.9	5.9 ^B	1.3

*The P balance was calculated from recorded P applications and crop P offtake with exported grains and residues.

REFERENCES

- (1) Jarvie, H. P.; Sharpley, A. N.; Spears, B.; Buda, A. R.; May, L.; Kleinman, P. J. A. Water Quality Remediation Faces Unprecedented Challenges from “Legacy Phosphorus.” *Environ. Sci. Technol.* **2013**, *47* (16), 8997–8998. <https://doi.org/10.1021/es403160a>.
- (2) Weng, L.; Vega, F. A.; Van Riemsdijk, W. H. Competitive and Synergistic Effects in PH Dependent Phosphate Adsorption in Soils: LCD Modeling. *Environ. Sci. Technol.* **2011**, *45*, 8420–8428. <https://doi.org/10.1021/es201844d>.
- (3) Warrinnier, R.; Goossens, T.; Amery, F.; Vanden Nest, T.; Verbeeck, M.; Smolders, E. Investigation on the Control of Phosphate Leaching by Sorption and Colloidal Transport : Column Studies and Multi-Surface Complexation Modelling. *Appl. Geochemistry* **2019**, *100* (November 2018), 371–379. <https://doi.org/10.1016/j.apgeochem.2018.12.012>.
- (4) Langmuir, D. *Aqueous Environmental Chemistry*; McConnin, R., Ed.; Pretice Hall, Inc.: New Jersey, 1997.
- (5) Rubæk, G. H.; Kristensen, K.; Olesen, S. E.; Østergaard, H. S.; Heckrath, G. Phosphorus Accumulation and Spatial Distribution in Agricultural Soils in Denmark. *Geoderma* **2013**, *209–210*, 241–250. <https://doi.org/10.1016/j.geoderma.2013.06.022>.
- (6) De Bolle, S.; De Neve, S.; Hofman, G. Rapid Redistribution of P to Deeper Soil Layers in P Saturated Acid Sandy Soils. *Soil Use Manag.* **2013**, *29* (SUPPL.1), 76–82. <https://doi.org/10.1111/j.1475-2743.2012.00426.x>.
- (7) Regelink, I. C.; Koopmans, G. F.; van der Salm, C.; Weng, L.; van Riemsdijk, W. H. Characterization of Colloidal Phosphorus Species in Drainage Waters from a Clay Soil

- 471 Using Asymmetric Flow Field-Flow Fractionation. *J. Environ. Qual.* **2013**, 42 (2), 464.
472 <https://doi.org/10.2134/jeq2012.0322>.
- 473 (8) Siemens, J.; Ilg, K.; Lang, F.; Kaupenjohann, M. Adsorption Controls Mobilization of
474 Colloids and Leaching of Dissolved Phosphorus. *Eur. J. Soil Sci.* **2004**, 55 (2), 253–263.
475 <https://doi.org/10.1046/j.1365-2389.2004.00596.x>.
- 476 (9) Beauchemin, S.; Simard, R. R.; Cluis, D. Forms and Concentration of Phosphorus in
477 Drainage Water of Twenty-Seven Tile-Drained Soils. *J. Environ. Qual.* **1998**, 27 (3), 721.
478 <https://doi.org/10.2134/jeq1998.00472425002700030033x>.
- 479 (10) Baken, S.; Regelink, I. C.; Comans, R. N. J.; Smolders, E.; Koopmans, G. F. Iron-Rich
480 Colloids as Carriers of Phosphorus in Streams: A Field-Flow Fractionation Study. *Water*
481 *Res.* **2016**, 99, 83–90. <https://doi.org/10.1016/j.watres.2016.04.060>.
- 482 (11) Cornu, S.; Samouëlian, A.; Ayzac, A.; Montagne, D. Soluble and Colloidal Translocation
483 of Al, Fe, Si and Mn in an Artificially Drained French Retisol. *Geoderma* **2018**, 330 (June),
484 193–203. <https://doi.org/10.1016/j.geoderma.2018.05.032>.
- 485 (12) Baken, S.; Moens, C.; Van Der Grift, B.; Smolders, E. Phosphate Binding by Natural Iron-
486 Rich Colloids in Streams. *Water Res.* **2016**, 98, 326–333.
487 <https://doi.org/10.1016/j.watres.2016.04.032>.
- 488 (13) Philippe, A.; Schaumann, G. E. C. *Environ. Sci. Technol.* **2014**, 48 (16), 8946–8962.
489 <https://doi.org/10.1021/es502342r>.
- 490 (14) Lofts, S.; Tipping, E.; Hamilton-Taylor, J. The Chemical Speciation of Fe(III) in

- 491 Freshwaters. *Aquat. Geochemistry* **2008**, *14* (4), 337–358. <https://doi.org/10.1007/s10498->
492 008-9040-5.
- 493 (15) Smolders, E.; Baetens, E.; Verbeeck, M.; Nawara, S.; Diels, J.; Verdievel, M.; Peeters, B.;
494 De Cooman, W.; Baken, S. Internal Loading and Redox Cycling of Sediment Iron Explain
495 Reactive Phosphorus Concentrations in Lowland Rivers. *Environ. Sci. Technol.* **2017**, *51*
496 (5), 2584–2592. <https://doi.org/10.1021/acs.est.6b04337>.
- 497 (16) Gu, S.; Gruau, G.; Dupas, R.; Petitjean, P.; Li, Q.; Pinay, G. Respective Roles of Fe-
498 Oxyhydroxide Dissolution, PH Changes and Sediment Inputs in Dissolved Phosphorus
499 Release from Wetland Soils under Anoxic Conditions. *Geoderma* **2019**, *338* (June 2018),
500 365–374. <https://doi.org/10.1016/j.geoderma.2018.12.034>.
- 501 (17) Kirk, G. *The Biogeochemistry of Submerged Soils*; John Wiley & Sons, Ltd: Chichester,
502 UK, 2004. <https://doi.org/10.1002/047086303X>.
- 503 (18) Henderson, R.; Kabengi, N.; Mantripragada, N.; Cabrera, M.; Hassan, S.; Thompson, A.
504 Anoxia-Induced Release of Colloid- and Nanoparticle-Bound Phosphorus in Grassland
505 Soils. *Environ. Sci. Technol.* **2012**, *46* (21), 11727–11734.
506 <https://doi.org/10.1021/es302395r>.
- 507 (19) Blackwell, M. S. A.; Brookes, P. C.; de la Fuente-Martinez, N.; Murray, P. J.; Snars, K. E.;
508 Williams, J. K.; Haygarth, P. M. Effects of Soil Drying and Rate of Re-Wetting on
509 Concentrations and Forms of Phosphorus in Leachate. *Biol. Fertil. Soils* **2009**, *45* (6), 635–
510 643. <https://doi.org/10.1007/s00374-009-0375-x>.
- 511 (20) Thompson, A.; Chadwick, O. A.; Boman, S.; Chorover, J. Colloid Mobilization during Soil

- 512 Iron Redox Oscillations. *Environ. Sci. Technol.* **2006**, *40* (18), 5743–5749.
513 <https://doi.org/10.1021/es061203b>.
- 514 (21) Gu, S.; Gruau, G.; Dupas, R.; Rumpel, C.; Crème, A.; Fovet, O.; Gascuel-Oudou, C.;
515 Jeanneau, L.; Humbert, G.; Petitjean, P. Release of Dissolved Phosphorus from Riparian
516 Wetlands: Evidence for Complex Interactions among Hydroclimate Variability,
517 Topography and Soil Properties. *Sci. Total Environ.* **2017**, *598* (November), 421–431.
518 <https://doi.org/10.1016/j.scitotenv.2017.04.028>.
- 519 (22) Borch, T.; Kretzschmar, R.; Skappler, A.; Van Cappellen, P.; Ginder-Vogel, M.; Voegelin,
520 A.; Campbell, K. Biogeochemical Redox Processes and Their Impact on Contaminant
521 Dynamics. *Environ. Sci. Technol.* **2010**, *44* (1), 15–23. <https://doi.org/10.1021/es9026248>.
- 522 (23) Madison, A. S.; Tebo, B. M.; Mucci, A.; Sundby, B.; Luther, G. W. Abundant Porewater
523 Mn(III) Is a Major Component of the Sedimentary Redox System. *Science* (80-.). **2013**,
524 *341* (6148), 875–878. <https://doi.org/10.1126/science.1241396>.
- 525 (24) Keiluweit, M.; Nico, P.; Harmon, M. E.; Mao, J.; Pett-Ridge, J.; Kleber, M. Long-Term
526 Litter Decomposition Controlled by Manganese Redox Cycling. *Proc. Natl. Acad. Sci.*
527 **2015**, *112* (38), E5253–E5260. <https://doi.org/10.1073/pnas.1508945112>.
- 528 (25) Jones, M. E.; Nico, P. S.; Ying, S.; Regier, T.; Thieme, J.; Keiluweit, M. Manganese-Driven
529 Carbon Oxidation at Oxic-Anoxic Interfaces. *Environ. Sci. Technol.* **2018**, *52* (21), 12349–
530 12357. <https://doi.org/10.1021/acs.est.8b03791>.
- 531 (26) Gilkes, R. J.; McKenzie, R. M. Geochemistry and Mineralogy of Manganese in Soils.
532 *Manganese in Soils and Plants* **1988**, *1*, 23–35. <https://doi.org/10.1007/978-94-009-2817->

533 6_3.

- 534 (27) Gasparatos, D.; Massas, I.; Godelitsas, A. Fe-Mn Concretions and Nodules Formation in
535 Redoximorphic Soils and Their Role on Soil Phosphorus Dynamics: Current Knowledge
536 and Gaps. *Catena* **2019**, *182* (June), 104106. <https://doi.org/10.1016/j.catena.2019.104106>.
- 537 (28) Keiluweit, M.; Wanzek, T.; Kleber, M.; Nico, P.; Fendorf, S. Anaerobic Microsites Have
538 an Unaccounted Role in Soil Carbon Stabilization. *Nat. Commun.* **2017**, *8* (1), 1–8.
539 <https://doi.org/10.1038/s41467-017-01406-6>.
- 540 (29) Ball, B. C. Soil Structure and Greenhouse Gas Emissions: A Synthesis of 20 Years of
541 Experimentation. *Eur. J. Soil Sci.* **2013**, *64* (3), 357–373.
542 <https://doi.org/10.1111/ejss.12013>.
- 543 (30) Brewer, P. E.; Calderón, F.; Vigil, M.; von Fischer, J. C. Impacts of Moisture, Soil
544 Respiration, and Agricultural Practices on Methanogenesis in Upland Soils as Measured
545 with Stable Isotope Pool Dilution. *Soil Biol. Biochem.* **2018**, *127* (February), 239–251.
546 <https://doi.org/10.1016/j.soilbio.2018.09.014>.
- 547 (31) Keiluweit, M.; Nico, P. S.; Kleber, M.; Fendorf, S. Are Oxygen Limitations under
548 Recognized Regulators of Organic Carbon Turnover in Upland Soils? *Biogeochemistry*
549 **2016**, *127* (2–3), 157–171. <https://doi.org/10.1007/s10533-015-0180-6>.
- 550 (32) Keiluweit, M.; Gee, K.; Denney, A.; Fendorf, S. Anoxic Microsites in Upland Soils
551 Dominantly Controlled by Clay Content. *Soil Biol. Biochem.* **2018**, *118* (December), 42–
552 50. <https://doi.org/10.1016/j.soilbio.2017.12.002>.

- 553 (33) Cambier, P.; Pot, V.; Mercier, V.; Michaud, A.; Benoit, P.; Revallier, A.; Houot, S. Impact
554 of Long-Term Organic Residue Recycling in Agriculture on Soil Solution Composition and
555 Trace Metal Leaching in Soils. *Sci. Total Environ.* **2014**, *499*, 560–573.
556 <https://doi.org/10.1016/j.scitotenv.2014.06.105>.
- 557 (34) Erickson, H. P. Size and Shape of Protein Molecules at the Nanometer Level Determined
558 by Sedimentation, Gel Filtration, and Electron Microscopy. *Biol. Proced. Online* **2009**, *11*
559 (1), 32–51. <https://doi.org/10.1007/s12575-009-9008-x>.
- 560 (35) Noirot-Cosson, P. E.; Vaudour, E.; Gilliot, J. M.; Gabrielle, B.; Houot, S. Modelling the
561 Long-Term Effect of Urban Waste Compost Applications on Carbon and Nitrogen
562 Dynamics in Temperate Cropland. *Soil Biol. Biochem.* **2016**, *94*, 138–153.
563 <https://doi.org/10.1016/j.soilbio.2015.11.014>.
- 564 (36) Vanden Nest, T.; Ruyschaert, G.; Vandecasteele, B.; Houot, S.; Baken, S.; Smolders, E.;
565 Cougnon, M.; Reheul, D.; Merckx, R. The Long Term Use of Farmyard Manure and
566 Compost: Effects on P Availability, Orthophosphate Sorption Strength and P Leaching.
567 *Agric. Ecosyst. Environ.* **2016**, *216*, 23–33. <https://doi.org/10.1016/j.agee.2015.09.009>.
- 568 (37) Chalhoub, M.; Garnier, P.; Coquet, Y.; Mary, B.; Lafolie, F.; Houot, S. Increased Nitrogen
569 Availability in Soil after Repeated Compost Applications: Use of the PASTIS Model to
570 Separate Short and Long-Term Effects. *Soil Biol. Biochem.* **2013**, *65*, 144–157.
571 <https://doi.org/10.1016/j.soilbio.2013.05.023>.
- 572 (38) Viollier, E.; Inglett, P. W.; Hunter, K.; Roychoudhury, A. N.; Van Cappellen, P. The
573 Ferrozine Method Revisited: Fe (II)/Fe (III) Determination in Natural Waters. *Appl.*

574 *Geochemistry* **2000**, 15 (6), 785–790. [https://doi.org/10.1016/S0883-2927\(99\)00097-9](https://doi.org/10.1016/S0883-2927(99)00097-9).

575 (39) Schwertmann, U. The Differentiation of Iron Oxides in Soils by Extraction with
576 Ammonium Oxalate Solution. *J. Plant Nutr. Soil Sci.* **1964**, 105, 194–202.

577 (40) Demaria, P.; Flisch, R.; Frossard, E.; Sinaj, S. Exchangeability of Phosphate Extracted by
578 Four Chemical Methods. *J. Plant Nutr. Soil Sci.* **2005**.
579 <https://doi.org/10.1002/jpln.200421463>.

580 (41) Gu, S. Release of Dissolved and Colloidal Phosphorus from Riparian Wetlands: A Field
581 and Laboratory Assessment of the Mechanisms and Controlling Factors, Université de
582 Rennes, 2017.

583 (42) Lofts, S.; Tipping, E.; Hamilton-Taylor, J. The Chemical Speciation of Fe(III) in
584 Freshwaters. *Aquat. Geochemistry* **2008**, 14 (4), 337–358. [https://doi.org/10.1007/s10498-](https://doi.org/10.1007/s10498-008-9040-5)
585 [008-9040-5](https://doi.org/10.1007/s10498-008-9040-5).

586 (43) Parc, S.; Nahon, D.; Tardy, Y.; Vieillard, P. Estimated Solubility Products and Fields of
587 Stability for Cryptomelane, Nsutite, Birnessite, and Lithiophorite Based on Natural Lateritic
588 Weathering Sequences. *Am. Mineral.* **1989**, 74 (3–4), 466–475.

589 (44) Chalhoub, M.; Coquet, Y.; Vachier, P. Water and Bromide Dynamics in a Soil Amended
590 with Different Urban Composts. *Vadose Zo. J.* **2013**, 12 (1), 0.
591 <https://doi.org/10.2136/vzj2012.0056>.

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