Short Term Effects of Salinization on Compound Release from Drained and Restored Coastal Wetlands

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Abstract: Over the past two decades, great efforts have been made to restore coastal wetlands through the removal of dikes, but challenges remain because the effects of flooding with saline water on water quality are unknown. We collected soil samples from two adjacent coastal fen peatlands, one drained and diked, the other open to the sea and rewetted, aiming at assessing the mobility and export of various compounds. Microcosm experiments with constant flow-through conditions were conducted to determine the effluent concentrations of dissolved organic carbon (DOC), ammonium (NH_4^+), and phosphate (PO_4^{3-}) during saline–fresh water cycles. Sodium chloride (NaCl) was used to adjust salinity (saline water, NaCl concentration of 0.12 mol L^{-1}; fresh water, NaCl concentration of 0.008 mol L^{-1}) and served as a tracer. A model analysis of the obtained chloride (Cl^-) and sodium (Na^+) breakthrough curves indicated that peat soils have a dual porosity structure. Sodium was retarded in peat soils with a retardation factor of 1.4 ± 0.2 due to adsorption. The leaching tests revealed that water salinity has a large impact on DOC, NH_4^+, and PO_4^{3-} release. The concentrations of DOC in the effluent decreased with increasing water salinity because the combination of high ionic strength (NaCl concentration of 0.12 mol L^{-1}) and low pH (3.5 to 4.5) caused a solubility reduction. On the contrary, saline water enhanced NH_4^+ release through cation exchange processes. The PO_4^{3-} concentrations, however, decreased in the effluent with increasing water salinity. Overall, the decommissioning of dikes at coastal wetlands and the flooding of once drained and agriculturally used sites increase the risk that especially nitrogen may be leached at higher rates to the sea.

Keywords: coastal wetlands; salinity; dissolved organic carbon; ammonium; phosphate; dual porosity

1. Introduction

Coastal wetlands—saltmarshes, mangroves, and seagrass beds—only cover approximately 0.3% of the Earth's land surface [1,2], but hold vast stores of carbon and play a critical role in regulating physical, chemical, and biological processes in tidal and non-tidal systems [3]. In the past, many marsh wetlands were diked and drained for pastural and agricultural use. It was estimated that about 25–50% of the world's coastal tidal wetlands were lost as a result of their direct conversion into agricultural land [2,4]. In addition to the direct land loss, a large number of coastal wetlands has been found to be eutrophic, which is considered one of the main causes for their ecological functional degradation [5,6].

Diking blocks the flow of seawater to wetlands, reducing their salinity [7]. The established drainage lowers the water table, accelerating organic matter decomposition [8,9]. It was reported that after long-term diking and drainage, coastal peatlands revealed low salinity (Cl concentration of 0.002 mol L^{-1}), acidification (pH, from 3 to 4), exchangeable Fe(II) mobilization, and organic matter mineralization [9]. To reestablish important wetland functions, a common practice is to return the formerly diked pasture to a salt marsh (NaCl concentration of 0.3 mol L^{-1}) through moving or altering barriers such as dams or dikes [10]. Although water salinity increased after removing dikes, previous

studies show contradictory effects of water salinity on carbon (C), nitrogen (N), and phosphorus (P) cycles. Salinization can directly influence the C cycles by increasing [11] or decreasing [12,13] dissolved organic carbon (DOC) release and the P cycles by increasing [8,14,15] or decreasing [16,17] sediment P availability. Moreover, the effect of salt on C, N, and P dynamics are generally derived from studies of salt gradients in estuaries or comparative studies between fresh water and the marine system rather than direct studies of de-salinization of coastal salt wetlands or re-salinization of coastal fresh wetlands [16].

In addition to salinization, the sediments of diked salt marshes that have been drained exhibit very distinct physical and chemical properties, such that they should respond differently to seawater restoration. Compared with seasonally flooded salt marshes, soils of diked salt marshes have a higher bulk density, lower organic matter content, and higher iron and sulfur content [8]. After re-salinization, high ferrous iron concentrations (0.05 mol L^{-1}) were observed in diked and drained peat, while sulfide accumulated in seasonally flooded diked peat [8,9]. Moreover, it has been proved that peat soils have a complex dual-porosity structure containing active pores and partially closed or dead-end pores. Water movement and solute transport occur basically through connected active pores (mobile soil water region), while partially closed pores (immobile soil water region) are diffusion controlled [18–21]. Some studies have concluded that a high pore water velocity in the mobile region may reduce DOC effluent concentrations [13] and that immobile water regions enhance nitrate reduction [20,21]. However, the soil structure of peat and its impact on C, N, and P cycles are not well understood yet. Thus, miscible displacement experiments were conducted and the mobile and immobile model (MIM) was applied to obtain more insight into the hydro-physical and solute transport properties of the system. The objectives of the present study were therefore to investigate (1) solute transport properties of organic soils and their effect on biogeochemical processes; and (2) the impact of salinity on C, N, and P release from coastal wetland sediments. The focus was laid on short saline fresh water cycles to unravel the operating processes of coastal wetlands, which are subjected to rewetting measures.

2. Materials and Methods

2.1. Study Sites and Soil Sampling

Two adjacent coastal wetlands were chosen. They were located approximately 10 km north of the city of Greifswald, northeastern Germany. Both sites have been diked and drained since 1800. The height of the dikes was increased between 1971 and 1974, coinciding with improvements in the drainage system. While one site was still subjected to drainage (coastal drained site; CD), the other site had been rewetted by removing the dike and thus had been open to the sea since 1993 (coastal rewetted site; CW; Figure 1). The first flooding of CW was recorded on 25 December 1993. Both sites were utilized as grassland, and their top soils (0–30 cm) were highly degraded peat. Beneath the peat horizon, the soil was classified as sandy loam. The pH values of the top soils were low at both sites due to the oxidation of reduced sulfur and iron minerals (Table 1). The ground water table at CD ranged from 50 cm to 100 cm and that at CW varied from 0 to 40 cm below the ground surface. The electrical conductivity (EC) of ground water in CW was approximately 13 mS cm^{-1}, which was significantly higher than at CD (1 mS cm^{-1}) due to the regular brackish water flooding after the dike removal. However, the EC of the ground water in CW was as low as 1 mS cm^{-1} after rainstorms in summer. It is expected that the drained site (CD) will be restored in the next 3 years and the dike will be removed, as was the case at the comparison site (CW). We intended to investigate the nutrient release after dike removal and the subsequent flooding of the formerly drained site. Soils from the CD site will then undergo saline–fresh water cycles. CW served as a reference.
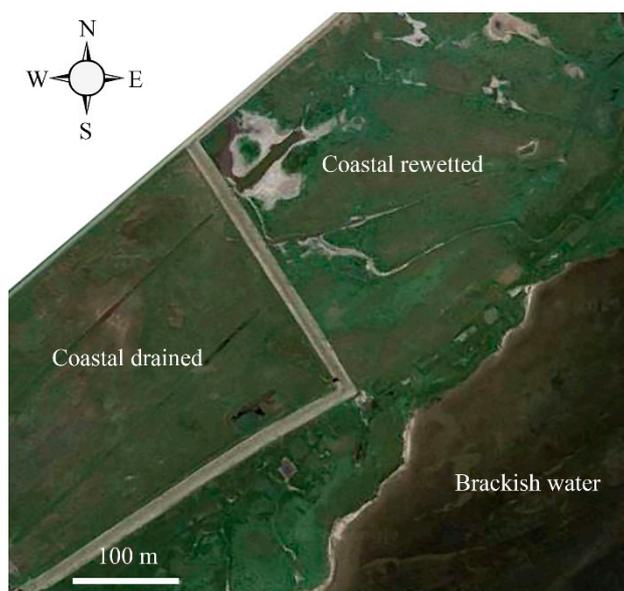
Figure 1. Two adjacent coastal wetlands, coastal drained (CD, with dike), and coastal rewetted (CW, dike removed).

Table 1. Physical and chemical properties of the investigated peat soils given as mean (standard deviation), n = 6.

Study Site	Soil Organic Matter Content	Bulk Density	Total Porosity	K_s [1]	pH	Total Phosphorus
	wt%	g cm^{-3}	vol%	cm h^{-1}	–	mmol g^{-1}
CD	35.1 (2.7)	0.65 (0.02)	68.8 (2.6)	−0.44 (0.25)	3.98 (0.29)	0.022 (0.001)
CW	37.3 (4.7)	0.60 (0.10)	71.4 (5.2)	−0.42 (0.24)	4.55 (0.39)	0.025 (0.002)

[1] Log$_{10}$-transformed saturated hydraulic conductivity (K_s), log$_{10}$ K_s.

At each site, an area of 8 m × 8 m was selected for sampling. Ten undisturbed soil cores (250 cm^3, 7.2 cm diameter, 6.1 cm long) were taken at a 10–20 cm depth at each site to determine soil hydro-physical and chemical properties (Table 1). All of the hydro-physical properties of the peat samples were obtained from standard measurements (e.g., ISO 11272:1998 for dry bulk density measurement; [22]). The soil organic matter content was determined by loss on ignition (four hours incineration at 550 °C). Bulk density was determined via the thermogravimetric method by drying the samples in an oven at 105 °C for 24 h. The total porosity was derived from the bulk density and gravimetric water content at saturation. The saturated hydraulic conductivity was determined by a constant-head upward-flow permeameter. For the determination of total phosphorus (TP), dried peat (60 °C, 48 h) was homogenized in a stainless-steel mill. The TP content of peat was determined as the soluble reactive phosphorus after an acid digestion procedure (circa 10 mg dry sample + 2 mL 10 M H_2SO_4 + 4 mL 30% H_2O_2 + 20 mL deionized water at 160 °C for 2 h; [23]). However, it should be noted that the value of TP in soil is related to the determination technique [24]. Two larger soil cores (8.0 cm diameter; 10 cm length) were collected from each site to conduct the leaching experiment. The larger soil cores were collected by cutting the soil with a sharp knife in front of the cylinder, which was slowly driven into the soil in order to avoid any compaction. The soil samples were stored in the fridge at 4 °C for two to three days prior to the experiment.

2.2. Leaching Experiment

For the initial flushing of the columns, we used a NaCl solution with an EC similar to the respective field conditions. The rewetted coastal wetland site (CW) was subjected to regular flooding with

brackish water while the coastal drained site (CD) was freshwater influenced. To this end, the large soil cores were saturated and flushed from the bottom to the top for 5 days using artificial NaCl solutions of different EC (CW, 13 mS cm^{-1} or 0.12 mol NaCl L^{-1}; CD, 1 mS cm^{-1} or 0.008 mol NaCl L^{-1}). The solutions were prepared using demineralized water; the final solution had a low oxygen content of 2.3 mg O$_2$ L^{-1} [11]. Thereafter, three cycles of artificial saline water (NaCl solution, 0.12 mol L^{-1}) and freshwater (NaCl solution 0.008 mol L^{-1}) were applied to all soil columns. Each cycle comprised leaching with saline water for 5 days and leaching with fresh water for 5 days. The flux was adjusted to 0.34 cm h^{-1}, which compared to the saturated hydraulic conductivity of soils from CD and CW (Table 1). The experiment was conducted under steady state conditions. A constant flow rate (both inflow and outflow) was kept by a peristaltic pump ensuring that no ponding occurred at the soil surface. For details of the experimental set-up, see Liu et al. [25]. The effluent was collected using fraction samplers to determine EC, pH, Na$^+$, Cl$^-$, SO$_4{}^{2-}$, DOC, NH$_4{}^+$, and soluble reactive P concentrations. The Na$^+$, Cl$^-$, and SO$_4{}^{2-}$ concentrations were analyzed using ion chromatography employing a 930 Compact IC Flex (Metrohm AG, Hamburg, Germany). The DOC concentrations were measured with a DIMATOC® 2000 (Dimatec Analysentechnik GmbH, Essen, Germany). The phosphate concentration in the effluent of the soil cores was analyzed after filtration with syringe filters (0.45 µm pore size) by using the molybdenum blue method (Cary IE; Varian, Darmstadt, Germany) according to Murphy and Riley [26]. Photometric determination of effluent NH$_4{}^+$ concentrations were determined using a Continuous Flow Analyzer (CFA, Seal Analytical GmbH, Norderstedt, Germany). Before DOC and NH$_4{}^+$ analyses, the effluent samples were filtered through a 0.45 µm cellulose mixed esters membrane.

2.3. Evaluation of Breakthrough Curves

The well-known mobile–immobile model (MIM) [27] was used to evaluate the obtained Cl$^-$ and Na$^+$ breakthrough curves (BTCs). The BTCs were plotted as relative concentrations (C/Co; C, effluent concentration; Co, initial concentration of influent) against exchanged pore volumes (volume of peat soil core occupied by fluid). The MIM allows one to distinguish two water fractions with the mobile region (v$_m$ > 0) and immobile region (v$_{im}$ = 0; v = pore water velocity). In its dimensionless form, the solute transport in a dual porosity medium is given as Equations (1)–(3). For details of the evaluation of breakthrough curves using the MIM, see Liu et al. [28].

$$\beta R \frac{\partial C_m}{\partial T} + (1 - \beta) R \frac{\partial C_{im}}{\partial T} = \frac{1}{Pe} \frac{\partial^2 C_{im}}{\partial X^2} - \frac{\partial C_m}{\partial X} \tag{1}$$

$$(1 - \beta) R \frac{\partial C_{im}}{\partial T} = \omega(C - C_{im}) \tag{2}$$

$$T = \frac{vt}{L} \tag{3}$$

where β is the fraction of the mobile zone, ω is the mass transfer coefficient between the mobile and immobile regions. The subscripts "m" and "im" represent the mobile and the immobile water fractions, respectively. The effluent concentration (C) was normalized with the influent concentration (Co). X is the spatial coordinate, t is the time and T is dimensionless time. v is the average pore water velocity. The Peclet number (= v$_m$L/D$_m$) expresses the ratio of advection to diffusion. v$_m$ is the velocity of water through pores of the mobile region and D$_m$ is the hydrodynamic dispersion coefficient in the mobile region. L is length. R is the retardation factor. In this study, the MIM parameters (β, D, and ω) were optimized using the least squares fitting procedure CXTFIT [29] with R fixed at 1 for Cl$^-$ BTCs [18]. It was assumed that the dispersion coefficient would be the same for Cl$^-$ and Na$^+$ [27,29]. Therefore, for Na$^+$ BTCs, the MIM parameters (β, R, and ω) were optimized with D kept fixed at values obtained from the Cl$^-$ BTCs.

3. Results

3.1. Nutrient Flushing Phase

For all investigated parameters and compounds, with the exception of pH and phosphorus, a similar flushing pattern with higher values at the onset and lower values at later stages of the leaching test was observed. During the early times of flushing, the effluent EC from all soil cores was higher than that of the applied background water. After several days of flushing, EC values decreased to those of the background water (CW, 13 mS cm^{-1}; CD, 1 mS cm^{-1}; Figure 2a). The soil samples from both sites contained a large amount of sulfate, which became obvious from the high sulfate concentrations at the early stage of flushing (3 to 9 mmol L^{-1}; Figure 2b). Sulfate concentrations of effluents remained low (<0.2 mmol L^{-1}) after 5 days of leaching. During the flushing period, the effluent pH had a narrow range from 4.3 to 5.3 (Figure 2c). For most soil cores, a relatively high DOC concentration was observed only during the early stage before it stabilized at a lower concentration of 20 to 40 mg L^{-1} (Figure 2d). The NH_4^+ concentrations ranged from 0.15 to 0.4 mmol L^{-1} and after 5 days of flushing, it varied around approximately 0.2 mmol L^{-1} (Figure 2e). Phosphate concentrations ranged from 0.04 to 0.07 mmol L^{-1} and no clear tendency over time was observed during the flushing experiment (Figure 2f).
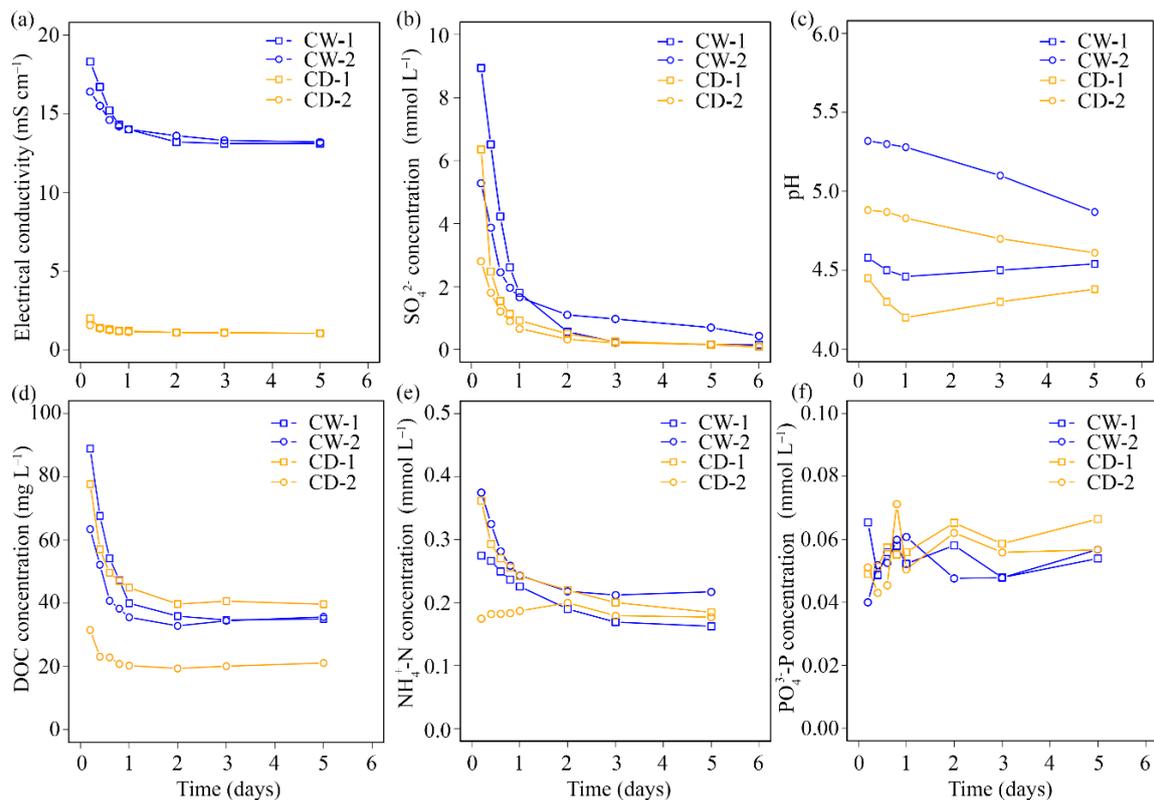
Figure 2. Initial nutrient flushing phase: (**a**) electrical conductivity, (**b**) sulfate (SO_4^{2-}), (**c**) pH, (**d**) dissolved organic carbon (DOC), (**e**) ammonium (NH_4^+-N), and (**f**) phosphate (PO_4^{3-}-P).

3.2. Breakthrough Curves

The obtained Cl$^-$ and Na$^+$ BTCs are presented in Figure 3. For all investigated soil cores, mass recovery for Cl was close to 100%, while it was 93% for Na. The relative Cl$^-$ concentration (C/Co) rose quickly and reached a value of approximately 0.7 after the exchange of one pore volume, indicating a non-equilibrium flow and transport situation. The Na$^+$ BTCs showed a similar pattern. However, the relative Na$^+$ concentrations were below 1, even after the exchange of five pore volumes, suggesting Na$^+$ was retarded in all the soil cores. In this study, the MIM adequately described all BTCs with a

fitting criterion of $R^2 > 0.99$ (Figure 3; Table 2). For Cl^- BTCs, the optimized dispersion coefficient ranged from 0.96 to 1.48 cm^2 h^{-1}. In contrast to the peat from CD, the peat soils from CW had a greater dispersivity but a lower mass transfer coefficient. The β values ranged from 0.66 to 0.90 and ω was found to vary from 0.003 to 0.368. For all the soil cores, the volumetric water content of the mobile region was calculated from the optimized β values as 0.54 ± 0.08 cm^3 cm^{-3} (mean ± standard deviation). The optimized retardation factor R for sodium varied from 1.2 to 1.7 (Table 2). Despite the similar basic soil properties (Table 1), the columns from the two experimental sites had different mobile water fractions and (Table 2) sodium retardation was likewise unequal.
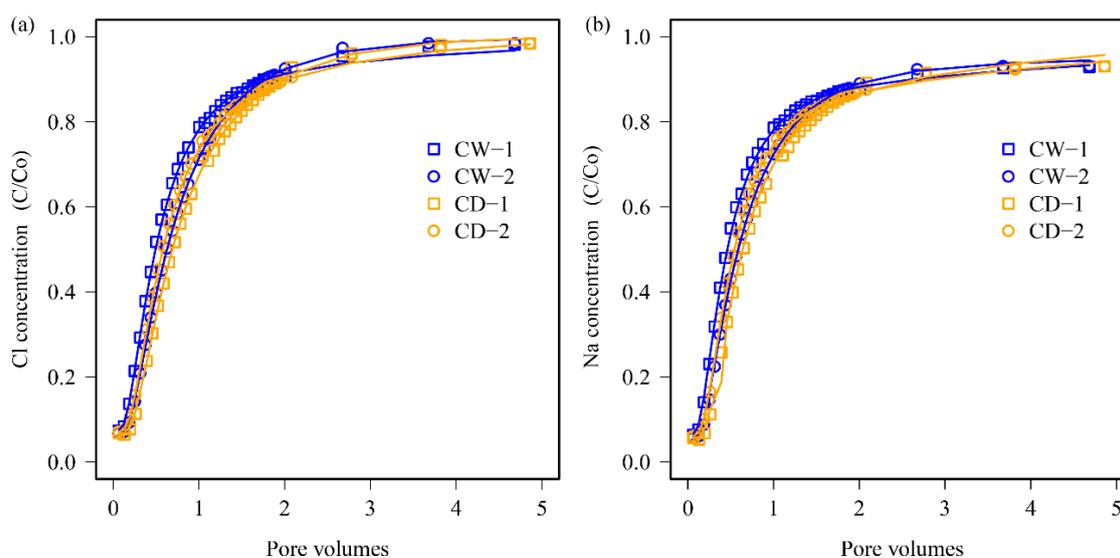
Figure 3. (**a**) Chloride (Cl^-) and (**b**) sodium (Na^+) breakthrough curves plotted as relative concentrations (C/Co) against the number of pore volumes. The lines represent the fitted breakthrough curves using the mobile and immobile model.

Table 2. Values of optimized parameters from MIM (average pore water velocity, v; dispersion coefficient, D; retardation factor, R; mobile water fraction, β; mass transfer coefficient, ω) and coefficient of determination, R^2.

Soil Core	Tracer	v	D	R	β	ω	R^2
		cm h^{-1}	cm^2 h^{-1}	–	–	–	–
CD-1	Chloride	0.434	0.96	1.00	0.79	0.368	0.999
	Sodium	0.434	0.96	1.24	0.60	0.220	0.997
CD-2	Chloride	0.434	1.05	1.00	0.70	0.213	0.999
	Sodium	0.434	1.05	1.32	0.50	0.205	0.999
CW-1	Chloride	0.418	1.33	1.00	0.66	0.112	0.999
	Sodium	0.418	1.33	1.37	0.44	0.161	0.999
CW-2	Chloride	0.418	1.48	1.00	0.90	0.003	0.999
	Sodium	0.418	1.48	1.71	0.47	0.082	0.999

3.3. Effect of Salinity on pH and C, N, and P Release

The use of artificial NaCl solution with a high EC caused a significant drop in pH of the effluents from 5.5 to 3.8. Decreasing water EC to 1 mS cm^{-1} raised the pH of the effluent to approximately 5.5. Figure 4 shows the temporal variance of DOC export from peat soil cores under saline–fresh water cycles. The effluent DOC concentrations were sensitive to influent water salinity (Figure 4). For all soil cores, decreasing water salinity (EC) from 13 to 1 mS cm^{-1} resulted in a DOC concentration increase to approximately 150 mg L^{-1}. At times of low salinities, colored dissolved organic matter (CDOM) was

visually observed in the water samples. Increasing water salinity to 13 mS cm^{-1} lowered the DOC concentrations to approximately 10 mg L^{-1}. When fresh water was applied, soil from CW exported a greater amount of DOC than those from CD. For soils from CW, no difference in DOC export pattern was observed between the three fresh-saline water cycles. In contrast, soils from CD exhibited higher DOC peak concentrations with an increasing number of fresh-saline water cycles.
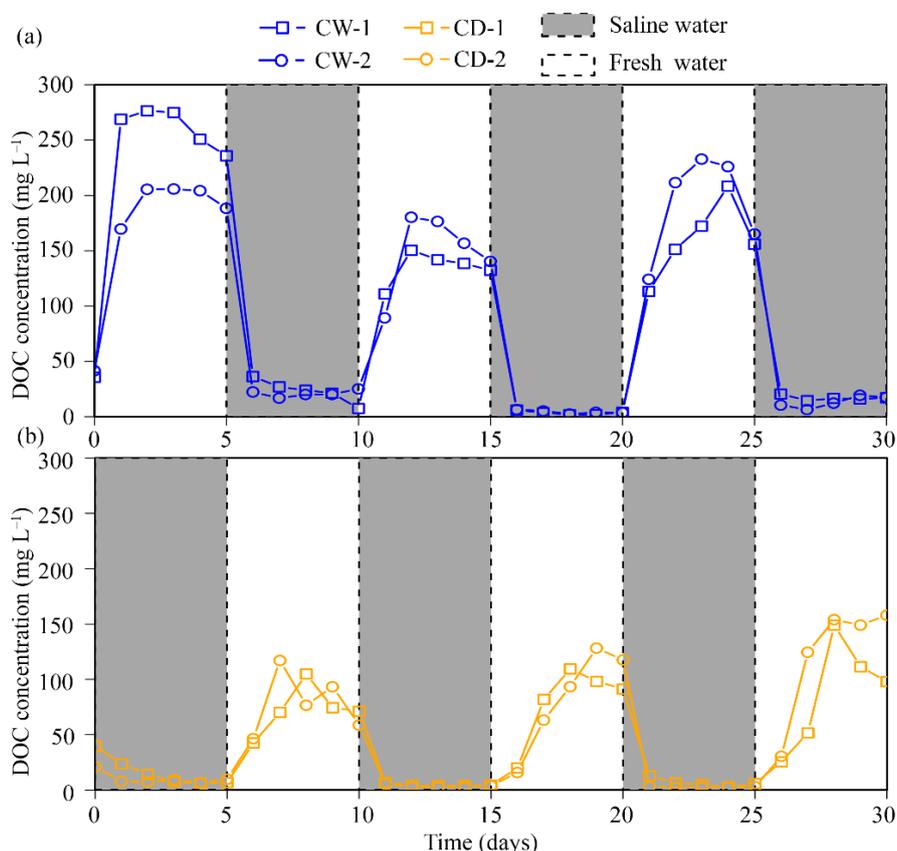
Figure 4. Dissolved organic carbon (DOC) release from peat soils under saline–fresh water cycles: (**a**) coastal rewetted, CW; and (**b**) coastal drained, CD.

Figure 5 shows the temporal variance of NH$_4^+$ release from peat soil cores under saline–fresh water cycles. For all soil cores, effluent NH$_4^+$ concentrations ranged from 0.01 to 0.25 mmol L^{-1}. In each cycle, effluent NH$_4^+$ concentrations were higher under saline water than under fresh water conditions. A significantly higher NH$_4^+$ concentration was observed in the first fresh-saline water cycle compared to the subsequent cycles. No difference between investigated sites was found with respect to NH$_4^+$ release.

The behavior of PO$_4^{3-}$-P was comparable to that of NH$_4^+$ due to the flooding history (CD vs. CW) having had no effect on the release pattern (Figure 6). Furthermore, it was observed that PO$_4^{3-}$-P concentrations decreased under elevated salinities (average 0.04 ± 0.02 mmol L^{-1}). Phosphorus concentrations were higher during the first saline–fresh water cycle in comparison to the two following cycles.
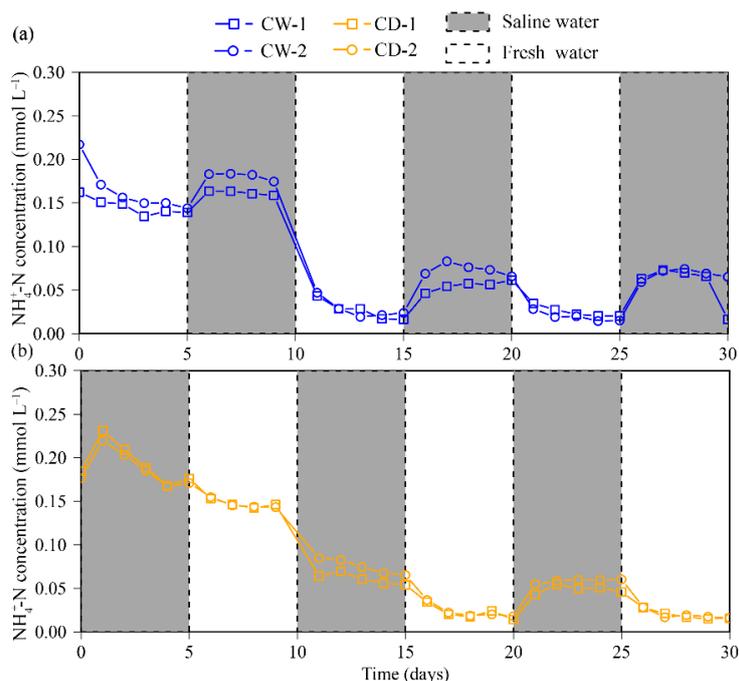
Figure 5. Ammonium (NH_4^+-N) release from peat soils under saline–fresh water cycles: (**a**) coastal rewetted, CW; and (**b**) coastal drained, CD.
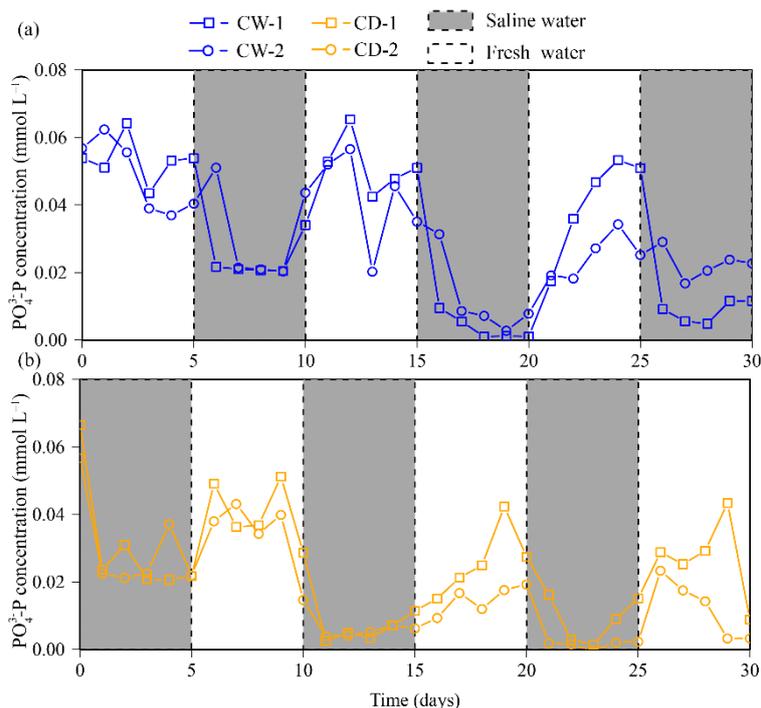
Figure 6. Phosphate (PO_4^{3-}-P) release from peat soils under saline–fresh water cycles: (**a**) coastal rewetted, CW; and (**b**) coastal drained, CD.

4. Discussion

4.1. Non-Equilibrium Flow and Transport

In this study, the Peclet number of the mobile water region ranged from 2.8 to 4.5, indicating that advection processes dominated in the leaching tests [30]. The optimized β values of all soil cores

ranged between 0.5 and 1 (Table 2), which can be taken as an indication that the investigated peat soils constituted a dual-porosity medium containing active and dead-end pores [31–33], where the active pores or mobile water region dominated the pore space of the four soil cores. The volumetric water content of the immobile region for all soil cores was 0.17 ± 0.07 cm^3 cm^{-3}; this water fraction did not participate in the convective transport of chloride. The fractions of immobile water found in this study were lower than those found for pristine peat or less decomposed peat soils [18,33], but comparable to those of highly degraded peat soils and peat sand mixtures [13,28]. The amount of immobile water content is related to peat type, the stage of peat degradation, and boundary conditions [32,33]. In pristine peat or less decomposed peat soils, the large number of inactive pores are formed by intact plant cell remains [32].

The smaller the value of β, the higher the pore water velocity in the mobile region. The soil core CW-1 had the highest pore water velocity. The largest differences in DOC and SO$_4^{2-}$ concentrations between early and late flushing stages were also observed for CW-1. It seems that high pore water velocities in the mobile region reduced DOC and SO$_4^{2-}$ effluent concentrations (Figure 2b,d). This finding is consistent with Tiemeyer et al. [13], who reported that higher pore water velocities in the mobile region reduce DOC. We postulate that the diffusional exchange between immobile and mobile water fractions is lower at high pore water velocities, which hinders DOC supply from the soil matrix to the advection zone. The impact of pore structure is, however, not as important as that of salinity on biogeochemical processes during saline–fresh water cycles.

The MIM adequately described all Cl$^-$ BTCs with R = 1, indicating that the sorption of Cl$^-$ on the investigated peat was neglectable. This result disagrees with previous studies questioning that Cl$^-$ is a conservative tracer [32,33]. However, it should be noted that the peat soils in the cited studies were pristine peat or weakly degraded peat soils having a much higher soil organic matter content (>80 wt%) than the investigated soils in this study (35 wt%), which may cause a higher adsorption coefficient of Cl$^-$ [34]. In our study, the retardation factor found for sodium was slightly smaller than the values of approximately 1.8 reported by Rezanezhad et al. [18] and Caron et al. [35]. The retardation was probably due to the adsorption of sodium to a solid phase [18,35]. We assume that the retardation is less in our study because of a lower organic matter content as compared to the aforementioned studies [36].

4.2. Effect of Salinity on C, N, and P Release

The pH values of effluents were lower (3.5 to 5) when the soil cores were flushed with saline water than with fresh water (5.5 to 6.5). In field studies, high sulfate (SO$_4^{2-}$) concentrations have been found to be responsible for low pH values [37–39]. However, SO$_4^{2-}$ cannot be the reason for a low pH value in this study because concentrations were low after initial flushing (<0.02 mmol L^{-1}; Figure 2b). The soil pH was low (Table 1), and the possible adsorption sites were loaded with H$^+$ ions. When NaCl is introduced in high concentrations, the Na$^+$ ions may replace the H$^+$ ions and the pH of the effluent drops, as shown in previous studies [11,13,37]. It has been reported that increasing water salinity (EC) from 0.1 to 1.0 mS cm^{-1} results in a pH decrease from 5.5 to 3.5 [13]. In this context the release of H$^+$ from carboxyl and hydroxyl groups may also be playing an important role [40,41].

After initial flushing, the concentrations of DOC decreased to a constant value. Such behavior has been observed when organic-rich soils were leached with an artificial water solution [12,42]. Increasing water salinity and ionic strength reduced the mobilization of DOC (Figure 4). The lower DOC concentrations under saline water conditions can be explained by the coagulation of a certain fraction of DOC to particles larger than 0.45 µm, which would not pass the 0.45 µm filter. This is a reversible process as has been documented previously [12,13,43]. The impact of water salinity on DOC release is related to carbon quality. A higher DOC release under salt water than fresh water conditions was observed for peat soils containing a large number of carbohydrates [11]. Also, the reduced DOC mobilization under saline water conditions may be caused by the lower pH of the effluent. Previous studies on organic soils reported that increasing pH values generally enhances DOC release [44,45]

because a higher pH can increase the charge of organic molecules and thus stimulates the detachment of DOC from organic surfaces [12]. Similar effects were observed for peat soils by Kang et al. [46]; these authors reported that higher pH values increase activate phenol oxidase, accelerating the release of DOC. It may be difficult to separate the effects of ionic strength from pH effects because both variables are strongly correlated [44,47]. Therefore, after the restoration of coastal wetlands by dike removal, the re-salinization of wetlands may constrain DOC release to the sea. This process is, however, reversible and large amounts of DOC may be released from restored peatlands to the sea during storm events with high rainfall intensities.

For all soil cores, nitrate concentrations in the effluent were low (<0.01 mmol L^{-1}) during the whole experiment because the study sites were not exposed to intensive nitrogen fertilization despite agricultural usage. We assume that denitrification and nitrate ammonification did not play a major role at the drained and rewetted sites. It has been reported that dissolved oxygen in soils has a large impact on denitrification and the nitrification rate [48]. In this study, the microcosm experiments were conducted under a fully saturated condition and the applied solutions were prepared with demineralized water with a low gas content (2.3 mg O_2 L^{-1}; [11]). We assumed a low and almost constant dissolved oxygen content during the entire experiment, which had a minor effect on nutrient release patterns (such as those presented in Figure 5). When saline water was applied, a rapid release of ammonium from the organic sediment was observed, which is in line with previous studies [16,49,50]. Elevated NH_4^+ concentrations occur under saline water conditions because the applied Na^+ cations compete with ammonium for binding sites, which results in NH_4^+ desorption from soil particles [16]. The difference between the NH_4^+ concentrations in effluent for fresh water and saline water treatments was approximately 0.07 mmol L^{-1}, which corresponds to the findings by Baldwin et al. [16]. In their study, an addition of 0.1 mol NaCl L^{-1} fostered a NH_4^+-N increase from 0.08 to 0.18 mmol N L^{-1}. There were no differences in the patterns of NH_4^+-N release between soils from CD and CW even though the CW had been rewetted for almost 30 years. The fluctuating water table at CW and low groundwater levels during summer facilitated a continuous mineralization of organic matter and an associated mobilization of nitrogen. The re-salinization of coastal wetlands by dike removal increased the risk of nitrogen (ammonium) release to the sea even after decades of rewetting.

There are different opinions in the literature concerning the impact of water salinity on phosphate release. Previous studies on phosphate sorption characteristics of coastal wetlands have shown that phosphate binding decreases with increasing water salinity [51,52], increasing the available phosphate in the water column. Here, the results show the opposite and phosphate concentrations decreased with an increasing water salinity in an acidic environment (Figure 6). One possible reason is that the sorption of phosphate onto soil is sensitive to the presence of cations such as Ca^{2+}, Fe^{2+}, or Fe^{3+} [16,53,54]. It has been reported that dissolved Fe^{2+} ion concentrations in sediments increased from 0.2 to 3.8 mmol L^{-1} with increasing NaCl loading from 0 to 0.1 mol L^{-1} [16,54]. We assumed in our study that phosphate bound to Fe^{3+} ions, which resulted in low phosphate concentration under saline conditions. Another possible reason for this was that a stronger phosphate adsorption capacity on metal (hydr)oxides occurred at lower pH values (high salinity in this study), decreasing phosphate concentrations [55]. Moreover, humic acid (HA) aggregates occur at low pH values, which may also have an impact on phosphate adsorption through humic/Fe-oxide mixtures [56]. The re-salinization of coastal wetlands does, thus, not necessarily increase phosphate release. The situation may, however, be different during storm events with high rainfall intensities.

5. Conclusions

The biogeochemical response of diked and drained coastal sites to restoration measures depends on the established water flow regime as well as water salinity. The heterogeneous pore structure of peat soils causes non-equilibrium flow and transport conditions, affecting DOC and SO_4^{2-} flushing patterns. The salinity reduces the solubility of DOC and its release. Under saline conditions, the sediments may release more dissolved Fe^{2+} ions, which when fixing phosphate, would result in low P concentrations in

the effluent. In addition, the lower pH values under saline conditions enhance the phosphate adsorption capacity on metal (hydr)oxides, which further constrains phosphate availability. The opposite was observed for nitrogen (NH_4^+), for which cation exchange increased aqueous concentrations upon salinity increase. The microcosm experiments showed that these processes are reversible. Although the export of DOC and phosphate to sea water may be low after dike removal, a certain leaching risk remains at times when soil pore water salinity decreases. For instance, fixed phosphate may be mobilized during storm events with high rainfall intensities and a consecutive freshwater flux from land to sea. Therefore, the effects of a dike removal as a restoration measure should be evaluated on the basis of expected water fluxes considering short (tidal) and long-term boundary conditions (e.g., storm events).

Author Contributions: H.L. designed the experiment and analyzed the data; H.L. wrote the original draft and B.L. contributed in reviewing and editing the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

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