Phosphorus cycling and spring barley crop response to varying redox potential

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Abstract
For arable soils, it is not clear whether closing a controlled drainage system leads to P mobilization due to water table rise and associated changes in redox-induced biogeochemical processes. Therefore, we investigated P mobilization at different redox conditions using three spring barley (Hordeum vulgare L.) cropped lysimeters filled with monoliths of arable northeastern German soil profiles. Pore water samples were collected weekly from three different depths, and dissolved (<0.45 μm) element concentrations of total C, P, Al, Fe, Mn, Ca, Mg, and K, as well as inorganic and organic C (DIC and DOC) and P (P<sub>i</sub> and P<sub>o</sub>), SO<sub>4</sub><sup>2-</sup> and NO<sub>2</sub>–N and NO<sub>3</sub>–N were determined. The total P concentration in pore water collected from a given lysimeter at a given time was 1.8 mg P L<sup>-1</sup> maximum. Organic P concentrations in subsoil solutions were positively correlated with Fe concentrations. Grain yield of spring barley ranged between 5.6 and 6.5 Mg ha<sup>-1</sup>, and total biomass P uptake was negatively correlated with the stable P stocks of the soil profiles. Results suggest that reductive conditions in subsoils led to dissolution of pedogenic Fe-(oxy)hydroxides and release of P<sub>o</sub> compounds, the latter of which were more important for biomass P uptake than P released from stable P compounds. Overall, closing the drainage at the field site could represent a moderate P mobilization risk, which would probably be lower compared with a P mobilization risk caused by a heavy rainfall event.

1 | INTRODUCTION

Phosphorus leaching from agricultural land into water bodies is a common problem (Xia et al., 2020). In the case of heavy rain events, leaching can be very high as reported by Zimmer, Kahle, & Baum (2016), who observed 141 mg P L<sup>-1</sup> in drain water of arable northern German soils. To diminish P leaching, controlled drainage is a possibility (Carstensen et al., 2019; Dagnew, Scavia, Wang, Muenich, & Kalcic, 2019), but closing the drainage and a subsequent water table rise may even initiate P mobilization due to a decrease in redox potential (Eh) (Ruiz, Delgado, & Torrent, 1997). Thereby, under oxic conditions, the terminal electron acceptor for electrons originating from soil microbial respiration of organic

Abbreviations: DIC, dissolved inorganic carbon; DOC, dissolved organic carbon; DRW, drying and rewetting; Eh, redox potential; ICP–OES, inductively coupled plasma–optical emission spectroscopy; P<sub>i</sub>, inorganic phosphorus; P<sub>o</sub>, organic phosphorus; PVC, polyvinyl chloride; TC, total carbon.

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matter (metabolic pathways) is O$_2$, whereas under reducing conditions, the terminal electron acceptors differ depending on the Eh (Megonigal, Hines, & Visscher, 2004). For example, at Eh values between about −100 to +100 mV, the main terminal electron acceptor is Fe(III), meaning that Fe(III) compounds could be reduced to Fe(II) compounds (Reddy & DeLaune, 2008). Phosphorous bound to Fe-hydroxides will be released into the soil solution if Fe(III) is reduced to Fe(II) (Moore & Reddy, 1994; Szilas, Borggaard, Hansen, & Rauer, 1998). This effect has been shown for wetland soils including rewetted peat soils (Meissner et al., 2008; Prem et al., 2015; Shenker, Seitelbach, Brand, Haim, & Litaor, 2005; Stepniewska, Borkowska, & Kotowska, 2006). On the other hand, flooding of two paddy soils increased oxalate-extractable Fe, which led to an increase in P adsorption (Zhang et al., 2003).

Besides these disagreeing results in the literature, effects of water table fluctuations on P mobilization in drained arable mineral soils of northeastern Germany are unclear and need to be understood to restrict undesirable P transfers into waterways.

Many studies investigated the effect of drying and rewetting (DRW) on soil nutrients including P (Blackwell et al., 2009; Bünemann et al., 2013; Butterly, Bünemann, McNeill, Baldock, & Marschner, 2009; Pezzola et al., 2019; Turner, Driessena, Haygarth, & Mckelvie, 2003). Bünemann et al. (2013), for example, related a strong P pulse after rewetting of dry soil to the lysis of microbial cells, as well as to soil aggregate disruption and subsequent P release. In contrast, Pezzola et al. (2019) could not find any effects of DRW cycles on water-extractable inorganic P (P$_i$) of the soil. Although most of the existing studies reported on soil extractable nutrient content after DRW events, only Tian, Dong, Karthikeyan, Li, & Harmel (2017) examined P$_i$ concentrations in pore water of artificially prepared soil columns and found that during reflooding, P$_i$ decreased over time. Most DRW studies did not investigate P concentrations in soil solutions as affected by measured Eh, nor did they investigate pore water P concentration of intact mineral soils. The original pore structure, however, is important not only for Eh, but also for drainage of the soil profile, since ions in pore water could potentially be leached during controlled drainage. Further, additional element or ion concentrations in pore water are of interest with respect to plant nutrient availability, toxicity for plants and microbes (e.g., Al$^{3+}$), element mobilization or dislocation, and thus leaching potential of plant nutrients such as nitrate (NO$_3^-$)-N, which may also contaminate water bodies. Also, dissolved organic C (DOC) concentration can enhance the effect of reducing conditions and thus could contribute to P mobilization (Khan et al., 2019). Already single factors such as the O$_2$ status of soil or plant nutrient concentrations in pore water are known to affect plant productivity (Poulton, Johnston, & White, 2013; Steffens, Hütsch, Eschholz, Lošák, & Schubert, 2005). Concentrations of elements and/or ions in pore water during fluctuating water table and their overall effect on crop growth and yield, however, have not yet been reported for temperate arable soils.

For the investigation of element and ion concentration changes in pore water, lysimeter studies can be used, which allows element monitoring in soil columns of intact soil structure, as well as a close monitoring of various related parameters such as the Eh (Meissner, Rupp, & Haselow, 2020; Rupp, Meissner, & Leinweber, 2018; Rupp, Rinklebe, Bolze & Meissner, 2010; Shaheen, Rinklebe, Rupp, & Meissner, 2014). Usually, leachate of whole soil columns has been investigated (Andersson, Bergström, Ulén, Djodijic, & Kirchmann, 2015; Siddique, Robinson, & Alloway, 2000), and studies analyzing pore water from different soil depths have most often been done with suction cups or suction plates (Koch, Kahle, & Lennartz, 2019; Siemens & Kaupenjohann, 2002). Pore water collection from different depths of lysimeters (experimental units of soil monoliths placed in polyvinyl chloride [PVC] tubes and installed open air), however, may lead to a better understanding of pore water chemistry depending on specific soil horizon characteristics.

The aims of the present study were (a) to assess the potential mobilization of P and other relevant elements and ions in different soils along a northern German hill slope by quantifying the dissolved element concentrations in solutions taken from different soil depths of these soils at different redox conditions, and (b) to examine the relation between P uptake by crops and soil P characteristics. We hypothesized that (a) high water levels cause low Eh values in soil that, in turn, contribute to Fe dissolution and P release, and (b) P uptake by crops is affected by soil P characteristics. The overarching practical question behind our research was: can drain water P concentration from fields be reduced by application of controlled drainage, or does controlled drainage pose a risk of additional P mobilization due to reductive dissolution of pedogenic oxides?
2 | MATERIALS AND METHODS

2.1 | Lysimeter installation

In May 2018, three lysimeters were installed in PVC tubes (30-cm i.d., 90-cm length) by taking the monoliths from an experimental field at Dummerstorf (Mecklenburg-Western Pomerania, Germany), at which studies on diffuse P losses had been done before (Tiemeyer, Kahle, & Lennartz, 2009). The intact monoliths were excavated by drilling at the upper slope (upper slope), at mid-slope position (mid-slope), and at the bottom of a slight slope (toe slope) (Umwelt-Geräte-Technik, Müncheberg, Germany; https://www.ugt-online.de/en/products/lysimeter-technology/). The description and analytical characterization of these monoliths at three different depths have been published by Baumann et al. (2020). In brief, the profiles were classified as Epiaquepts according to the U.S. Soil Taxonomy (Soil Survey Staff, 2014) and represented a Stagnic Eutric Cambisol (CM-st.eu), upper slope profile), Eutric Stagnosol (ST-eu, mid-slope profile), and Eutric Stagnosol (colluvic) (ST-eu-co, mid-slope profile) according to the World Reference Base for Soil Resources (IUSS Working Group WRB, 2015), respectively, with the soil textures loamy sand consisting of 9–15% clay (generally dominated by illite and illite-rich mixed layer minerals), 27–36% silt, and 52–58% sand (Baumann et al., 2020). The P sorption capacity (PSC) based on oxalate-extractable Al + Fe + Mn varied between 13 and 32 mmol kg⁻¹, with the highest values for the upper soil depth of each profile and decreasing PSC with increasing soil depth in each profile. In almost all depths, PSC decreased in the order upper > toe > mid-slope profile (Baumann et al., 2020).

Each lysimeter was instrumented with three ceramic suction cups (P80, Umwelt-Geräte-Technik; at −20, −45, and −70 cm), three redox electrodes (ecoTech redox electrodes, ecoTech Umwelt-Meßsysteme; at −15, −40, and −65 cm), three moisture and temperature sondes (SMT-100, Umwelt-Geräte-Technik; at −15, −40, and −65 cm), and three tensiometers (Tensio 160, Umwelt-Geräte-Technik; at −15, −40, and −65 cm). Below, the lysimeter monolith of a specific site is referred to as the “upper slope,” “mid-slope,” and “toe slope” profile, and monolith depth is given as “1,” “2,” or “3” (Depth 1 = top soil, Depth 2 = upper subsoil, Depth 3 = lower subsoil). The lysimeters were placed outside the University of Rostock, Agriculture Building (54.075060° N, 12.098802° E, 38 m asl), where they were exposed to open-air conditions. Water level heights in the lysimeters were individually adjusted from the bottom upwards by a logger-controlled pump system using tap water to simulate closed drainage (high water level) or open drainage (low water level). All parameters were recorded by a data logger. Natural precipitation was collected by a rain trough and is given as cumulative weekly amount (Figures 1–3, a).

In April 2019 (Week 16 of 2019 starting with Monday 15 April), the water level of all lysimeters was set to −5 cm, resulting in high water levels during Weeks 17–21 (Figures 1–3, b). This high-water equilibration period was followed by a low-water equilibration period for which water levels were adjusted at −80 cm in lysimeters of the upper and mid-slope position and −50 cm in the lysimeter of the toe slope position. In the third week after low water level adjustment (Week 24), the sampling campaign lasting 22 wk was started. During the sampling campaign, dry periods of 3 wk were alternated with wet periods of 3 wk. Thereby, the water levels in lysimeters of the upper and mid-slope position were set to −25 cm (wet period) and −80 cm (dry period), respectively, and in the lysimeter of the toe slope position it was set to −25 and −50 cm, respectively, to account for natural ground water fluctuations at different slope positions.

In Week 17, the original grass–lucerne (Medicago sativa L.) mixture for fodder was removed manually from the lysimeter monoliths, and spring barley (Hordeum vulgare L. cultivar Planet RGB) was sown at a density of 50 seeds lysimeter⁻¹ (Figures 1–3, b), which was then thinned to 25 plants lysimeter⁻¹ in Week 23. After harvest of spring barley in Week 36, lysimeters were catch cropped with 0.25 mg sarradella (Ornithopus sativus L.) lysimeter⁻¹.

2.2 | Solution sampling and plant harvest

From Week 24 onwards, soil solutions were sampled weekly for 22 wk from each lysimeter by sucking on average 70-ml solution from each depth using a vacuum pump (MVF-120, Umwelt-Geräte-Technik) operated at −75 kPa. To avoid collection of long-standing solution (in suction cups or tubes), the first few milliliters of collected solutions were discarded. During dry periods, solution could not be collected from some of the lysimeters. An overview of missing solution samples and thus analytical values for elements is given in Supplementary Table S1. For each soil solution, pH was determined (pH-meter pH540 GLP WTW) before solutions were filtered <0.45 μm (cellulose nitrate membrane, Whatman) and stored at −20 °C until further analyses.

Spring barley plants were harvested after 19 wk of growth by manually cutting the plants at the soil surface. Plants were dried at 60 °C before straw and grains were finely ground and further analyzed.
2.3 Analyses of element concentrations in pore water and plant material

Total dissolved concentrations of Al, Fe, Ca, K, Mg, Mn, and P in the filtered soil solutions were determined by inductively coupled plasma–optical emission spectroscopy (ICP–OES, Perkin-Elmer Optima 8300 DV). Total and inorganic C was analyzed using Dimatoc 2000 (Dimatec Analysentechnik), and organic C was calculated by difference. The anions NO$_2^-$, NO$_3^-$, PO$_4^{3-}$, and SO$_4^{2-}$ were determined by ion chromatography (930 Compact IC Flex, Metrohm) equipped with a Metrosep A Supp 5–150/4.0 column (Metrohm) and using 3.2 mmol L$^{-1}$ Na$_2$CO$_3$ and 1 mmol L$^{-1}$ NaHCO$_3$ as eluent.

Finely ground plant material (0.1 g) was analyzed in duplicate for total element concentrations after microwave assisted digestion with 5 ml 65% HNO$_3$ and 3 ml 30% H$_2$O$_2$ (after Zimmer et al., 2018). Element concentrations (Al, Fe, Ca, K, Mg, Mn, and P) were determined by ICP–OES (Perkin-Elmer Optima 8300 DV). Total C, N, and S concentrations were determined fourfold by dry combustion using an elemental analyzer (VARIO EL, Elementar Analysensysteme).
FIGURE 2  Time series of precipitation, water level, redox potential, pH, and dissolved element concentrations in soil solution samples from Depths 1 to 3 in the mid-slope lysimeter. For details of a–o, see caption of Figure 1.

2.4 Calculations and statistics

The weighted mean of the total P concentration in pore water of a lysimeter at a given time was calculated based on soil layer thickness, lysimeter area, pore volume, soil moisture (Supplemental Table S2, Supplemental Figure S1) and total P concentration as outlined in Equation 1:

\[
c_{P,\text{lys}} = \frac{\sum_{i=1}^{3} (d_i AV_{\text{pore,}i}/100 w_i/100,000c_{P,i})}{\sum_{i=1}^{3} (d_i AV_{\text{pore,}i}/100 w_i/100,000)}
\]

where \(c_{P,\text{lys}}\) is the weighted mean of total P concentration in pore water of a lysimeter at a given time (mg L\(^{-1}\)), \(d_i\) is the thickness of the \(i\)th soil layer (cm), \(A\) is the area of the lysimeter (709 cm\(^2\)), \(V_{\text{pore,}i}\) is the pore volume of the \(i\)th soil layer (% v/v), \(w_i\) is the soil moisture of the \(i\)th soil layer (% v/v), and \(c_{P,i}\) is the total P pore water concentration in the \(i\)th soil layer (mg L\(^{-1}\)).

Soil profile stocks of P- and oxalate-extractable fractions (\(\text{H}_2\text{O}-\text{P}\), resin P, \(\text{NaHCO}_3-\text{P}\), labile P [\(\text{H}_2\text{O}-\text{P} + \text{resin P} + \text{NaHCO}_3-\text{P}\)], NaOH-P [moderately labile P], \(\text{H}_2\text{SO}_4-\text{P}\) [stable P], residual P, and oxalate-extractable P, Fe, Al, and Mn) were based on soil layer depth (Supplemental Table S2), bulk density, and element concentration data taken from Baumann et al. (2020). The stocks were calculated according to Xu et al. (2019) and were expressed in grams per square meter for a profile depth of 87 cm (Equation 2):

\[
\text{stock}_X = \sum_{i=1}^{3} (c_{X,i} bd_i d_i 10)
\]

where \(\text{stock}_X\) is the stock of the parameter \(X\) of the soil profile down to 87-cm depth (g m\(^{-2}\)), \(c_{X,i}\) is the concentration of the parameter \(X\) of the \(i\)th soil layer (g kg\(^{-1}\)), \(bd_i\) is the soil bulk density of the \(i\)th soil layer (g cm\(^{-3}\)), and \(d_i\) is the thickness of the \(i\)th soil layer (cm).

Since a Shapiro–Wilk test showed non-normal distribution of the lysimeter element data, Spearman’s rank correlation coefficient (\(\rho\)) was calculated to estimate dependence of parameters. Only for correlations between spring barley...
FIGURE 3  Time series of precipitation, water level, redox potential, pH, and dissolved element concentrations in soil solution samples from Depths 1 to 3 in the toe slope lysimeter. For details of a–o, see caption of Figure 1.

RESULTS

3.1 Precipitation, Eh, and pH

Precipitation above the long-term weekly mean was recorded for Weeks 24, 25, 32, 36, 37, 40, 43, and 45 (Deutscher Wetterdienst, precipitation data since 1951) (Figures 1–3, a). In those weeks, the amount of precipitation ranged between 14 and 49 mm, which was an enhancement of 27–86% of the long-term weekly mean. In all other weeks, the precipitation was below the long-term weekly mean.

Generally, for all depths below the adjusted water level, the Eh decreased for the duration of water saturation and increased again once the water level was lowered again (Figures 1–3, b, c). The minimum Eh of all soil profiles ranged between $-248$ and $-212$ mV (Depth 1), $+163$ and $-159$ mV (Depth 2), and $+188$ and $+105$ mV (Depth 3). The maximum Eh for all depths of all profiles ranged between $+575$ and $+685$ mV. Although permanently above the adjusted water level after Week 21, the Eh of Depth 1 of all profiles also showed a more or less strong response to high water level periods. The permanently water-saturated Depth 3 of the toe slope profile did not respond to water level changes after Week 26 but stayed between $+188$ and $+258$ mV throughout the experiment.

The pH of all samples varied between 6.4 and 8.2. Although showing some fluctuations, the pH slightly decreased over time except for Depth 3 of the mid- and toe slope soil in which it remained almost constant (Figures 1–3, d). The pH was not correlated with Eh (Table 1).
| Lysimeter Depth | Lysimeter | Depth | \( n^a \) | Eh vs. & pH vs. & Al vs. & Fe vs. & Mn vs. & \( P_\text{O} \) vs. & TC vs. & OC vs. |
|-----------------|-----------|-------|-----------|-----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Upper slope | 1 | 19 | Ca = .77*** | Ca = −.76*** | Mn = .71*** | Fe = .71*** |
| & | Mg = .73*** | Mg = −.71*** |
| & | NO\(_3\)-N = .75*** | Fe = .76* | Al = .76*** | Eh = −.83*** |
| & | SO\(_4\)-S = .71*** |
| & | Mn = −.83*** |
| & | NO\(_3\)-N = .85*** |
| & | Ca = .77*** |
| & | Fe = .77* |
| & | P\(_\text{O} \) = .81*|
| & | P\(_\text{T} \) = .80*** |
| & | Fe = .89*** |
| Mid-slope | 1 | 12 | TC = .88*** | TC = .77* | OC = .83*** | Fe = .73* | pH = .88*** | SO\(_4\)-S = −.78* |
| & | IC = .73* |
| & | Mn = .73* |
| & | NO\(_3\)-N = −.73* |
| & | SO\(_4\)-S = −.77* |
| & | Ca = −.78* |
| & | Mg = −.74* |
| & | Fe = .76* |
| & | TC = .71*** |
| & | Al = .76*** |
| & | Fe = .71*** |
| & | P\(_\text{O} \) = .74*** |
| & | Fe = .74*** |
| & | P\(_\text{T} \) = .78*** |
| & | P\(_\text{O} \) = .84*** |
| & | Fe = .84*** |
| Toe slope | 1 | 19 | Fe = .82* | Al = .82*** |
| & | Mn = −.76*** |
| & | TC = .74*** |
| & | Eh = −.76*** |
| & | OC = .75*** |
| & | Fe = .78*** |
| & | P\(_\text{O} \) = .78*** |
| & | P\(_\text{T} \) = .71*** |

Note. \( n \), number of solutions from which all parameters could be analyzed and which hence were used for correlation; \( P_\text{O} \), organic P; TC, total C; OC, organic C; \( P_\text{T} \), total P; IC, inorganic C.

*Significant at the .05 probability level. ***Significant at the .001 probability level.
3.2 | Element concentrations in pore water

Across all soil profiles, the maximum total dissolved P concentration in pore water samples was 2.0, 1.8 (toe slope profile), and 2.1 mg L$^{-1}$ (upper slope profile) for Depths 1, 2, and 3, respectively (Figures 1–3, e). The proportion of P, thereby varied between <1.5 and 100%. In Weeks 24–28, P$_{o}$ dominated, whereas from Week 29 onwards, detectable P concentrations were dominated by organic P (P$_{o}$). The total P concentration in pore water collected from a given lysimeter at a given time was 1.8 mg P L$^{-1}$ maximum.

Total dissolved Fe was mainly present in soil solutions of Weeks 24 and 27–35 (Figures 1–3, f). Maximum Fe concentrations for the upper and toe slope profiles were found in solutions of Depth 1 (0.02 and 0.03 mg L$^{-1}$, respectively), whereas in the mid-slope profile, it was Depth 3 (0.01 mg L$^{-1}$). In the upper soil profile, total dissolved Mn was mainly detected in Depth 3 throughout the experiment, with highest concentrations in Week 24 (3.7 mg L$^{-1}$, Figures 1–3, g). In the mid-slope profile, Mn was mainly detected in solutions of Depth 1 during high water levels in Weeks 27–29 and 34–36 (maximum = 0.3 mg L$^{-1}$). In the toe slope profile, the highest Mn concentrations occurred in Week 24 in Depth 1 (3.4 mg L$^{-1}$), whereas in Depth 2, concentrations were highest during the high-water period in Weeks 27–29 (maximum = 1.4 mg L$^{-1}$).

Maximum total C (TC) concentrations were 138, 64, and 78 mg L$^{-1}$ in the upper slope profile, 90, 89, and 177 mg L$^{-1}$ in the mid-slope profile, and 173, 93, and 73 mg L$^{-1}$ in the toe slope profile for Depths 1, 2, and 3, respectively (Figures 1–3, h). Generally, dissolved inorganic C (DIC) was present in all analyzed solutions. In the upper slope profile, DIC concentrations from Depth 1 were generally highest (20–88 mg L$^{-1}$) except for Weeks 24–26, in which not enough sample solution could be collected to perform this analysis. In Week 24, the highest DIC concentration was detected in Depth 1 of the toe slope profile (173 mg L$^{-1}$). Concentrations of DOC were highest in solutions of Depth 1 with a maximum of 74, 32, and 41 mg L$^{-1}$ for the upper, mid-, and toe slope profile, respectively. With this, maximum DOC concentrations corresponded to 66, 47, and 64% of TC in the upper, mid-, and toe slope profile, respectively.

Nitrite-nitrogen was generally high from Week 33 onwards, except for the toe slope profile, in which NO$_2^-$ was already found in solutions from Week 24 onwards. Nitrate-nitrogen was particularly detected from Week 31 onwards and peaked during Weeks 40 and 41 (Figures 1–3, j). Sulfate-sulfur was detected constantly throughout the experiment and was mainly found in Depth 1 solutions (Figures 1–3, k). Similarly, Ca, K, and Mg were constantly detected, with the highest concentrations in Depth 1, except for K in the upper slope profile where its concentration was generally highest in solutions of Depth 2 (Figures 1–3, m–o). Concentrations of Al were mainly detected in Depth 3 solutions and peaked between Weeks 28 and 33 (Figures 1–3, l).

3.3 | Correlation of parameters

Strong positive correlations between Eh and dissolved element concentrations were almost exclusively observed for the upper slope profile (Table 1). Here, more Ca and Mg were present in solutions of Depths 1 and 3, if the Eh was high. Similarly, NO$_3^-$ was positively correlated with Eh in Depth 2 and 3. In Depth 2 of the upper and toe slope profiles, Mn concentration was negatively correlated with Eh.

The Fe concentrations correlated positively with concentrations of Mn in solutions of Depth 1 of the upper and mid-slope profile. In Depth 1 of the toe slope profile, the Fe concentration in solution was positively correlated with the Al concentration. Similar observations were made for Depth 2 for the mid-slope and Depth 2 and 3 for the upper slope profile. Further, Fe concentrations were correlated positively with P$_{o}$ in solutions of Depth 3 of the upper and toe slope profile and Depths 2 and 3 of the mid-slope profile. The TC concentration was positively correlated with the Al concentration in solutions of Depth 1 of the mid-slope profile, and with PO$_4^{3-}$ in solution of Depth 2 of the toe slope profile.

3.4 | Plant mass and element concentrations of spring barley

The dry mass for spring barley straw ranged between 19 and 27 g lysimeter$^{-1}$, and the mass of grain was between 40 and 46 g lysimeter$^{-1}$ (Table 2), which was equivalent to a grain yield of 5.6–6.5 Mg ha$^{-1}$. The grain/straw dry mass ratio increased in the order upper < toe < mid-slope lysimeter (1.6, 2.1, and 2.0, respectively). Concentrations of P were similar in spring barley from the upper and mid-slope lysimeter (15 g kg$^{-1}$) but were slightly lower in the toe slope lysimeter (13 g kg$^{-1}$). Total biomass P of spring barley was 0.71, 0.63, and 0.64 g biomass P lysimeter$^{-1}$ for the upper, mid-, and toe slope lysimeter, respectively. From all the soil profile stocks of P- and oxalate-extractable fractions, calculated from Baumann et al. (2020) (H$_2$O-P, resin P, NaHCO$_3$-P, labile P [H$_2$O-P + resin P + NaHCO$_3$-P], NaOH-P [moderately labile P], H$_2$SO$_4$-P [stable P], residual P, oxalate-extractable P, Fe, Al, and Mn; Supplemental Table S3), only stable P (H$_2$SO$_4$-P) profile stocks were significantly negatively correlated with biomass P uptake lysimeter$^{-1}$ ($r^2 = .995$).
### Table 2

| Lysimeter     | Plant part | Dry mass | C (g kg⁻¹) | N (g kg⁻¹) | S (mg kg⁻¹) | Al (mg kg⁻¹) | Fe (mg kg⁻¹) | Mn (mg kg⁻¹) | Mg (mg kg⁻¹) | P (mg kg⁻¹) | P uptake (mg kg⁻¹) |
|---------------|------------|----------|------------|------------|-------------|-------------|-------------|-------------|-------------|------------|-------------------|
| Upper slope   | Straw      | 27.0     | 441.2      | 1.7        | 5.0         | 860.1       | 1.3         | 21.9        | 16.6        | 3.5        | 0.06              |
|               | Grain      | 43.1     | 412.9      | 13.3       | 1.1         | 40.2        | 4.2         | 15.1        | 5.5         | 5.5       | 0.05              |
| Mid-slope     | Straw      | 19.1     | 433.6      | 1.6        | 4.6         | 870.8       | 1.3         | 27.7        | 17.5        | 3.2        | 0.03              |
|               | Grain      | 39.5     | 414.0      | 13.1       | 1.2         | 47.2        | 1.2         | 15.0        | 5.6         | 5.6       | 0.03              |
| Toe slope     | Straw      | 23.3     | 434.1      | 4.5        | 1.8         | 679.5       | 1.2         | 24.8        | 17.8        | 4.8        | 0.04              |
|               | Grain      | 46.1     | 413.3      | 13.5       | 1.2         | 49.3        | 0.3         | 12.9        | 4.8         | 5.6       | 0.06              |

### DISCUSSION

#### 4.1 Redox potential pattern

In all lysimeters, waterlogging up to −5 cm resulted in the lowest Eh values for Depth 1 indicating strongly reducing conditions during Weeks 17–21 (Figures 1–3, c). An Eh of down to −248 mV points towards a SO₄²⁻ reduction pathway in Depth 1, at which all electron acceptors starting from O₂, over NO₃, Mn, down to Fe were saturated so that mainly S as an electron acceptor was left over (Langmuir, 1997; Megonigal et al., 2004). The high electron production can be explained by microbial decomposition of large amounts of organic matter, since it is well known that the amount of labile organic C, functioning as an electron donor, is critical for the reduction of the final electron acceptors (Lu, Wassmann, Neue, & Huang, 2000; Megonigal et al., 2004; Reddy & DeLaune, 2008). These conditions are plausible because of a high organic matter content of 10–14 mg soil organic C kg⁻¹ at Depth 1 (Baumann et al., 2020), as well as intensive rooting by the barley crops and resulting microbial activity in the rhizosphere. The lower amounts of soil organic C in Depths 2 and 3 (1–7 g kg⁻¹ soil in Depth 2 and 3; Baumann et al., 2020) most probably have contributed to a relatively high minimum Eh of +180 mV, indicating reduction of mainly Mn(IV) and/or Fe(III) in those depths (Megonigal et al., 2004). In addition, the quality of the organic matter and differences in the abundance and activity of microbial communities could have restricted the decomposition of organic matter and thus prevented the Eh to drop as intensive as at Depth 1 (Baumann, Marschner, Smernik, & Baldock, 2009; Fierer & Schimel, 2002; Moche, Gutknecht, Schulz, Langer, & Rinklebe, 2015). It should be noted that all reduction processes are subject to microbial competition and hence may coexist (Megonigal et al., 2004; Reddy & DeLaune, 2008). In the following rewetting cycles in the toe slope profile, Eh in Depth 1 was strongly affected at high water levels. Here, it decreased down to −240 mV again (Weeks 27–29) but did not reach those low values in the following high-water periods. In fact, it leveled out with time, meaning that Eh changes became smaller with each reoccurring high-water event. This phenomenon was also observed for Depth 2 and 3 of the upper and mid-slope profiles, as well as for Depth 2 of the toe slope profile, and was noted before in a lysimeter study conducted by Shaheen et al. (2014) investigating heavy metals. In the present study, as well as in the study by Shaheen et al. (2014), it may be explained by a general decrease in dissolved C concentration over time, which could be due to an exhaustion of the labile soil organic matter pool, as well as a decrease or change in microbial biomass due to reoccurring rewetting events (Chen, Lai, Zhao, Li, & Lin, 2016; Van Gestel, Mecck, & Vlassak, 1993). This explanation is well in line with...
declining CO₂ respiration flushes frequently observed during soil DRW cycles in laboratory studies (Chow, Tanji, Gao, & Dahlgren, 2006; Fierer & Schimel, 2002; Mikha, Rice, & Mil liken, 2005) and suggests a relationship between CO₂ flush and Eh intensity. Redox potential, however, was not correlated with dissolved TC or organic C concentrations, confirming that organic matter quality is a main driver for microbial activity and, thus, CO₂ flush intensity (Butterly et al., 2009; Wang, Dalal, Moody, & Smith, 2003).

A permanently high water level resulted in minimum Eh values of about +200 mV for Depth 3 of the toe slope profile, indicating the theoretical possibility of NO₃⁻/Mn(IV) but not Fe(III) reduction (Reddy & DeLaune, 2008) at any time. However, the occasional detection of dissolved Fe and dissolved P, which could have potentially been bound to Fe, disagrees with that theoretical redox range. This observation suggests that other factors such as element leaching from upper parts of the soil column probably affected the pore water concentration of these elements in Depth 3.

No substantial effect on the solution pH had been observed during an Eh decrease, which may be due to a very fast pH response that, in our study, was not captured by weekly sample collection. In fact, Ponnamperuma (1972) reported a stabilization at about neutral pH within only a few weeks after low Eh due to long-term regulation of the pH by CO₂ partial pressure. Further, the collection of several milliliters of sample solution could have masked any small-scale spatial heterogeneity in pH (Husson, 2013).

4.2 Effects of water table fluctuation on P mobilization

The calculated total P concentration in pore water collected from a given lysimeter at a given time was 1.8 mg P L⁻¹ at most. This concentration range was fivefold higher than that usually observed in waters at drain outlets at the field site where the lysimeters were collected (Kahle, Bauwe, & Lennartz, 2019). This larger concentration range indicates stronger redox effects in our partly water-saturated lysimeter soils compared with field conditions and also may point to P traps along the pathway from soil profiles to drainage outlet. On the other hand, P concentrations detected in the lysimeter soil solutions were far below that found by Zimmer et al. (2016) after a heavy rainfall event in drain water of the Dummerstorf field site (141 mg P L⁻¹). This also points to the same explanation given above for the lower P concentrations in base flow: the existence of P traps along the flow pathways that had been flushed during the storm event and had resulted in a large P release and heavy preferential flow events. It should be noted that our results are based on total pore volume only and did not take into account differences in pore size distribution when calculating P concentrations from different depths at different soil moistures. This may suggest that fine pores and associated positively charged reactive surfaces could have been one part of the hypothesized P traps. The results suggest that closing the drains may be a useful temporal procedure to cut off drainage peaks and related flushes of P. Especially in summer, when the heaviest rainfall events usually occur in northeastern Germany (Miegel, K., personal communication, 2020), soil profiles would not be completely saturated and thus pore space for water storage should be available. Therefore, irrespective of preferential flow, which definitely would occur, cutting off the drainage peaks in the first instance could prevent P losses from the field since P in pore waters may not necessarily leave the field but could also be taken up by crops and microorganisms.

In all three soils, the highest P i concentrations were observed at the beginning of solution sampling during Weeks 24–27, which may be due to the dispersion of colloid particles during the preceding reducing conditions. Thereby, Fe(III) compounds would have been reduced, resulting in mineral dissolution as suggested by Yan, Lazouskaya, and Jin (2016). Further, Fe(III) compound reduction could have increased the pH, which in turn could have affected particle dispersion via changes in colloid surface charge and changes in particle coating that glue or bind clay and organic matter together (Henderson et al. 2012; Thompson, Chadwick, Boman, & Chorover, 2006). After the first DRW (Week 30 onwards), P i concentrations were generally negligible, which could be due to altered colloid surface properties that were modified by changes in solution chemistry (e.g., pH, organic matter) and the processes of dissimilatory Fe reduction under anaerobic conditions (Yan et al., 2016). Also, the mineralizing or turning over microbial community and/or the spring barley root activity, both of which could have contributed by their activity to high P i concentrations in solution as before (Nagarajah, Posner, & Quirk, 1970), seemed to have been affected by high water levels. Further, Bünemann et al. (2013) reported that P released from microorganisms during DRW was trapped inside microaggregates and only became water extractable again in combination with soil dispersion. Similarly, P released from soil also could have been trapped inside those microaggregates. Additionally, the increased amount of water may have diluted and/or relocated P i, thus leading to the negligible P i concentrations.

The concentration of P o in pore water showed the reverse pattern of that observed for P i with high concentrations mainly between Weeks 29 and 33. This suggests that during the rewetting event (Weeks 27–29), microorganisms (e.g., aerobic bacteria) could have been killed, which led to a flush in P o afterwards. Interestingly, this P o flush was not short-living but stretched over the whole second dry phase (Weeks 30–33). One reason for this may be a lag phase in which the solution still reflects the situation of some weeks before (Moloney, Fenton, & Daly, 2020), because it may take some time for the P o compounds to find their way to the medium and
macropores to be finally sucked out of the system. In our case, this lag phase may have been 2 wk judging from the first occurrence of $P_0$. Secondly, a stepwise adaptation of the microbial community to the dry period may have caused high $P_0$ concentrations occurring in solution over a long time. Since different microorganisms can cope differently with DRW, this may have resulted in a long-lasting continuous change in the microbial community (DeAngelis, Silver, Thompson, & Firestone, 2010; Fierer & Schimel, 2002; Fierer, Schimel, & Holden, 2003; Moche et al., 2015; Pett-Ridge & Firestone, 2005). Also, Turner and Haygarth (2001) and Turner, Baxter, and Whitton (2003) found high $P_0$ concentrations in water samples of U.K. grassland soils that—as they speculated—had partly derived from lysed microbial cells as well as native soil organic matter.

High $P_0$ concentrations in Weeks 38 and 39 were observed in pore water of the upper and toe slope profile, respectively (Figures 1–3, e). They may be related to high precipitation in Weeks 36 and 37 (Figures 1–3, a) with the effects visible after a lag phase of 2–3 wk, during which rainwater percolated through the soil and adsorption–desorption–turnover processes took place. The precipitation coincided with the harvest of spring barley and the sowing of the catch crop serradella (Figures 1–3, b). Hence, decomposing root biomass (spring barley) and tillage of the upper soil centimeters for serradella seed bed preparation most probably also contributed to a $P$ concentration peak 2–3 wk later (could not be shown for the mid-slope profile because no solution could be collected from Depth 1 during Week 38; Figure 2e, Supplemental Table S1). Also, the detected $P_0$ may have originated from the disruption of intact soil aggregates and subsequent release of $P$ and $Fe$. Further, serradella roots may have contributed to $P$ mobilization, since legumes are known to increase $P$ mobilization by low pH, high organic acid concentrations, and phosphatase activity in the rhizosphere (Eichler-Löbermann, Köhne, Kowalski, & Schnug, 2008; Maltais-Landry, 2015).

In the present study, there was no general positive relationship observed between concentrations of total $P$ and $Fe$, $Al$, $Mn$, or DOC, suggesting that structural effects of the intact soil columns with nonhomogeneous situations for biogeochemical processes could have affected the relations. In particular, different mechanisms including aggregation of particles under slightly drier and more oxidative conditions and dispersion of colloids under slightly wetter and more reductive conditions taking place at the same time but in different spots may have affected the result. Only in Depth 3 of all lysimeter solutions was $P_0$ concentration strongly positively correlated with $Fe$ concentration, pointing to the important role of $Fe$ minerals in $P$ binding at this depth.

For almost all soil depths, $Fe$ and $Al$ concentrations were positively correlated in pore waters of the present study. Their peak during Weeks 29–33 coincided with high $P_0$ concentrations, suggesting that $P_0$ had not only been complexed by $Fe$ but also by $Al$, and/or bound in $Al$-substituted $Fe$-(oxy)hydroxides (Schwertmann, 1991). Although it is assumed that during the wet period mainly $Eh$-driven oxide reductions and dispersion of colloid particles were responsible for the release of $P$, decomposition and desorption reactions initiated by excretion of plant and microbial-derived organic acids could also have contributed during the dry phase (Nagarajah et al., 1970).

For all lysimeters, a main increase in $NO_3^−$ but also in $Ca$ and $Mg$ concentrations was observed after Week 36 for pore waters of Depth 1, which coincided with spring barley harvest and serradella planting. Hence, the increase in element concentrations was most probably related to spring barley root decomposition and/or the lack of nutrient uptake by the living plants. Since $NO_3^−$ inhibits dissimilative $Fe$(III) reduction (Turner & Patrick, 1968), an increase in nitrification could have added to the stability of $Fe$-$P$ compounds, thus contributing to low $P$ concentrations in pore water as generally observed after Week 36 (Figures 1–3, e).

### 4.3 | Spring barley yield and $P$ uptake

Spring barley grown in the lysimeter monoliths reached a grain yield of 5.6–6.5 Mg ha$^{-1}$, which was in the range of grain yields reported for different spring barley genotypes before (4.6–7.3 Mg ha$^{-1}$; Chen, Svane, & Thorup-Kristensen, 2019). This suggests a representative development of this crop in the lysimeter monoliths and, moreover, the general relevance of the experimental approach.

Phosphorus uptake of plants was reported to strongly correlate with the labile $P$ pool of soils (Sanntner et al., 2015; Tran, Simard, & Fardeau, 1992; Zheng, Parent, & MacLeod, 2003). However, in the present study, spring barley $P$ uptake (Table 2) was only negatively correlated with $H_2SO_4$–$P$ soil stocks of the original soil monoliths as calculated from Baumann et al. (2020). Stable $P$, generally interpreted as $P_1$ and $P_0$ associated with $Ca$ and $P$ occluded within sesquioxides, thus plausibly did not promote plant growth in the present study. In contrast, a substantial portion of total $P$ occurring as stable $P$ in the subsoil (Baumann et al., 2020) affected barley $P$ uptake negatively. This result suggests that reoccurring reducing conditions had no substantial positive effect on the mobilization of stable $P$, which in turn could have been used by barley to increase its $P$ uptake.

### 4.4 | Limitations of the study

The maximum total $P$ concentration discrepancies between field observation (141 mg P L$^{-1}$; Zimmer et al., 2016) and lysimeter study (1.8 mg P L$^{-1}$) could indicate that our lysimeter profiles did not include so called “sensitive areas” of
high predictive power for matter transport of this study site (Sommer, 2006). However, it should be noted that heavy rain extreme situations were not simulated in our lysimeters. Further, it cannot be ruled out that a slightly higher P concentration may have been leached from a lysimeter during the initial drainage (Weeks 22 and 23).

In the present study, element concentrations but no element fluxes (P concentration times the flow rate) were analyzed. However, the latter may be useful to evaluate the amount of P that could potentially be lost through soil pore water and should be examined in future studies. Thereby, it may turn out that high P pore water concentrations along with low P mobility during dry periods may be less harmful than low P pore water concentrations along with high P mobility during wet periods. The latter may be more challenging to control, and the soil could be more vulnerable to P loss through leaching. However, the P concentrations are critical target values for the quality of freshwaters (Leinweber et al., 2016) and are hence presented in this study.

For our correlation analyses between elements and Eh or pH, we pooled all samples of a given lysimeter rather than looking at single dry–wet periods separately. Thereby different mechanisms of complex reactions were considered together. Hence, all relations include the factor time.

5 | CONCLUSIONS

Lysimeter experiments conducted in the present study were useful to assess pore water P concentrations in soil pore systems during the course of fluctuating water level. Although the study was not designed to investigate single processes, the combination of all pore water element results and parameters together led to plausible explanations of the observed patterns.

Elevated water levels were demonstrated to cause low Eh values in soil, which could be related to the soil organic matter content. During solution sampling, the Eh was not related to Fe or P concentrations in the natural, largely undisturbed pore system of the lysimeter soils, probably reflecting all the different mechanisms and processes of an inhomogeneous soil.

A maximum of 1.8 mg total P L$^{-1}$ in pore water of a given lysimeter at a given time was observed, suggesting that closing a drain may cause a moderate P mobilization risk for the investigated temperate arable soils. This would probably be lower compared with a P mobilization risk caused by a heavy rain event.

A negative relationship between stable P of the soil, determined in disturbed soil samples during the lysimeter excavation, and crop biomass P suggested that water table fluctuation did not mobilize much P of this fraction, which could have been used by the crops.

Overall, the study contributed to finding solutions for reducing the diffuse P pollution of freshwater by pointing to a relatively low risk of controlled drainage systems for undesired P mobilizations.

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AUTHOR CONTRIBUTIONS

Karen Baumann: Conceptualization; Formal analysis; Investigation; Visualization; Writing-original draft; Writing-review & editing. Samer Nastah: Investigation. Sabry M. Shaheen: Writing-review & editing. Peter Leinweber: Conceptualization; Funding acquisition; Project administration; Supervision; Writing-review & editing.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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**SUPPORTING INFORMATION**

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