



# Salinization lowers nutrient availability in formerly brackish freshwater wetlands; unexpected results from a long-term field experiment

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**Abstract** Worldwide, coastal freshwater wetlands are facing salinization at an increasing rate due to large-scale land use change, freshwater extraction, climate-driven sea level rise, droughts and land subsidence. Although it is known that increased surface water salinity does influence wetland functioning, effects on nutrient dynamics reported in literature are contradictory and evidence from controlled, long-term field experiments is scarce. We therefore tested the effects of 4 levels of increased surface water salinity, from oligohaline to mesohaline conditions (0.9, 2.25, 4.5, 9 PSU), on biogeochemical and physicochemical processes in the

sediment of a formerly brackish freshwater wetland. For this, we used 16 enclosures in a controlled, 5-year field experiment. Salinization unexpectedly led to a dose dependent decreased availability of nitrogen and phosphorus in the sediment, both in the short and in the long term, even though sulfate reduction rates increased. Decreased phosphorus availability was probably caused by co-precipitation with calcium that was mobilized from sediment adsorption sites. Mobilization of ammonium from the sediment and coupled nitrification–denitrification most probably explained decreased nitrogen availability. Increasing sulfate concentrations associated with increased salinity shifted the dominant mineralization process from methanogenesis to sulfate reduction, also in the long term. We show surface water salinization to have major short-term and long-term consequences for the ecological and biogeochemical functioning of coastal freshwater wetlands.

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## Introduction

Salinization of freshwater wetlands

Anthropogenic forcing in response to changes in land use and water management in combination with sea

level rise and climate change (Church et al. 2013) has led to a worldwide increase in the intrusion of saltwater into coastal freshwater wetlands (Herbert et al. 2015). Surface water salinization has large biogeochemical and physiological consequences, and threatens groundwater and surface water resources for drinking water abstraction, agricultural practices and the ecological functioning of freshwater wetlands (Lamers et al. 2002b; Pitman and Lauchli 2002; Katerji et al. 2003; Bonte and Zwolsman 2010; Oude Essink et al. 2010; Rengasamy 2010; Brouns et al. 2014; Herbert et al. 2015; van Dijk et al. 2017). Coastal wetlands can be under the direct or indirect influence of increased salinity from various sources and via several pathways, e.g. decreased freshwater inflow due to summer droughts (Milly et al. 2005), anthropogenic land and water use change in the coastal zone, and via salinization of groundwater aquifers (Barlow and Reichard 2010; Ferguson and Gleeson 2012; Taylor et al. 2013). Salinization not only alters ionic concentrations, but also physical processes, chemical equilibria and microbiological pathways. Due to the myriad of effects of salinization on (biogeo)chemical processes, as linked to microbiological functioning, it is challenging to predict net effects on nutrient biogeochemistry. To better predict potential effects of salinization, more knowledge on potential effects of salinization on the nutrient cycling, (nitrogen (N), phosphorus (P) and carbon (C)) of coastal wetlands is urgently needed.

#### Direct effects on nutrient cycling

Previous studies show that salinization can either enhance or decrease nutrient availability. It is known that salinization can influence sediment nutrient cycles via several direct and indirect pathways. Increased ionic concentrations change physicochemical processes and chemical equilibria, facilitate aggregation and sedimentation of suspended matter, and induce fast displacement of cations [incl. calcium (Ca) and ammonium ( $\text{NH}_4^+$ )] bound to the cation adsorption complex in the sediment (Rysgaard et al. 1999; Weston et al. 2006, 2010; van Dijk et al. 2015). Salinization can directly influence the N cycle including nitrification (Rysgaard et al. 1999; Magalhaes et al. 2005; Noe et al. 2013) and denitrification rates (Giblin et al. 2010; Marks et al. 2016) and the P cycle by increasing (Chambers et al. 1995; Portnoy and Giblin

1997; Lamers et al. 2002a; Weston et al. 2006) or decreasing (Baldwin et al. 2006; Van Diggelen et al. 2015; van Dijk et al. 2015) sediment P availability.

#### Indirect effects on nutrient cycling

Apart from these contrasting direct effects of salinization on nutrient availability, more indirect effects may also occur by affecting the sulfur (S) and iron (Fe) cycles (Smolders et al. 2006). Salinization leads to an increased sulfate ( $\text{SO}_4^{2-}$ ) concentration which is an alternative terminal electron acceptor in anaerobic sediments (Roden and Edmonds 1997; Lamers et al. 1998a, 2002a; Smolders et al. 2006), and may thus lead to increased P and N mineralization in wetlands (internal eutrophication; (Smolders et al. 2006)). Additionally,  $\text{SO}_4^{2-}$  reduction and consequential sulfide ( $\text{S}^{2-}$ ) production is closely coupled to the Fe and P cycle.  $\text{S}^{2-}$  may mobilize P by reducing  $\text{Fe(III)(O)OH}$  complexes to which P is adsorbed, while the precipitation of  $\text{Fe}^{2+}$  sulfides ( $\text{FeS}_x$ ) strongly lowers dissolved  $\text{Fe}^{2+}$  concentrations (Lamers et al. 2002a; Smolders et al. 2006; DeLaune and Reddy 2008). As a result,  $\text{Fe}^{2+}$  to P ratios in sediment porewater decrease, which may enhance the release of P to the water layer (Geurts et al. 2008). The influence of enhanced  $\text{SO}_4^{2-}$  levels on nutrient cycles, as an indirect effect of salinization, should therefore not be underestimated, especially with respect to the P cycle.

#### Indirect effects on C cycling

Although enhanced ionic concentrations can affect the C cycle (Chambers et al. 2011), it is generally accepted that enhanced  $\text{SO}_4^{2-}$  reduction resulting from increased  $\text{SO}_4^{2-}$  concentrations can strongly affect the C cycle in wetlands (Weston et al. 2006; Lamers et al. 2013). As increased  $\text{SO}_4^{2-}$  concentrations can enhance net organic matter breakdown (C mineralization),  $\text{CO}_2$  emissions may increase after salinization (Weston et al. 2006, 2011; Craft et al. 2009; Chambers et al. 2011; Marton et al. 2012). Simultaneously, increased  $\text{SO}_4^{2-}$  reduction rates generally decrease the rates of methanogenesis (Weston et al. 2006; Loeb et al. 2007) because (1) methanogens are outcompeted for organic compounds such as acetate (Lamers et al. 1998b; Smolders et al. 2002) as  $\text{SO}_4^{2-}$  reduction is thermodynamically more favorable (Segers 1998) and (2) increased salinity and

the production of toxic  $S^{2-}$  can lead to physiological stress for methanogens (Chambers et al. 2011; Lamers et al. 2013). However, a comparison of different systems along a salinity gradient shows that more saline systems often show lower net C emissions to the atmosphere (Bartlett et al. 1987; Poffenbarger et al. 2011; Weston et al. 2014; Vizza et al. 2017).

### Contradictory results

The contrasting effects of salinization on N, P and C cycles indicate that biogeochemical and ecological effects of salinization are influenced by a range of biogeochemical factors and probably depend on local differences in biogeochemical and physical sediment characteristics (Herbert et al. 2015). The fact that coastal wetlands often show strong differences in the historical influence of brackish or saline water, resulting in increased salinity and increased S concentrations in their aquatic sediment, makes the prediction of the effects of enhanced salinity even more complex. In recent years more knowledge has been gained about the effects of salinization. This knowledge is mostly derived from short-term laboratory experiments, as long-term controlled field experiments are scarce.

### This study

We carried out a 5 year field experiment to study long-term effects of four increasing levels of salinization on biogeochemical processes in organic sediments, with a main focus on the resulting availability of N, P and C. These effects were tested in a coastal freshwater wetland that was formerly influenced by saline water (see Materials and Methods). We hypothesized that salinization would cause major biogeochemical changes leading to cation mobilization (H1), increasing porewater N concentrations (especially  $NH_4^+$ ) and P concentrations (H2), and decreasing porewater  $CH_4$  concentrations (H3). Furthermore we hypothesized that the effect of salinization will be dose dependent (H4). We hypothesized rapid short term effects (within-weeks) of salinization on the N, P and C cycles in the sediment and hypothesized the effects to become more pronounced in the long term (months–years) (H5).

## Materials and methods

### Site description

The experiment was carried out in a former brackish freshwater wetland (Ilperveld, 1300 ha), located to the north of Amsterdam (the Netherlands). The coastal wetland harbors a large surface area of open water connected to the Noord-Holland Canal. Between 500 B.C. and 500 A.D. a raised bog landscape was formed here, dominated by *Sphagnum* mosses (Bakker and Van Smeerdijk 1982; Witte and Van Geel 1985; Willemsen et al. 1996). As many European former coastal wetlands, however, the area has suffered from large-scale anthropogenic disturbances since the middle ages (Vos 2015; van Dijk et al. 2018), including drainage, burning, increased agricultural activity, construction of ditches and canals, creation of low-lying tracts of land enclosed by dikes (polders), and peat extraction. This led to a strong land subsidence and to increased influence of brackish water due to several floods with brackish and saline water from the Zuiderzee, a former lagoon attached to the North Sea (Van't Veer 2009; Raats 2015). Since the 1930s the influence of brackish water decreased and salinity levels dropped due to the construction of a large dam (Afsluitdijk) converting the brackish Zuiderzee into a freshwater lake (Lake IJsselmeer), eliminating seawater influence from the study area (de Beaufort 1954). Since then, surface water Cl concentrations have decreased from approximately 13 PSU (200 mmol Cl  $L^{-1}$ ) to approximately 1 PSU (15–20 mmol Cl  $L^{-1}$ ). Although the study area is classified as a freshwater wetland under the present conditions, the historic influence of brackish water (i.e. increased Cl, Na and  $SO_4^{2-}$  levels) is still noticeable in the aquatic sediment and groundwater (Table 1). The high S versus low Fe contents and high Na contents indicate the former influence of brackish water.

The experiment was carried out in a dead-end peatland canal (52°27.225 N–4°55.885E), approximately 250 m long and 10–15 m wide. In this wetland, a strict surface water level management is maintained only allowing water level fluctuations of up to 5 cm. The canal is surrounded by reedlands and peat meadows in extensive agricultural use. The underwater sediment at the study site consists of a top layer (14 cm) of unconsolidated peat on top of several meters of stratified, consolidated peat and clay layers

**Table 1** Average organic matter content (%) and total element concentrations of (Na, Ca, S, Fe, P and N) (mmol kg DW<sup>-1</sup>) at three depth sections at de experimental location (S.E.M. in superscript, [n = 4]) (DW = dry weight)

Sediment depth (cm)	OM (%)	Na (mmol kg DW <sup>-1</sup> )	Ca (mmol kg DW <sup>-1</sup> )	S (mmol kg DW <sup>-1</sup> )	Fe (mmol kg DW <sup>-1</sup> )	P (mmol kg DW <sup>-1</sup> )	N (mmol kg DW <sup>-1</sup> )							
0–15	68.7	1.1	249.2	5.2	485.6	5.9	737.2	29.9	176.7	14.4	25.7	1.6	1105.1	29.6
15–30	81.4	3.4	243.2	9.6	393.6	26.8	619.9	56	98.1	29.2	14.0	3.4	821.0	110.7
30–45	91.5	0.3	270.2	25.4	306.9	13.4	451.6	26.9	18.8	5.5	5.0	0.2	560.0	32.4

(Westland formation), based on a sand layer (Formation of Twente, National DINO Database, TNO) (Fig. 1a).

### Experimental design

To test the effects of increased surface water salinity, 16 enclosures (95 cm diameter) were placed in the middle of the canal to avoid side effects (Fig. 1a–d). We randomly assigned four different salinity levels treatments ( $n = 4$ ) to the enclosures. Additional measurements were carried out at fixed locations ( $n = 4$ ) in the surrounding canal, as a control for enclosure effects. The enclosures consisted of stainless steel frames in which cylinders of flexible PVC foil ( $\approx 1$  mm thick, 130 cm long) were placed in June 2010 (Fig. 1b). The PVC enclosures were open at the top and bottom and connected to the steel frame by rubber bands, keeping the upper part (30 cm) above the water surface (Fig. 1b). At the bottom the foil was fastened to a steel ring (30 cm length) placed 40 cm below the sediment–water interface. In this way miniature ponds with flexible volumes were created, in which interactions between the atmosphere (precipitation and evaporation) and the enclosed surface water remained intact.

The different salinity levels [in a range from fresh to mesohaline; 0.9, 2.25, 4.5 and 9.0 PSU (14, 35, 70 and 140 mmol Cl L<sup>-1</sup>)] were established by adding concentrated solutions of artificial sea salt (Tropic Marin<sup>®</sup>, which is similar to the element composition of the North Sea) to the surface water in the enclosures (Table 2). The salinity levels were selected to (1) test dose dependency of salinization on biogeochemical processes and (2) to test salinity levels within a range historically observed at the study area or that might occur due to future climate change or active management. To avoid precipitation from affecting the treatment, dissolved sea salt was added twice a year, to keep surface water ion concentrations stable (Fig. 2).

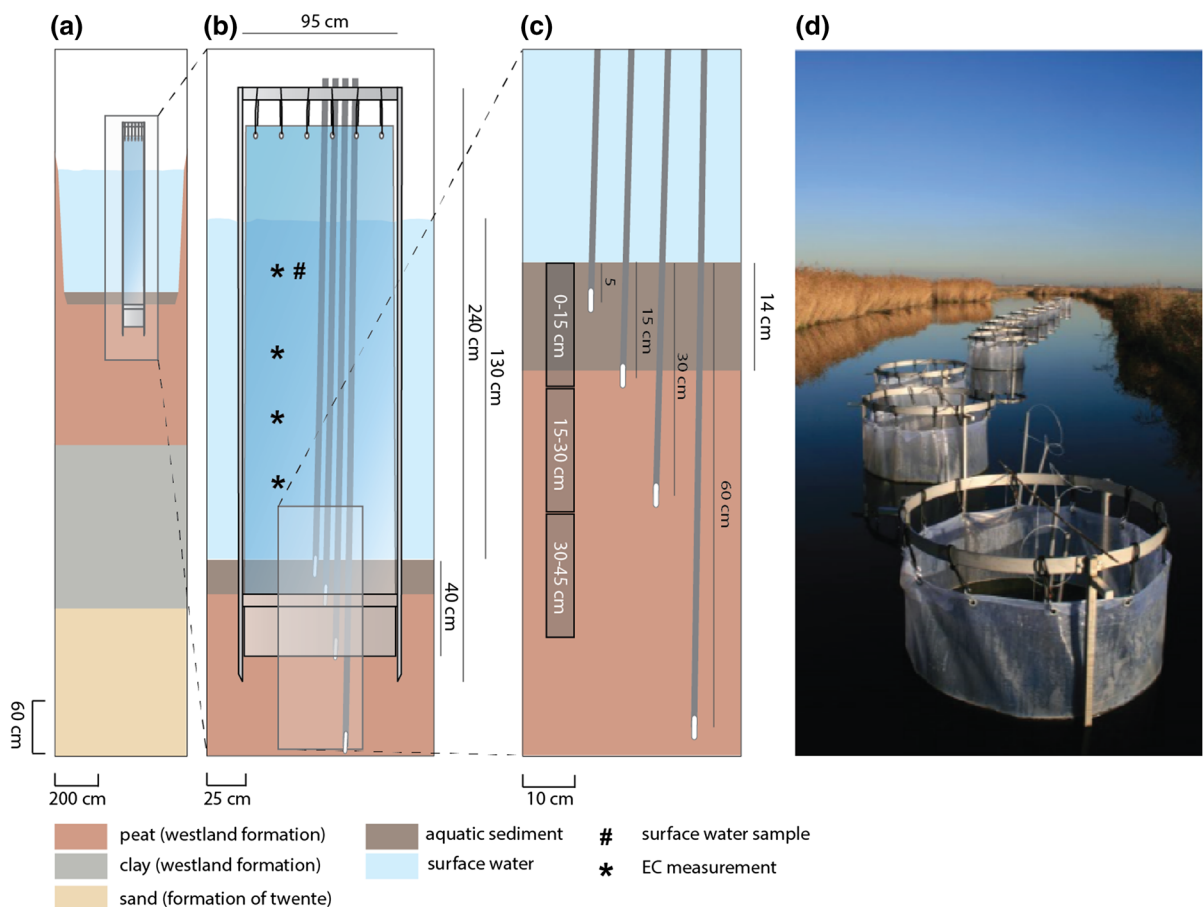
### Sampling

The experiment lasted 5 years (2010–2015). During the first 1.5 years, the experiment was sampled monthly, followed by 3.5 years with less intensive sampling (1 to 4 times a year). Surface water and sediment porewater were collected from all replicates.

During the first 6 months of this experiment we noted increasing surface water stratification within the enclosures that did not occur outside. To reduce stratification in the enclosures, over the following year we mixed the surface water within the enclosures every 2 weeks, slowly, by hand, for 2 min. The remaining 3.5 years of the experimental period no additional mixing was applied due to less intensive sampling and the exclusion of surface water sampling. Due to stratification of the surface water layer over time, surface water results are only presented for the 1st months of the experimental period. Sediment porewater samples were not significantly affected by surface water stratification (no difference before and after the period with additional surface water mixing)

and are presented for the complete five-year duration of the experiment.

Surface water samples were taken from the upper 15 cm. Electrical conductivity (EC) measurements (HQD Conductivity probe, Multi 2 channels, HACH, Germany) were carried out at four depths in the water column (Fig. 1b). Sediment porewater samples were taken anaerobically at a depth of 15 cm in the aquatic sediment with a 50 mL syringe connected to a ceramic cup by a Teflon tube (Fig. 1c). Porewater gas was collected by connecting an evacuated 12 mL glass exetainer (Labco exetainer®, High Wycimbe, UK) to the same ceramic cup, and CH<sub>4</sub> measurements were subsequently measured in the headspace. After 2.5 years, additional porewater samples were



**Fig. 1** **a** Enclosure placed in the surface water of a canal with peat soil on top of clay and sand layers, **b** schematic representation of an enclosure showing steel frame, flexible PVC foil cylinder, and ceramic cups; **c** detailed overview showing sampling method including ceramic cups for porewater

sampling at different depths and in shaded rectangles sediment sample depths (0–15, 15–30 and 30–45 cm below the water–sediment border). Scales in cm, **d** experimental set-up in the field (photo G. van Dijk)

collected at three additional depths, at 5 cm of depth for all treatments and at 30 and 60 cm in the control (0.9 PSU) and highest salinity (9.0 PSU) treatment (Fig. 1c). At the same time, sediment cores (4 randomly selected subsamples pooled per enclosure) were also collected in all treatments using a sediment suction corer (diameter 4 cm; Piston sampler, Eijkelkamp Soil and Water, the Netherlands) and divided into three depth sections 0–15 cm, 15–30 cm and 30–45 cm (Fig. 1c). All samples were cooled during transportation and stored under dark and cool conditions (4 °C) until analyses.

### Chemical analyses

The pH values of surface water and porewater samples were measured using a combined pH electrode with a Ag/AgCl internal reference (Orion Research, Beverly, CA, USA) and a TIM800 pH meter. Turbidity was measured using a Turb 550 turbidity meter (WTW GmbH, Weilheim). Total dissolved inorganic C concentrations were measured using infrared gas analysis (IRGA, ABB Advance Optima, Zürich, Switzerland), after which CO<sub>2</sub> and HCO<sub>3</sub><sup>-</sup> were calculated based on the pH equilibrium. After removing the vacuum of the exetainers with N<sub>2</sub> gas, CH<sub>4</sub> concentrations were measured in the headspace with a Hewlett-Packard 5890 gas chromatograph (Avondale, California) equipped with a flame-ionization detector and a Porapak Q column (80/100 mesh) operated at 120 °C with N<sub>2</sub> as carrier gas. CH<sub>4</sub> concentrations were recalculated for the water volume using Henry's constant. H<sub>2</sub>S concentrations were determined directly after sampling by fixing 10.5 ml of porewater with 10.5 ml S<sup>2-</sup> Anti Oxidant Buffer, and using an Orion H<sub>2</sub>S electrode and a Consort Ion meter (type C830) for analyses (Van Gernerden 1984). Prior to elemental

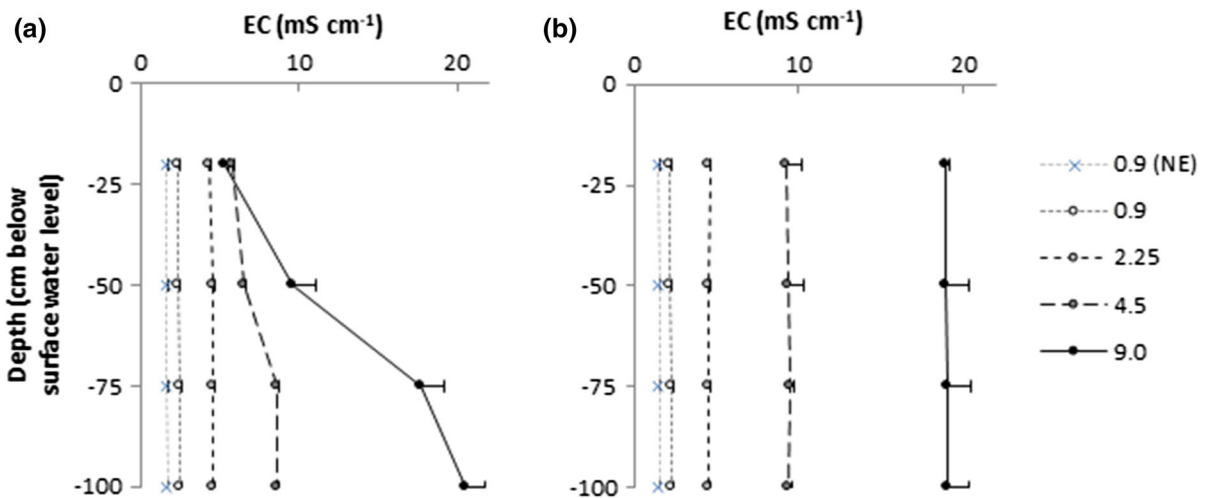
analyses, 10 ml of each sample was stored at 4 °C until analyses after adding 0.1 ml (65%) HNO<sub>3</sub><sup>-</sup> to prevent metal precipitation. For the analyses of P, Ca, Mg, Mn, Fe, S, K and Al, inductively coupled plasma spectrophotometry (ICP-Optical Emission Spectrometer, Thermo Scientific iCAP 6000 Series ICP) was used. To determine NO<sub>3</sub><sup>-</sup> (Kamphake et al. 1967), NH<sub>4</sub><sup>+</sup> (Grasshoff and Johannsen 1972), PO<sub>4</sub><sup>3-</sup> (Henriksen 1965), Na and Cl concentrations, 20 ml of each sample was stored at - 20 °C and analyzed colorimetrically with an Auto Analyzer 3 system (Bran and Luebbe).

Dry weights and bulk densities of the sediment samples were measured by drying a known volume of fresh sediment at 70 °C until constant weight was obtained. The organic matter content was determined by loss-on-ignition for 4 h at 550 °C. Total concentrations of Fe, S and P in the sediment samples were determined by digesting 200 mg of dried (24 h, 70 °C) and homogenized sample in 4 mL concentrated HNO<sub>3</sub> and 1 ml 30% H<sub>2</sub>O<sub>2</sub> (Milestone microwave MLS 1200 Mega). Sample extracts were analyzed after dilution with de-ionized water by ICP, as described above. Exchangeable cation concentrations of the sediments (Na, Mg, Mn, Ca, K and NH<sub>4</sub>) were determined at the end of the experiment by shaking (105 r.p.m.) 17.5 g of fresh sediment for 60 min with a 0.2 M SrCl<sub>2</sub> solution. The supernatant was analyzed using ICP and Auto Analyzers (see above). Concentrations of P for different fractions (labile, Ca, Fe and Al bound) were determined according to the sequential extraction method of (Golterman 1996) and the remaining residue was digested with HNO<sub>3</sub> (as described above) to determine the concentration of organically bound P (refractory non-labile organic P). In November and December 2012 (year 2), extra sediment samples were collected

**Table 2** Overview of the chemical composition of the surface water of all treatments at the start of the experiment

Solutes (unit)	Salinity (PSU)	Cl <sup>-</sup> (g L <sup>-1</sup> )	Cl <sup>-</sup> (mmol L <sup>-1</sup> )	Na <sup>+</sup> (mmol L <sup>-1</sup> )	S <sub>(tot)</sub> (mmol L <sup>-1</sup> )	Ca <sup>2+</sup> (mmol L <sup>-1</sup> )	HCO <sub>3</sub> <sup>-</sup> (mmol L <sup>-1</sup> )
Fresh (outside control)	0.9	0.5	14	12	1.3	2	3
Fresh (inside control)	0.9	0.5	14	12	1.3	2	3
Oligohaline	2.25	1.25	35	32	2.5	2.5	3
Oligo-mesohaline	4.5	2.5	70	64	5	3	3
Mesohaline	9	5	140	128	10	5	3





**Fig. 2** Depth profiles of electrical conductivity (EC, in  $\text{mS cm}^{-1}$  average + SEM, [ $n = 4$ ]) in the surface water of all treatments (in PSU; NE no enclosure), under **a** stratified

conditions at  $t = 6$  months and **b** under non-stratified conditions at the start of the experiment and for the 1-year period when manual mixing was applied

with an Eckman sediment sampler [three subsamples of  $180 \text{ cm}^2$  and 8 cm depth per enclosure, (in total < 10% of the total enclosure sediment surface)] for benthic macro-invertebrate analyses. Samples were taken to the laboratory and stored at  $4^\circ \text{C}$  until analysis within 3 days. The three subsamples were carefully mixed and a subsample was passed through three different mesh sizes (2, 1, and 0.4 mm). The retained benthic macro-invertebrates were sorted and identified to genus level.

#### Data analyses

Treatment effects were tested with SPSS 21 (IBM SPSS Statistics) on  $\ln(x + 1)$  transformed data to make the data distribution less skewed and achieve a closer fit to a normal distribution, except for pH as it is already log-transformed. Treatment effects for surface water and sediment porewater were tested for the period of June 2010 to September 2011 (16 months, 16 measurement points in time) and for surface water from June 2010 to September 2010 (4 months, 5 measurement points in time). Data was tested using Linear Mixed Models, using replicas as subject factor, treatment as factor and time as co-factor [AR (1): Heterogeneous was used as co-variance type, based on AICC values]. Differences between treatments within the Linear Mixed Models were further analyzed using LSD post hoc tests. Treatment effects for sediments

and porewater in depth profiles were tested among depth sections using One-Way ANOVA and LSD post hoc tests.

## Results

### Salinity effects on surface water biogeochemistry

Due to reduced water movement and the exclusion of the influence of surrounding surface water, precipitation caused stratification of the surface water layer in the enclosures in 4.5 and 9.0 PSU treatments, during the first 6 months (Fig. 2a). Despite the periodical stratification near the surface and the regular addition of sea salt, salinity concentrations always remained at treatment levels below a depth of about 30 cm above the aquatic sediment (Fig. 2a). As the chemical composition of the top layer of the surface water was affected by the above-mentioned processes, we only present surface water results of the first four months. Cl concentrations increased in all salinity treatments and differed significantly from the control treatment ( $p < 0.001$ ) (Fig. 3a). A significant ( $p < 0.01$ ) decrease in the surface water P concentration at an increased salinity was observed (78% decrease between control treatments and the two highest salinity treatments (4.5 and 9.0 PSU) after four months) (Fig. 3b). A short, although not significant,

increase in surface water  $\text{NH}_4^+$  concentrations was observed after salinization in the higher salinity treatments (Fig. 3c). The total inorganic C concentration (TIC, Fig. 3d) decreased faster in the 4.5 and 9.0 PSU treatments. Furthermore, after reaching the targeted treatment concentrations in July 2010 (1 month after the start), Ca concentrations (Fig. 3e) in the highest salinity treatment decreased faster (38% decrease in July, 51% in August) than Cl concentrations (31% decrease in July, 43% in August) (Fig. 3a). This difference in the rate of decrease between concentrations of Ca and Cl was less prominent in intermediate salinity treatments. In the short term, Ca concentrations (Fig. 3e) increased in the two highest salinity treatments. In the short term, no significant differences were found between the inside and outside control treatments, indicating that the placement of enclosures didn't have major short-term effects on these ions.

#### Salinity effects on porewater nutrient concentrations

Porewater concentrations of salinity-related ions, such as Cl, Na and  $\text{SO}_4^{2-}$ , were increased in all salinity treatments ( $p < 0.001$ ) (Cl shown in Fig. 4a,  $\text{SO}_4^{2-}$  in Fig. 4c). Cl and Na concentrations even increased ( $p < 0.05$ ) up to a depth of 60 cm as measured 2.5 years after the start of the experiment (Cl in Fig. 5a, Na in Fig. 5b, Ca in Fig. 5c). Sediment porewater Cl and Ca concentrations at a depth of 15 cm showed a very rapid response (increasing within a month) to increased surface water salinity and increased in all three salinity treatments (Cl is shown in Fig. 4a, Ca in Fig. 4b). Porewater pH was not influenced by salinity (data not shown), but TIC levels decreased in all salinity treatments ( $p < 0.01$ ) (Fig. 4f). Within months porewater P concentrations showed a salinity dependent decrease in all treatments, significant ( $p < 0.01$ ) in the highest salinity treatment (9 PSU), leading to a 60% decrease after 5 months compared to the control treatment (Fig. 4d). During the following months porewater P concentrations further decreased ( $p < 0.05$ ) in the two highest salinity treatments. After 1 to 1.5 years, average P concentrations were 33% lower in the 2.25 PSU, 54% lower in the 4.5 PSU and 69% lower in the 9 PSU treatment compared to the control treatment (Fig. 4d). Less intensive long term sampling proved P concentrations

to remain low for 5 years in high salinity treatments (Fig. 4d).

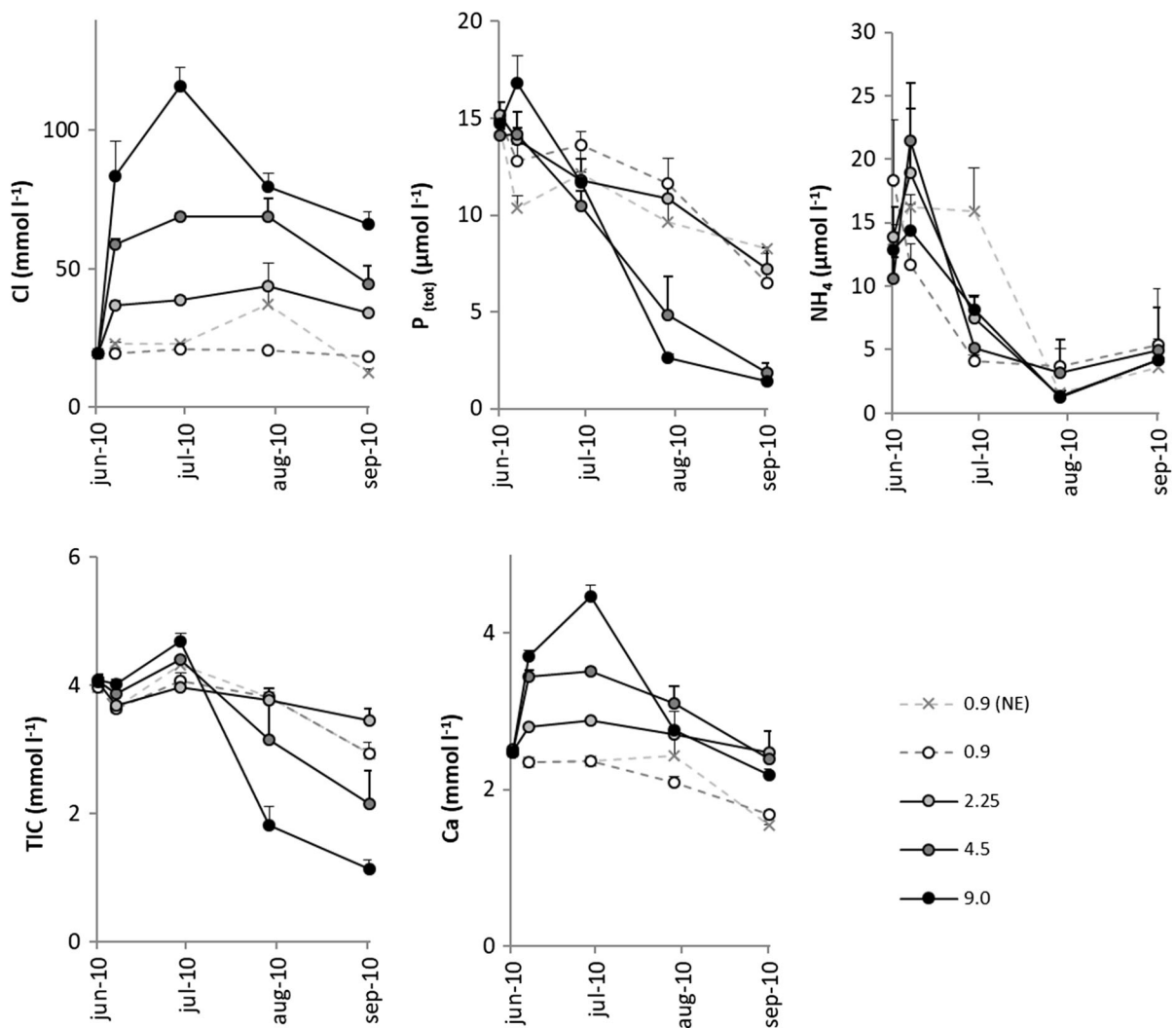
Although surface water salinization initially led to a short-term increase of porewater  $\text{NH}_4^+$  concentrations (n.s.),  $\text{NH}_4^+$  concentrations decreased in the longer term (Fig. 4e). After 1.5 years, a 30% decrease was reached in the 4.5 PSU treatment (n.s.) and a 60% ( $p < 0.01$ ) decrease in the 9 PSU treatment, as compared to the control. In contrast to porewater P concentrations, which stabilized after a gradual decrease during the first 10 months, porewater  $\text{NH}_4^+$  concentrations showed a decrease in all treatments during autumn and winter, and an increase again during spring and summer of the 2nd year (Fig. 4e). The strongest increase was observed in the control treatments, almost back to ambient levels, whereas  $\text{NH}_4^+$  concentrations in all salinity treatments remained lower (Fig. 4e).

All salinity related elements did increase down to 60 cm of depth in the sediment (Fig. 5). Porewater depth profiles after the first 2.5 years, showed ( $p < 0.01$ ) lower  $\text{NH}_4^+$  and P levels at both 15 and 30 cm depth for the 9 PSU treatment compared to the control treatment. At a depth of 60 cm nutrient concentrations did not differ between the treatments (Fig. 5g, h). Less intensive long term sampling proved  $\text{NH}_4^+$  concentrations to remain low for 5 years in high salinity treatments (Fig. 4e). Effects on porewater  $\text{CH}_4$ ,  $\text{SO}_4^{2-}$  and  $\text{S}^{2-}$  will be discussed in greater detail in the subsequent section. In the long term (years) however, some inevitable enclosure effects were found leading to lower sediment porewater concentrations ( $p < 0.05$ ) of  $\text{NH}_4^+$ , TIC and P in the control (0.9 PSU) treatment compared to the control treatment outside of the enclosures (0.9 PSU) (Fig. 4).

#### Salinity effects on sediment chemistry including cation exchange

High Na (and also Mg) concentrations caused the mobilization of cations from the cation exchange complex of the sediment. Sediment analyses showed increased total and exchangeable Na concentrations (Fig. 6a, d) decreased total and exchangeable Ca concentrations (Fig. 6b, e) and decreased exchangeable  $\text{NH}_4^+$  concentrations in the increased salinity treatments (Fig. 6f). Exchangeable ion concentrations were significantly increased, for  $\text{NH}_4^+$  in the deeper sediment layer of the 9.0 PSU treatment ( $p < 0.05$ )



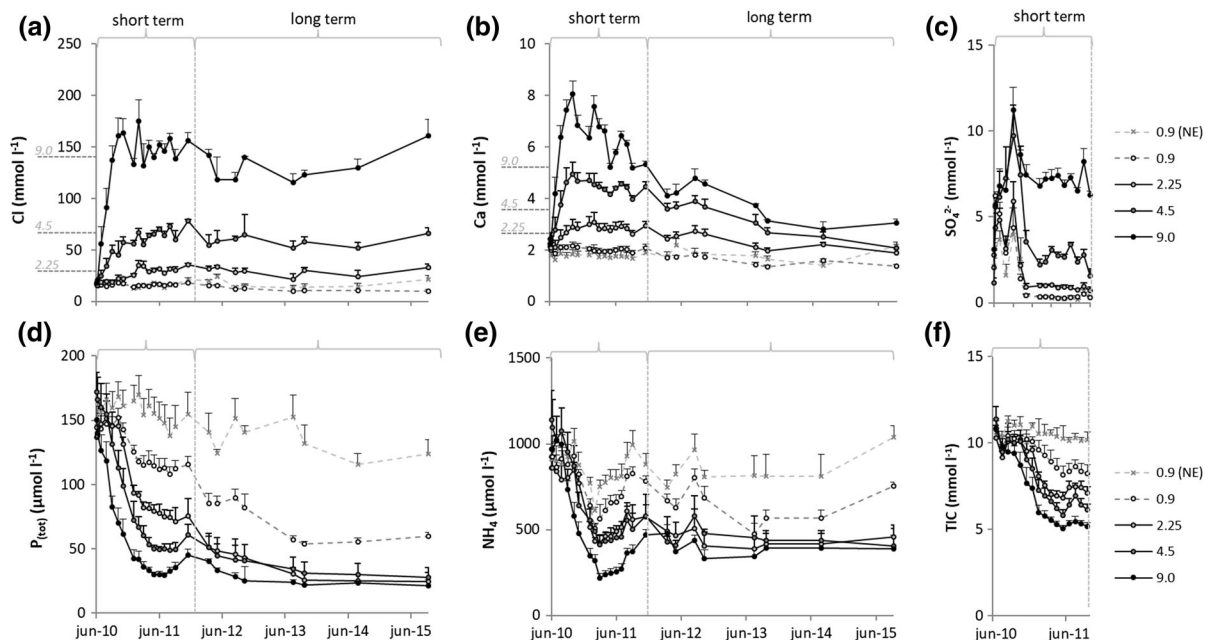


**Fig. 3** **a** Surface water chloride concentration, **b** phosphorus concentration, **c** the ammonium concentration, **d** the total inorganic carbon concentration (TIC), and **e** the calcium

concentration in all treatments during the first four months of the experiment (given in PSU, NE no enclosure), (+ SEM, [n = 4])

and for Na and Ca in both sediment layers in the 9.0 PSU treatment ( $p < 0.05$ ) (Fig. 6d–f). The sediment total C:N ratio was not affected by salinity (Fig. 6c). In contrast to porewater concentrations, total sediment P and N concentrations did not differ between treatments (data not shown). Most P (about 70%) was present as organic-P, about 15% was bound to Ca (carbonates) and about 10% to Fe or Al, without treatment effects (data not shown). Mobilization of  $\text{NH}_4^+$  in the porewater was observed in the short term (Fig. 4e), but we also found mobilization of Ca (Fig. 4b) and Mn (data not shown). Porewater Ca and Mn concentrations increased in the two highest

salinity treatments ( $p < 0.05$  for 4.5 PSU;  $p < 0.01$  for 9.0 PSU). However, porewater  $\text{Fe}^{2+}$  concentrations remained very low,  $< 2 \mu\text{mol L}^{-1}$  in all treatments (data not shown). Although Ca was also supplied via the addition of sea salt, porewater concentrations became higher than surface water concentrations (Fig. 4b), indicating Ca mobilization in the sediment. After this initial mobilization pulse, porewater Ca concentrations showed a slight decrease and stabilized at higher levels in the highest salinity treatments (Fig. 4b).



**Fig. 4** Porewater concentrations of **a** chloride, **b** calcium, **c** sulfate, **d** total phosphorus (TIC), **e** ammonium, and **f** total inorganic carbon through time at 15 cm of depth in the sediment for all treatments (given in PSU; NE no enclosure). Averages + SEM [ $n = 4$ ]. Concentrations are given in  $\mu\text{mol L}^{-1}$  for

$\text{P}_{(\text{tot})}$  and  $\text{NH}_4^+$ , and in  $\text{mmol L}^{-1}$  for other substances. **a**, **b**, **d** and **e** do present short and long term data, **c** and **f** only short term. In **a** and **b** treatment concentrations (indicated in PSU) are given in grey with dotted lines on the y-axes

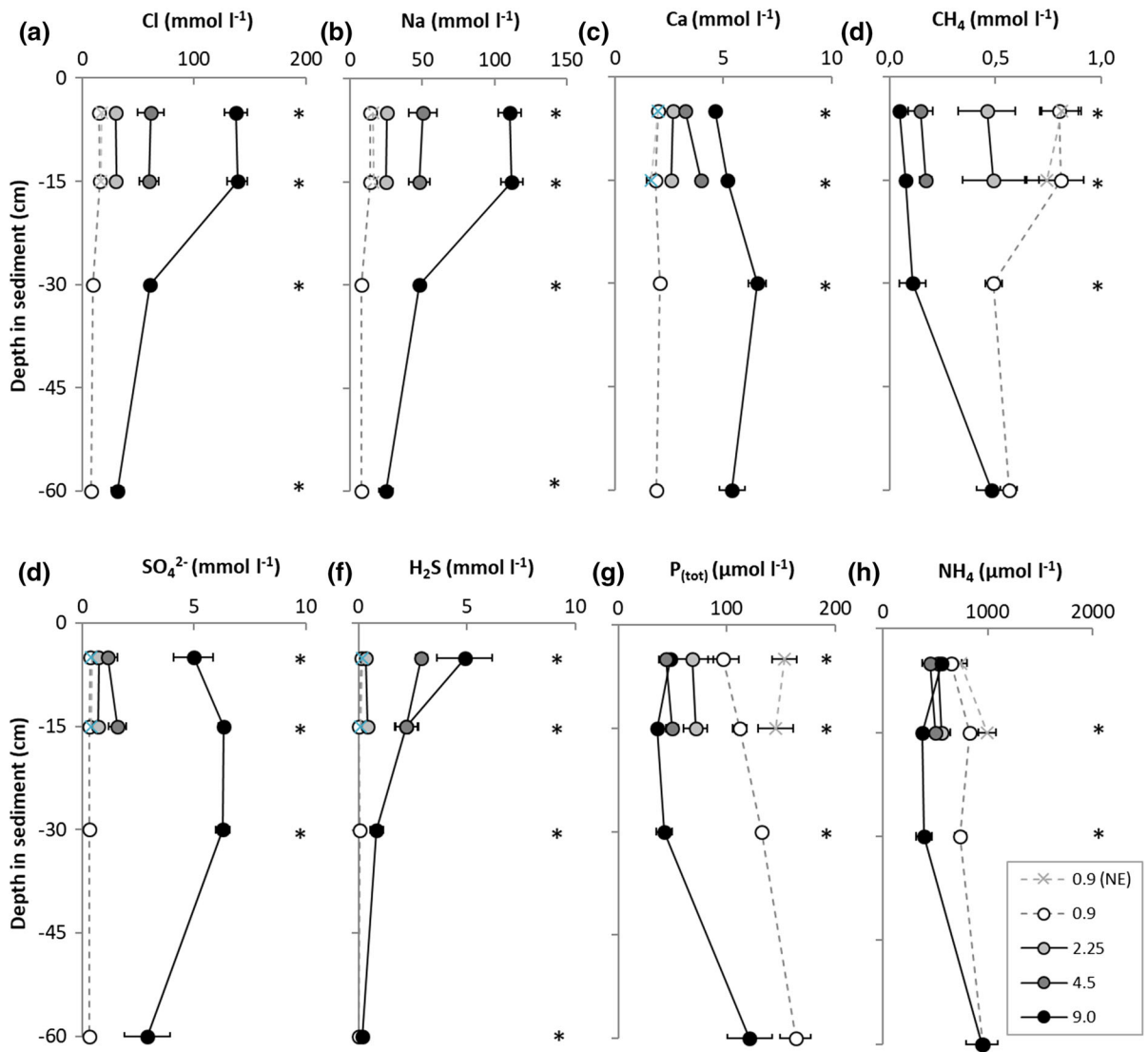
#### Salinity effects on methanogenesis and sulfate reduction

Increased surface water salinity strongly decreased porewater  $\text{CH}_4$  concentrations (Fig. 5d), down to a depth of 30 cm ( $p < 0.05$ ) (in the 9 PSU treatment). After 2.5 years, concentrations were lowered by 94% in the 9.0 PSU treatment, 82% in the 4.5 PSU treatment and 42% in the 2.25 PSU treatment, respectively in the upper sediment layers (5 cm and 15 cm depth). Porewater  $\text{SO}_4^{2-}$  concentrations were higher in all salinity treatments ( $p < 0.05$ ) (Figs. 4c, 5e). Porewater  $\text{S}^{2-}$  concentrations strongly increased in the sediment top layer from approximately  $0.13 \text{ mmol L}^{-1}$  in the control treatment to  $4.9 \text{ mmol L}^{-1}$  in the 9.0 PSU treatment (40 times increase;  $p < 0.05$ ), but decreased with depth (Fig. 5f).

#### Salinity effects on benthic invertebrate community

Benthic invertebrates sampled between 0 and 8 cm depth at the end of the second year showed a strong

decrease in numbers of individuals, from 2000 to  $3000 \text{ m}^{-2}$  sediment in the control and 2.5 PSU treatment, to almost absence ( $< 50 \text{ individuals m}^{-2}$ ) in the 4.5 and 9.0 PSU treatments ( $p < 0.01$  for all invertebrates, Oligochaeta ( $p < 0.01$ ), Gammaridae ( $p < 0.05$ ) and Chironomidae ( $p < 0.01$ ). Community composition also changed: the control community was dominated by worms (*Oligochaeta*), gammarids (*Gammaridae*) and chironomid larvae (*Chironomidae*), with a total spp. density of  $1800 \text{ m}^{-2}$ , whereas in the highest salinity treatments only a small selection of species of chironomid larvae and one gammarid species remained (total spp. density of  $50 \text{ m}^{-2}$ ). During the experimental period, no aquatic vegetation was present in the enclosures.



**Fig. 5** Porewater concentrations for **a** chloride, **b** sodium, **c** calcium, **d** methane, **e** sulfate, **f** sulfide, **g** total P, **h** NH<sub>4</sub><sup>+</sup> in depth profiles (0.9 and 9 PSU at 4 depths, 2.25 and 4.5 PSU at 2 depths), 2.5 years after the start of the experiment for all

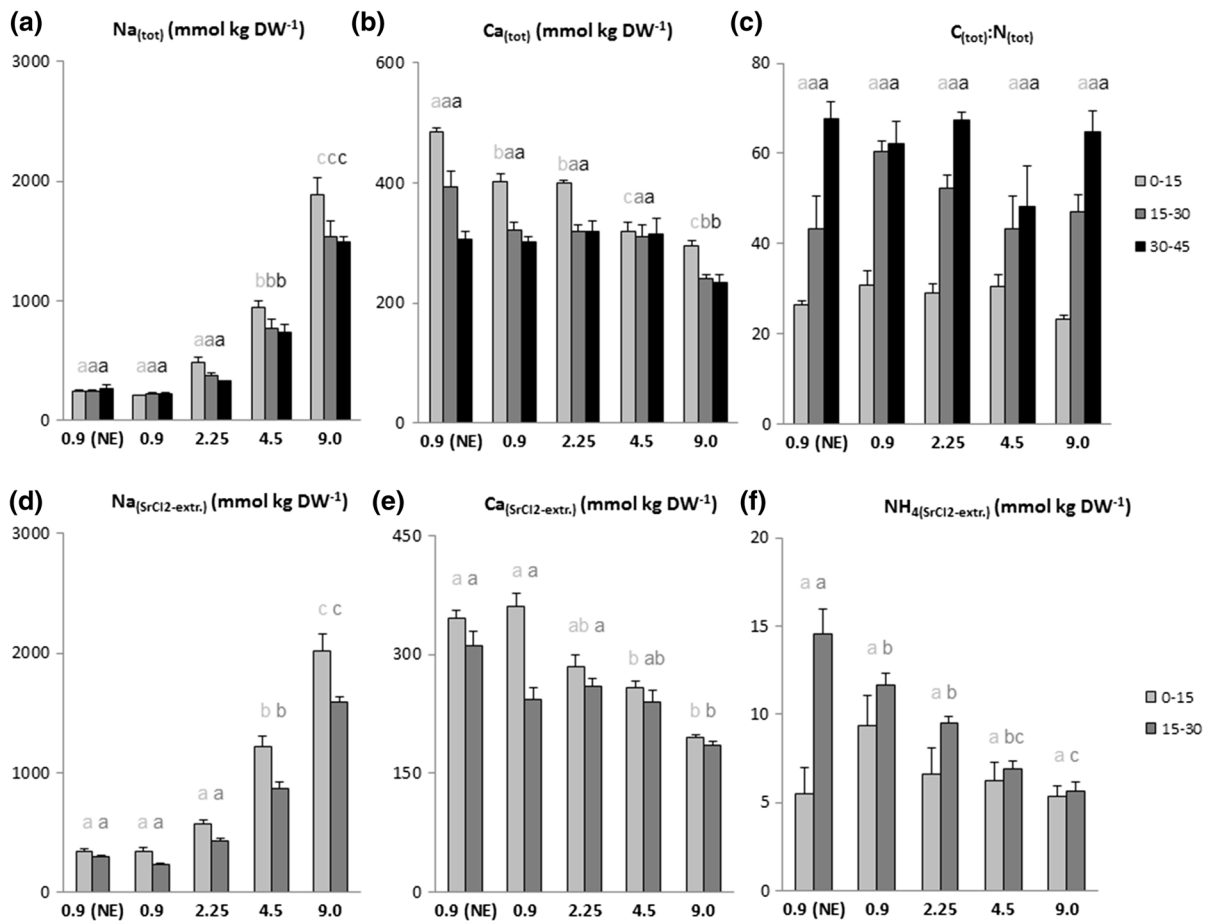
treatments (PSU), average  $\pm$  SEM [ $n = 4$ ]; note different scales on the x-axes. Statistical differences were tested between 0.9 and 9 PSU treatment, \* $p < 0.05$

## Discussion

### Long-term salinization lowers sediment phosphorus availability

Increased salinity (increasing PSU) significantly lowered porewater total P concentrations on both the short and long term (Figs. 4d, 5g). Although some earlier studies also showed this effect (Baldwin et al. 2006; Weston et al. 2006; van Dijk et al. 2015), others

showed the opposite (Sundareshwar and Morris 1999; Beltman et al. 2000; Jun et al. 2013). Our study indicates that lowered porewater P concentrations may well be caused by co-precipitation of P with Ca or with CaCO<sub>3</sub> (calcium carbonate) (Bale and Morris 1981; Morris et al. 1981; House 1999). This mechanism seems to be very likely given the combination of enhanced Ca concentrations due to the sea salt addition and increased Ca mobilization from sediment cation adsorption sites at increased salinities.



**Fig. 6** Sediment characteristics for three depth sections (0–15, 15–30 and 30–45 cm of depth) in all treatments (given in PSU; NE = No Enclosure); **a** total Na concentration, **b** total Ca concentration, **c** total C:N ratio (mol/mol), **d** SrCl<sub>2</sub>

extractable Na concentration, **e** SrCl<sub>2</sub> extractable Ca concentration, **f** SrCl<sub>2</sub> extractable NH<sub>4</sub><sup>+</sup> concentration (average + SEM, [n = 4]). Different letters indicate statistical differences between treatments (p < 0.05)

Subsequent precipitation of Ca in the surface water is indicated by the faster decrease of Ca over time compared to Cl (Fig. 3a, e). The observed decrease in TIC concentrations (Fig. 4f) of the sediment porewater also indicates precipitation of CaCO<sub>3</sub> following Ca mobilization in the sediment. During the first 4 months, surface water P concentrations also decreased more quickly than Cl, due to salinization (Fig. 3). It is known that high porewater Fe:P ratios prevent P mobilization to the water layer (Geurts et al. 2008). However, as was shown by (Geurts et al. 2010), porewater P concentration and P release from the aquatic sediment to the overlying water layer are linearly correlated under aerobic surface water conditions for sediments showing low (< 1 mol mol<sup>-1</sup>) porewater Fe:P ratios, which is the case in our study

(Fe:P < 0.001 in all treatments). This implies that lower porewater P concentrations due to salinization will also result in decreased P release to the overlying water layer.

#### Minor influence of Sulfate-induced P mobilization

An important issue related to P availability in wetlands is the potential role of increased SO<sub>4</sub><sup>2-</sup> input on sediment P mobilization. Several studies showed SO<sub>4</sub><sup>2-</sup>-induced P mobilization and enhanced decomposition (Roden and Edmonds 1997; Lamers et al. 1998b, 2002a; Zak et al. 2006) leading to internal P eutrophication in the longer term (Smolders et al. 2006). Interestingly, in our study the opposite was found, as lower porewater P concentrations correlated

with elevated  $\text{SO}_4^{2-}$  concentrations related to salinization. Low porewater  $\text{Fe}^{2+}$  in combination with high  $\text{SO}_4^{2-}$  reduction rates, as indicated by high  $\text{S}^{2-}$  levels, indicate that adsorption of P onto iron hydroxides, or precipitation of P and  $\text{Fe}^{2+}$ , is not a key mechanism in the sediments in the present study. This can be explained by the fact that our study site was rich in Ca and showed increased total S contents of the sediment as a result of the brackish history (see Table 1). Therefore, most Fe in the sediments was already bound to reduced S ( $\text{S}^{2-}$ ), resulting in a minor effect of enhanced  $\text{S}^{2-}$  production on the adsorption of P onto Fe compounds. As a result, P immobilization caused by precipitation of P with Ca is greater than potential P mobilization by enhanced  $\text{SO}_4^{2-}$  reduction rates. S-poor sediments, such as freshwater wetlands without historic influence of saline water, will most probably react differently and will probably show P mobilization after salinization.

#### Long-term salinization lowers sediment nitrogen availability

The observed salinity-induced decrease in  $\text{NH}_4^+$  availability in the long term is contrary to our hypothesis and to the results of many other studies reporting an increase due to displacement of  $\text{NH}_4^+$  from sediment cation exchange sites by increased cation concentrations (Seitzinger et al. 1991; Weston et al. 2006, 2010; van Dijk et al. 2015; Steinmuller and Chambers 2018). Although rapid  $\text{NH}_4^+$  mobilization can take place within hours after salinization (Weston et al. 2010), long-term increased or fluctuating salinity may deplete the amount of  $\text{NH}_4^+$  bound to cation exchange sites, depending on sediment characteristics (Weston et al. 2010; Noe et al. 2013; van Dijk et al. 2015; Steinmuller and Chambers 2018). In the present study, fast  $\text{NH}_4^+$  mobilization was indeed found during the 1<sup>st</sup> weeks. Porewater  $\text{NH}_4^+$  concentrations were on average 14% higher in the 4.5 and 9.0 PSU treatments during the first 4 months compared to the control treatment (Fig. 4e). Even surface water  $\text{NH}_4^+$  concentrations were, on average 8% higher in these treatments during the first 4 months (n.s.) (Fig. 3c). The seasonal fluctuations in porewater  $\text{NH}_4^+$  concentrations in 2010/2011 were most probably related to temperature-related changes in decomposition rates. In contrast to the observed short-term effect, porewater  $\text{NH}_4^+$  concentrations remained 30% lower in all

salinity treatments (vs. control) during the last 3 years (Fig. 4e). Our analyses indicated rapid  $\text{NH}_4^+$  mobilization from cation exchange sites in the short term, which supports our hypothesis of short-term mobilization (H4), but in the long-term depletion of  $\text{NH}_4^+$  was found does not support the second half of the hypothesis (H5) of more pronounced effects in the long term. The decrease in exchangeable  $\text{NH}_4^+$  concentrations observed in deeper sediment layers of all salinity treatments further supports this decrease and depletion of  $\text{NH}_4^+$  in time and depth in the long term (Figs. 4e, 6f). The observed decrease could be explained by short term  $\text{NH}_4^+$  mobilization and coupled nitrification and denitrification at the sediment water interface (Strauss et al. 2002; Burgin and Hamilton 2007), leading to long-term N depletion. In  $\text{S}^{2-}$ -rich ecosystems S-driven  $\text{NO}_3^-$  reduction by chemo-autotrophic denitrifying bacteria may also play an important role, next to chemo-organotrophic denitrification (Hayakawa et al. 2013). In literature, however, there is no consensus on the effects of salinization on the N cycle and nitrification and denitrification in particular, which warrant further research (Herbert et al. 2015).

#### Salinization effects on decomposition—sulfate reduction versus methanogenesis

There is no clear consensus in the literature on how increased salinity affects sediment C cycling. In general, salinization will lead to increased concentrations of the alternative terminal electron acceptor  $\text{SO}_4^{2-}$ , which may enhance anaerobic microbial mineralization of organic matter in coastal wetlands (Lamers et al. 1998b; Weston et al. 2006; Chambers et al. 2011, 2013; Marton et al. 2012; Neubauer 2013; Vizza et al. 2017). Although actual C mineralization rates and microbial activity were not determined in the present study, porewater concentrations of the end products of methanogenesis ( $\text{CH}_4$ ) and of  $\text{SO}_4^{2-}$  reduction ( $\text{S}^{2-}$ ) could be used as proxies. Our study shows a clear shift from methanogenesis dominance under control conditions to dose-dependent  $\text{SO}_4^{2-}$  reduction dominance under increased salinity (> 2.25 PSU) (Fig. 5d for  $\text{CH}_4$ , Fig. 5e for  $\text{SO}_4^{2-}$  and Fig. 5f for  $\text{S}^{2-}$ ). This shift has also been found in several other studies (Bartlett et al. 1987; Weston et al. 2006; Chambers et al. 2011; Vizza et al. 2017) as  $\text{SO}_4^{2-}$  reduction is a thermodynamically more favorable

process than methanogenesis. As a result, methanogens are outcompeted by  $\text{SO}_4^{2-}$  reducers, or even directly inhibited by an increase in ionic strength or  $\text{S}^{2-}$  (Weston et al. 2006; Chambers et al. 2011). Apart from effects on  $\text{SO}_4^{2-}$  reduction and methanogenesis, Weston et al. (2006) also showed a temporary enhancement of Fe reduction rates after salinity increase. In our study, enhanced Fe reduction was unlikely due to the low availability of  $\text{Fe}^{2+}$  (as discussed above). Even after 5 years of increased salinity, methanogenesis was still suppressed in the 4.5 and 9.0 PSU treatments in contrast to the control (data not shown). This means that increased surface water salinity will also in the long term decrease  $\text{CH}_4$  emissions from former brackish coastal freshwater wetlands. Based on the results from the present study, however, it is difficult to speculate on the effects of salinization on the total C emissions to the atmosphere.

#### Short term versus long term effects of salinization

As confirmed by the present paper salinization has large effects on the N, P and C cycles on the short term. However hardly any field experiments have studied the long term effects of salinization. Our results does show that, in contrast to what was hypothesized (H5), the dose-dependent effects of salinization were found to increase on the short term (weeks–months) but did stabilize on the long term (months–years). From this it can be concluded that great care should be taken to extrapolate the outcome of short-term studies (days to weeks) to longer-term effects. Semi-long term effects (months) can already give a more appropriate prediction for long term effects (years).

#### Enclosure effects

The observed differences between treatments within enclosures provided important evidence-based insights to understand differential, short-term and long-term effects of enhanced salinity on sediment biogeochemistry under field conditions. As expected, the comparison with control sites outside enclosures (NE) also revealed some inevitable enclosure effects. The most noticeable effects were lower long term sediment porewater concentrations of  $\text{NH}_4^+$ , TIC and P in the 0.9 PSU treatment compared to the 0.9 PSU (NE) treatment (Fig. 4). These differences are very

likely caused by decreased input of dissolved and particulate organic matter into the enclosures compared to open water, affecting long term sediment decomposition and nutrient mineralization rates. Although dissolved organic C (as a substrate for microorganisms) has a large effect on  $\text{SO}_4^{2-}$  reduction and methanogenesis (Vizza et al. 2017; Welti et al. 2017), we found no proof that reduced input of organic matter as a consequence of enclosure placement affected these processes. Porewater depth profiles did not show differences between the control treatments with and without enclosure for  $\text{CH}_4$ ,  $\text{SO}_4^{2-}$  and  $\text{S}^{2-}$  (Fig. 5). We therefore feel that the outcome of our enclosure approach still warrants our conclusions.

#### Consequences of surface water salinization for the benthic community

In addition to the effects of increased salinity on biogeochemical cycling, some important consequences were observed for the benthic fauna community. It is well known that brackish conditions result in lower biodiversity than in freshwater ecosystems (Remane 1934; Hart et al. 1991). In the present study nutrient levels decreased but they were probably not limiting for primary production as a food source for benthic fauna, so we expect ionic and osmotic stress and  $\text{S}^{2-}$  toxicity to overrule the effects of decreased nutrient availability on benthic fauna. Free  $\text{S}^{2-}$  is highly toxic and known to increase mortality and other toxicity effects of macroinvertebrates and to delay population recovery after recolonization (Lamers et al. 2013; Kanaya et al. 2015). Characteristic brackish benthic fauna and aquatic plants are most probably absent due to dispersal limitation which was inherent to our experimental set-up.

#### Conclusion

Here we show a strong, dose-dependent negative impact of long-term (5 years) salinization on nutrient (N and P) availability in coastal freshwater wetland sediments. Although many short-term, lab studies report the opposite, our long-term, field study clearly shows that combined physicochemical and biogeochemical effects may well lead to a reduction of the N ( $\text{NH}_4^+$ ) and P availability in formerly brackish freshwater wetlands, both in the short-term and in



the longer term (5 years), ( $H_2$  rejected). Increased cation exchange appeared to be one of the key processes involved ( $H1$  accepted), resulting in  $NH_4^+$  and Ca mobilization, Ca–P precipitation and N losses due to coupled nitrification–denitrification. Furthermore we demonstrated a clear and lasting shift from methanogenesis to  $SO_4^{2-}$  reduction as the dominant C mineralization process leading to decreased  $CH_4$  production ( $H3$  accepted). As a consequence salinization led to enhanced  $S^{2-}$  levels, toxic to both plants and animals. Overall all salinization effects found showed to be dose dependent ( $H4$  accepted). And effects did increase on the semi-long term (months) but did stabilize on the long term (years) ( $H5$  rejected).

As worldwide salinization of coastal (and inland) systems is occurring at an alarming rate and scale (Herbert et al. 2015), results from long-term field experiments such as the one presented here are vital to better predict the future effects of increasing surface water salinity on biogeochemical processes, including sediment nutrient cycling. Our study shows that in formerly brackish systems nutrient availability may decrease due to salinization even though  $SO_4^{2-}$  reduction rates increase. As a large percentage of coastal wetlands are geologically or historically characterized by former influence of saline water and, as a consequence are S-rich, processes and mechanisms described in the present paper may well apply to many coastal wetlands.

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