#### Chemosphere 275 (2021) 129928

Contents lists available at ScienceDirect

# Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

# Redox-induced mobilization of phosphorus in groundwater affected arable soil profiles



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## HIGHLIGHTS

# G R A P H I C A L A B S T R A C T



- The reductive dissolution of Feoxides caused an increase in P mobilization.
- Phosphorus was more mobilized in the toe-than the mid- and upperslope soil.
- Phosphorus was more mobilized in the top-than the sub-soil samples.
- The loss of P is higher under reducing than oxidizing conditions.

#### ARTICLE INFO

Article history: Received 2 July 2020 Received in revised form 2 February 2021 Accepted 7 February 2021 Available online 11 February 2021

Handling Editor: X. Cao

*Keywords:* Redoximorphic soils Redox chemistry



# ABSTRACT

Mobilization of phosphorus (P) in arable soils might be affected by groundwater fluctuations and the associated changes in redox potential ( $E_H$ ). However, the impact of systematic changes of  $E_H$  on P mobilization in redoximorphic arable soils along a catena has not been studied so far. Therefore, we investigated P mobilization under different redox conditions in top- and sub-soil horizons of three groundwater affected arable soils along a slight slope (toe-, mid-, and upper-slope position) in Northern Germany using an automated biogeochemical microcosm system. The impact of pH, Al, Fe, Mn, and dissolved organic carbon (DOC) on P mobilization was also studied. The initial  $E_H$  (+351 to +431 mV) and pH (6.5–7.0) decreased in all soil samples ( $E_H = -280$  mV; pH = 4.4) when creating a slury. Thereafter, the pH increased to 7.1 and 6.4 with increasing  $E_H$  in the mid-and toe-slope soil, respectively. Concentrations of dissolved P ranged between 20.8 mg L<sup>-1</sup> under low  $E_H$  in the toe slope topsoil and 0.69 mg L<sup>-1</sup> under high  $E_H$  in the toe- and mid-slop subsoil. Concentrations (mg L<sup>-1</sup>) of dissolved Fe (0.31–13.3) and

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Phosphorus solubility Governing factors DOC (92–2651) increased under low  $E_H$  and decreased under high  $E_H$ . The increase of P mobilization under low  $E_H$  and pH in the soils might be due to the release of P via the reductive and acidic dissolution of Fe-(oxhydr)oxides and/or due to soil organic matter mineralization. The high mobilization of P under reducing conditions may increase its bioavailability; however, it may increase its loss in the soils, particularly in the toe slope profile.

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#### 1. Introduction

Phosphorus (P) is an essential nutrient for plant growth. However, the high mobilization of P in soil may increase its loss to the surface and groundwater. The aquatic environmental pollution caused by P has raised the interest in this element because it is considered to be the main element responsible for the eutrophication process (Abdulkareem et al., 2018; Barcellos et al., 2019).

Redox-induced mobilization of nutrients and pollutants in groundwater affected arable soils has large agro-environmental implications, because the redox processes affect the bioavailability of P and also affect its loss to ground and surface water (Sosa, 2018; Chen et al., 2019). Mobilization, bioavailability, and potential loss of P in soils could be affected by redox potential ( $E_H$ ) and pH changes via regulating P biogeochemical processes in soils (Gasparatos et al., 2019; Zhao et al., 2019; Baumann et al., 2020a). For example, the interactions between P and soil constituents (e.g., Fe–Mn-(oxhydr)oxides, calcium carbonates, organic matter) are affected by the dynamics of  $E_H$  and pH (Gu et al., 2019; Bai et al., 2020).

In soils, P can be bound to soil organic matter (SOM), Fe, Al, and Mn -(oxhydr)oxides, and/or calcium compounds (Shaheen et al., 2007; Baumann et al., 2020b). These fractions can be influenced by soil properties and the changes of soil  $E_H$  and pH (Yang et al., 2019). Therefore, these soil components are important factors in driving P mobilization in soils (Cui et al., 2019). The mobilization of P under anaerobic conditions has been studied in peat soils (Meissner et al., 2008). However, the impact of systematic changes of  $E_H$  and the  $E_H$ -dependent changes of governing factors such as pH, dissolved organic (DOC) and inorganic (DIC) carbon, and the Fe-and Mn- (oxhydr)oxides on the mobilization of P in groundwater affected arable soils is not known yet.

Worldwide, arable land is covering around 1.5 billion hectares (Hens and Quynh, 2016). Approximately 40% of this arable land is naturally acidic, which may have developed with intensive agriculture, particularly when rainfall exceeds evapotranspiration (Kamprath and Smyth, 2005). Further, around 80 million hectares are affected by water logging (Hens and Quynh, 2016). In arable soils, particularly in Northern Germany, the closure of drainage systems and high precipitation may cause an increase in the water table (Svoboda et al., 2015; Zimmer et al., 2016), which can lead to reductive conditions. Arable soils on a single slope (catena) display different characteristics depending on slope position. For example, the toe slope position soil may have longer periods of water saturation due to rising groundwater level than the upper slope soils. Also, the subsoil might be more affected by water saturation than the topsoil. These in situ environmental conditions do not only affect soil properties but may also affect the mobilization of P in arable soils. Particularly under intensive applications of P fertilizers and/or manure the risk of P loss in these soils under changing environmental conditions may be increased. Consequently, in this study we investigated soil samples from the top- and subsoil of a toe-, middle-, and upper-slope arable soil profile to study P mobilization under different redox conditions.

We hypothesize that redox changes from reducing to oxidizing conditions and vice versa in groundwater affect arable soils as a result of water table fluctuations governing the release of P and its mobilization, through the direct impact of E<sub>H</sub> and/or the associated changes of soil pH, Fe-Mn oxides and DOC/DIC. We also hypothesize that if soil conditions become reducing, the P bound to the Fe and Mn-(oxhydr)oxides might be released due to the dissolution of these oxides. Also, we assume that redox-induced changes in soil organic and inorganic carbon affect P solubility and that the decomposition of SOM under reducing/oxidizing cycles leads to the release of P into soil solution. Moreover, we hypothesize that the slope position affects the water table level and thus affects the redox-induced mobilization of P in a soil catena differently. Therefore, our aim was to study the impact of rising groundwater level and the associated changes in E<sub>H</sub>, pH, Fe–Mn–Al-(oxhydr) oxides, DOC and DIC concentrations on P mobilization in the topand sub-soil horizons of toe-, mid-, and upper-slope arable soil profiles.

#### 2. Materials and methods

#### 2.1. Soil sampling and characterization

In a field at Dummerstorf, near Rostock, Germany, soil samples were collected from three soil profiles excavated by drilling along a slight slope at different positions (toe-, mid-, and upper-slope) i.e. different distances to groundwater (Baumann et al., 2020b). At each soil profile, four soil replicates were sampled from three horizons at different depths (Appendix A; Table S1). Soil classification, basic soil properties, and total element content as well as content of poorly crystalline oxides of Al, Fe, Mn, and P in the studied soil samples are reported in the supporting information (Appendix A; Table S1), and were described in detail in Baumann et al. (2020a,b). The top-(7–14 cm) and sub-soil horizon (55–72 cm) of the toe- and mid-slope profile and the topsoil horizon (7–14 cm) of the upper slope soil were used for the present microcosm experiment (section 2.2).

#### 2.2. Automated biogeochemical microcosm experiment

In the studied soil samples,  $E_H$  might be decreased due to raising groundwater level that might originate from precipitation plus restricted drainage; on the other hand, the  $E_H$  may increase again with decreasing groundwater level. Therefore, we incubated the soil samples and controlled the redox conditions from reducing to oxidizing status in the laboratory using an automated biogeochemical microcosm system (MC). The MC enabled us to simulate redox cycles that may occur in the soils when the groundwater level changes (Yu and Rinklebe, 2011). This system was used before to study the redox-induced mobilization of nutrients and trace elements in different soil samples (e.g., Yu et al., 2007; Frohne et al., 2011; Shaheen et al., 2014; Rinklebe et al., 2016, 2020). Briefly, the MC glass vessel was filled with 210 g of soil +15 g wheat straw +10 g glucose and 1680 mL of tap water, sealed air-tight and the slurry was continuously stirred. The powdered straw and glucose were added to the soil in each MC to serve as carbon sources for microorganisms. We controlled E<sub>H</sub> by adding N<sub>2</sub> to lower  $E_H$  or synthetic air to increase  $E_H$ . The  $E_H$  was decreased from oxidizing (+351 to+431 mV; 1 h after flooding) to reducing (-280 mV; 24 to 48 h after flooding) conditions by flushing with nitrogen. Then, the  $E_H$  was controlled from reducing (-280 mV) to oxidizing conditions (+485 mV) by flushing with synthetic air (20%)oxygen + 80% nitrogen) or oxygen. This process was controlled gradually by setting nine E<sub>H</sub> windows. The E<sub>H</sub> and pH values were recorded every 10 min using a data logger. The redox probes usually do not show the redox potential of the solution as a reference to the standard hydrogen electrode (SHE), but as the potential of the probe in relation to the solution (Wolersdorfer, 2008). Therefore, we calculated the redox potential relative to the SHE (to be close to the real situation) using the oxidation-reduction potential (ORP) Sensor reading (electrode Et, mV) and the solution temperature as well as the Nernst-Equation, as published by Wolkersdorfer (2008).

A sample (60 mL) of the slurry was sampled approximately 48 h after reaching equilibrium at each  $E_H$  window. The slurry was centrifuged at 4000 rpm (2257×g) for 15 min and filtered using 0.45 µm Millipore membranes. Concentrations of P, Fe, Mn, Al, and S in the filtrate were analyzed using inductively coupled plasma-optical emission spectroscopy. All processes were done in a glove box. The incubation time was approximately 440 h. More details about the MC experiment, further analyses, and the quality assurance of data are included in Appendix A.

## 3. Results and discussion

## 3.1. E<sub>H</sub>/pH dynamics

The  $E_H$  of all soil samples ranged from -280 mV to +485 mV (Fig. 1). The toe slope soil samples showed a wider range of  $E_{H}$ (-280 to +471 mV) than the mid slope (-272 to +442 mV) and the upper slope topsoil (UST) samples (-230 to +485 mV) (Fig. 1; Table 1). The E<sub>H</sub> range differed between the soil horizons; the toe slope subsoil (TSS) sample reached a lower  $E_H$  value (-280 mV) than the toe-slope topsoil (TST) sample (-232 mV), while both the mid slope top- (MST) and sub-soil (MSS) sample showed similar E<sub>H</sub> values (-270 mV) (Fig. 1). We assume that the E<sub>H</sub> changes between the profile position and horizon depth might be due to the effects of rising groundwater which had shaped these soils in situ. For example, due to its lower topographical position, the toe- and midslope soils may have had longer periods of water saturation due to raising groundwater level than the upper slope soil. This could have led to changes in soil biogeochemical properties and the nature and content of electron acceptors in the potentially saturated toe- and mid-slope soils. These differences may have affected the E<sub>H</sub> dynamics of the soil samples in the microcosms, and thus might be a reason for decreasing the E<sub>H</sub> in the toe-, and mid-slope soil more than the upper-slope soil (Fig. 1), because the  $E_H$  reduction is microbially mediated (Reddy and DeLaune, 2008).

The initial pH of the three soil samples ranged between 6.6 and 7.0 and decreased under reducing conditions to 4.3 in the TST, 5.4 in the TSS, 5.0 in the MST, 5.3 in the MSS, and 4.4 in the UST (Fig. 1). The pH was almost constant (4.3–4.6) during the increase of  $E_H$  in the TST and in the UST but increased to 7.5, 7.7, and 7.6 with increasing  $E_H$  in soils in the TSS, MST, and MSS, respectively (Fig. 1). However, the relationship between  $E_H$  and pH was significantly positive only in the mid slope soil (R = 0.72; P < 0.01; Appendix A; Table S2). The decrease of pH under reducing conditions might be due to production of CO<sub>2</sub> and organic acids by the microbial decomposition of SOM as has also been mentioned by Yu et al. (2007) and Shaheen et al. (2014). Also, an increase in partial

pressure of CO<sub>2</sub> and the associated increase of carbonic acid formation could be a reason for a decreasing pH under reducing conditions (Scalenghe et al., 2002; Jayarathne et al., 2016). Furthermore, the decrease of pH under low  $E_H$  might be caused by the hydrolysis of Fe-ions, which may occur with the release of Fe under low  $E_H$  (Sparks, 2003).

# 3.2. Redox-induced mobilization of P

#### 3.2.1. Impact of $E_H$ changes

Concentrations of dissolved P in different E<sub>H</sub> windows differed largely between the studied soil samples, as affected by the slope and depth (Table 1; Fig. 2). In all soil samples, the concentrations of dissolved P ranged from 8.8 to 20.8 mg  $L^{-1}$  under low  $E_{H}$ , while varying from 0.69 to 1.76 mg  $L^{-1}$  under high E<sub>H</sub>. Accordingly, the regression analysis showed that the relationship between P and E<sub>H</sub> was significantly negative for all soil samples ( $R^2 = 0.81-0.93$ ,  $P \le 0.05$ ; Fig. 2). The E<sub>H</sub> changes may affect P species and thus affect their solubility. The dramatic changes of E<sub>H</sub> and pH may alter the geochemical fractions and species of P in soils from the residual fractions to the potential mobile fractions and vice versa. For example, the E<sub>H</sub> and pH affect the distribution of P with Fe oxides, calcium carbonates, and organic matter, and thus affect its mobilization. We also assume that the redox-induced changes in P mobilization under low E<sub>H</sub> can be explained by the impact of E<sub>H</sub> on P oxidation states in soil solution, and thus may affect its mobilization. For example, the reduction of the higher redox states of P (+5) to the lower redox states (+3) under low  $E_{\rm H}$  and vice versa under high E<sub>H</sub> may affect the solubility of P in soils and aqueous environments. In this respect, Van Mooy et al. (2015) and Pasek et al. (2014) found that the lower redox states of P are common in water samples and account for up to 15% of dissolved phosphorus.

#### 3.2.2. Impact of slope position and soil depth

The TST showed the highest concentrations (mg L<sup>-1</sup>) of dissolved P (1.7–20.8) (Fig. 2). This was followed by the UST (1.7–16.7), MST (0.7–15.2), as well as the TSS (0.7–11.6), and the MSS (0.7–8.8) (Table 1). The toe slope soil revealed higher concentrations of dissolved P than the mid-and upper slope soil under the given E<sub>H</sub> course. This can be likely explained by the higher labile P concentrations shown in the toe slope soil than the mid-and upper-slope soils (Table S1). For example, the labile-P concentration of the TST (103 mg kg<sup>-1</sup>) was higher than that of the MST (80 mg kg<sup>-1</sup>) and UST (76 mg kg<sup>-1</sup>) (Table S1). In addition, the lower E<sub>H</sub> in the toe slope soil than the other soil samples (Fig. 1) might be a reason for the higher P mobilization in this soil sample (Fig. 2) as discussed in sections 3.2.1 and 3.2.3.

The results also indicated that concentrations of dissolved P were 2-fold higher in the topsoil samples (mean values =  $9.2-11.2 \text{ mg L}^{-1}$ ) than the subsoil samples (mean values =  $4.2-5.4 \text{ mg L}^{-1}$ ) (Table 1), which might be due to the higher oxalate-P and labile P in the topsoil samples than the subsoil samples (Table S1). For example, the concentrations of labile P in the topsoil samples (76–103 mg kg<sup>-1</sup>) were clearly higher than in the subsoil samples ( $8.5-24.7 \text{ mg kg}^{-1}$ ) (Table S1), which might be a reason for the high content of dissolved P in the topsoil samples (Fig. 2).

We summarize that the slope position of soils and thus effects of groundwater level can affect the redox cycles and E<sub>H</sub>/pH dynamics of soils. Associated changes in the microbial communities/activities and the chemistry of Fe-(oxyhydr)oxides and soil organic matter can then affect the mobilization of P in these soils. This implies that also *in situ* a lower topographical position may cause higher P mobilization in soil than an upper slope position.



Fig. 1. Temporal course of E<sub>H</sub> and pH in the soil suspensions of the studied soil samples as well as sampling times of suspension collection.

# 3.2.3. Impact of $E_H$ -dependent changes on pH, Fe-Mn-(oxhydr) oxides, sulfur, and soil carbon

3.2.3.1. Impact of pH. The concentrations of dissolved P increased under acidic conditions and decreased under alkaline conditions, particularly in the mid- and toe-slope soil samples. The regression analysis showed that although relatively weak, the relationships between dissolved P and pH were significantly negative ( $R^2 = 0.33-0.48$ ; Fig. 2). The impact of pH was stronger in the MST, MSS, and TSS than the other two soil samples (TST and UST), because the pH of these soils increased under oxic conditions up to

7.7, while it was less than 5.0 in the TST and UST. The pH of the water-sediment interface is a factor that can affect different geochemical processes, and thus influencing P release to soil solution (Sparks, 2003). We assume that the increase of P solubility under low pH might be due to the acidic dissolution of Fe–Mn-(oxyhydr)oxides and carbonates and the release of the associated P. On the other hand, the decrease of P solubility under alkaline conditions can likely be due to P bound to the precipitated Fe–Mn-(oxyhydr)oxides and/or carbonates. This interpretation is in agreement with Young and Ross (2001) who reported that released

#### Table 1

Variations of  $E_{H}$ , pH, and concentrations of P, Fe, Mn, Al, S, DOC, and DIC in soil suspension of the studied soils.

Parameter	Unit	n	Minimum	Maximum	Mean	SD
Toe slope topsoil						
E <sub>H</sub>	[mV]	2559	-232	+471	+183	212
pН		2615	4.29	6.74	4.68	0.34
Р	$[mg L^{-1}]$	9	1.72	20.81	11.25	8.55
Fe		9	0.74	13.21	8.67	4.99
Mn		9	0.74	14.78	10.94	4.25
Al		9	0.63	2.12	1.29	0.50
S		9	1.55	12.61	8.51	3.62
DOC		9	1161.6	2651.4	1655.2	480.6
DIC		9	0.00	8.73	1.49	2.80
Toe slope subsoil						
E <sub>H</sub>	[mV]	2605	-280	+433	+91	220
pH	. ,	2614	5.43	7.55	6.08	0.48
P	$[mg L^{-1}]$	9	0.69	11.67	5.44	3.99
Fe	1 0 1	9	0.34	13.26	5.71	5.35
Mn		9	0.41	13.34	8.31	5.21
Al		9	0.22	1.33	0.55	0.38
S		9	5.84	12.42	994	2.18
DOC		9	92.2	24293	1359.0	306.1
DIC		9	1.62	93.14	39 59	33 37
Middle slope topsoil						
Fu	[mV]	2562	-272	+433	+68	223
nH	[]	2601	5.04	7 74	5 79	0.72
P	$[m \sigma I^{-1}]$	9	0.75	15.21	9.84	5 99
Fe	[IIIg L ]	9	0.73	13.21	8.11	5.72
Mn		9	1.00	12.00	7 59	4 50
Δ1		0	0.24	0.02	0.54	0.28
S		9	8 10	13 70	10.74	1 03
5		0	1196	2606.2	1267.2	700.0
DIC		0	0.00	114.00	22 51	12 61
Middle clone subsoil						
F	[mV]	2507	270	442	100	214
LH DU	[IIIV]	2597	-270	7 57	5.06	0.51
рп	[mg I -1]	2001	0.60	0.01	1.30	2.00
F	[IIIg L ]	9	0.09	12.26	726	2.99
Mp		9	0.31	10.09	1.00	2.02
A1		9	0.30	10.06	4.00	2.99
AI C		9	0.24	2.42	10.00	1.04
3		9	0.90	12.34	10.00	1.84
DUC		9	163.0	2592.9	1329.9	818.0
DIC Unnen elene	tomoo:1	9	2.01	112.92	55.71	45.52
opper slope	lopson	2002	220	405	242	205
EH	[mv]	2603	-230	485	243	205
рн	rr11	2603	4.36	7.06	4.6	0.40
P	[mg L ·]	9	1.76	16.72	9.21	6.51
ге		9	0.70	13.21	8.41 0.20	5.31
win		9	1.13	13.29	9.38	3.62
AI		9	0.23	2.//	2.01	0.85
5		9	8.41	12.63	10.40	1.39
DOC		9	1045.1	2619.4	1544.1	506.9
DIC		9	0.00	7.74	1.15	2.52

 $E_{\rm H}=$  Redox potential; DOC = dissolved organic carbon; DIC = dissolved inorganic carbon; SD = standard deviation.

P can be retained by soil components and/or can be re-precipitated at the oxidized/alkaline soil layer in redox-affected soils.

3.2.3.2. Fe–Mn–Al-(oxhydr)oxides and sulfur. The concentrations of dissolved P as well as Fe (in all soil samples), Mn (TST, TSS and MST), Al (TSS and MST), and S (all soil samples except for TST) increased under reducing conditions and decreased under oxic conditions. Therefore, the relationships between dissolved P on the one hand and Fe, Mn, Al, and S on the other hand were significantly positive in these soil samples (Fig. 3; Table S2). The relationship between P and Fe ( $R^2 = up$  to 0.85) was stronger than Al ( $R^2 = up$  to 0.51), and Mn ( $R^2 = up$  to 0.62) (Fig. 3). However, the impact of Fe, Al, and Mn on P mobilization in the mid-and toe-slope soils (TSS and MST) was stronger than in the UST. These results demonstrate that the redox chemistry of Fe–Mn–Al oxides, particularly Fe



**Fig. 2.** Relationships between  $E_H$  and pH in the soil suspension vs. concentrations of dissolved P in the soil suspension of the studied soil samples. TST = Toe slope topsoil; TSS = Toe slope subsoil; MST = Mid slope topsoil; MSS = Mid slope subsoil; UST = Upper slope topsoil.

oxides, affect the redox-induced mobilization of P in the studied soil samples, particularly in the TSS and MST. Under reducing conditions, anaerobic bacteria could have used NO<sub>3</sub>, Mn<sup>4+</sup>, and Fe<sup>3+</sup>, as alternative electron acceptors to maintain their metabolism thus reducing  $Mn^{4+}$  to  $Mn^{2+}$  and  $Fe^{3+}$  to  $Fe^{2+}$  (e.g., Weber et al., 2006; Unger et al., 2009; Sánchez-Alcalá et al., 2011), which increase the mobilization of Fe and Mn under reducing conditions. The concentrations of dissolved P showed a similar pattern as Fe and Mn. We therefore assume that the reductive and acidic dissolution of Fe-Mn (oxhydr)oxides may have led to the release of the bound and/or occluded P to those (oxhydr)oxides to soil solution. This is supported by a strong significantly positive relationship between dissolved Fe and Mn with dissolved P concentrations (Fig. 3; Table S2). On the other hand, the decrease of dissolved P under high E<sub>H</sub> and pH can be explained by re-adsorption of P to the precipitated Fe oxides and carbonates under oxic/alkaline conditions, especially in the mid slope top- and subsoil samples and the toe slope subsoil sample (pH = 7.5-7.7; Fig. 1).

Earlier results on the P K-edge X-ray absorption near edge



**Fig. 3.** Relationships between concentrations of dissolved P in the soil suspension vs. concentrations of dissolved iron (Fe), manganese (Mn), aluminum (Al), sulfur (S), dissolved organic (DOC) and inorganic carbon (DIC) in the studied soil samples. TST = Toe slope topsoil; TSS = Toe slope subsoil; MST = Mid slope topsoil; MSS = Mid slope subsoil; UST = Upper slope topsoil.

structure (XANES) and sequential extraction analyses on the same soil samples revealed that high portion of total P (49%) was bound to Al– Fe-(oxhydr)oxides (Baumann et al., 2020b), which demonstrates that the soils indeed had a sufficient capacity of P which could be released from Al– Fe-(oxhydr)oxides. Also, the soil samples were shown to contain high concentrations of total and oxalate extracted Fe, Al, and Mn (Table S1).

3.2.3.3. DOC and DIC. The concentrations of dissolved P and DOC increased under low  $E_H$  and decreased under high  $E_H$  values. Consequently, the relationship between dissolved P and DOC was significantly positive in all soil samples ( $R^2 = 0.71$  in TSS to 0.85 in

MST; Fig. 3). The impact of DOC on P mobilization was stronger in the topsoils (particularly TST) than the subsoils, which can be likely explained by the high total carbon content in the topsoils (15.3%) than the subsoils (3.6%; Table S1). Most likely this association was due to microbial decomposition of SOM under low E<sub>H</sub> (Reddy and DeLaune, 2008). Decomposition of SOM may have led to the release of DOC as well as P to soil solution under reducing conditions indicating that some of the P. which was previously bound to organic matter, was released under low E<sub>H</sub>. The reductive microbial decomposition of SOM may also have led to a release of the sorbed and organo-complexed P to soil solution under low E<sub>H</sub>. The competition between sorbed phosphate on mineral surfaces and organic ligands might be a reason for the release of P to soil solution (Hutchison and Hesterberg, 2004; Abit et al., 2013). Also, DOC may interact with Fe–Al oxides and promote their dissolution and thus increase the release of the oxides bounded P (Yan et al., 2016; Yang et al., 2019).

Concentration of DIC increased under oxic conditions, particularly in the MST, MSS, and TST samples. Consequently, the relationships between dissolved P and DIC in these soil samples were significantly negative ( $R^2 = 0.38$  in TST and 0.62 in MST;  $P \le 0.05$ ; Fig. 3). This might be a reason for the decrease of P mobilization under these conditions. The higher impact of DIC on P mobilization in MST, MSS, and TST samples than TSS and UST can be explained by the increase of pH to 7.7 in these three soils (Fig. 1) under oxic conditions, which may cause precipitation of P carbonates and retention of P on these carbonates. Inorganic carbon solubility is very dependent on soil pH (Bargrizan et al., 2020). Under alkaline conditions and the presence of calcium (Ca), as it occurred in our soils (Table S1), the divalent Ca ions could have gotten into soil solution and phosphates might have been precipitated to form insoluble calcium phosphates. Phosphates can react with Ca<sup>2+</sup> ions and Ca or Mg carbonates and form insoluble Ca and/or Mg phosphates thus explaining our results of a negative relationship between DIC and dissolved P.

We summarize that the concentrations of P, Fe, Mn, and DOC in soil solution were high under anaerobic acidic conditions and decreased under aerobic alkaline conditions. The higher mobilization of P under low  $E_H$  and pH can be likely happening via the reductive/acidic dissolution of  $Fe^{3+}$  oxides and/or during SOM mineralization. The lower mobilization of P under high  $E_H$  and pH can be due to the increase of P sorption to the precipitated oxides and/or calcium carbonate.

# 4. Conclusions

The release of P in groundwater affected arable soils might increase under high precipitation and surface irrigation if drainage is restricted, which may increase the ground water level and cause reductive conditions. Reducing acidic conditions increased P mobilization up to 30 folds and thus may cause increased leaching if the groundwater level increases in the soils under study. Therefore, mitigating the potential loss of P under reducing acidic conditions using low cost and environmentally friendly soil amendments plus improvement of drainage system is needed, which is in consistence with the targets of the Helsinki convention (HELCOM, 2007) to decrease the leaching and loss of P from arable land in North-Eastern Germany. The results collected at micro-scale using the biogeochemical microcosm system should be verified on various scales (such as lysimeters) and in the field. Also, the impact of different redox cycles on the release of P in groundwater affected arable soils is needed to study the impact of water table level seasonal fluctuation and the associated wetting-drying cycles on the bioavailability and potential loss of P in these soils. Moreover, spectroscopic techniques can be used to investigate the redoxinduced changes on P species in the solid phase and elucidate the fate of P and predict its release and potential loss.

The gained results may help in evaluating the bioavailability and potential loss of P in groundwater affected arable soils and assessing the potential risks associated with the leaching of P. The collected results may also help the decision support system in north-eastern Germany to develop applicable practices to prevent water resources from diffuse P pollution and to conclusively evolve the traditional soil P management practices.

# Credit author statement

Sabry M. Shaheen: Performing the experiment, Writing – original draft. Jianxu Wang: Performing the experiment, Software and visualization. Karen Baumann: Editing and proof reading. Shan-Li Wang: Editing and proof reading. Peter Leinweber: Review, editing, and proof reading. Jörg Rinklebe: Concept, Supervision, review, editing, and foundation

# **Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgements

We thank the German Federal Ministry of Education and Research (BMBF) who funded the InnoSoilPhos-project (http:// www.innosoilphos.de/default.aspx), in the frame of the BonaResprogram (No. 521 031B0509A). Also, we thank the team of Laboratory of Soil- and Groundwater-Management at Wuppertal University for the technical support.

# Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2021.129928.

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