

1 **Carbon dioxide release driven by organic carbon in minerogenic**  
2 **salt marshes**

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13 **Abstract**

14 Coastal wetlands play an important role in the global carbon cycle by sequestering carbon (referred to as  
15 “blue carbon”). At the same time, organic carbon (OC) in the subsurface is decomposed, releasing greenhouse gases  
16 (GHGs) such as carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>). To predict how this carbon balance in salt marshes will  
17 change under future climate scenarios (e.g., higher temperatures, sea level rise), it is essential to understand the controls  
18 on OC decomposition in these systems. Here, we investigated OC turnover and CO<sub>2</sub> release in a minerogenic salt marsh  
19 at the Wadden Sea, Germany. We first characterized the porewater and sediment of a pioneer marsh and adjoining  
20 intertidal flat to identify key biogeochemical processes. We then performed an in situ experiment by injecting two OC  
21 sources (labile (acetate)/complex (humic acid)) and subsequently monitored GHG release over four injection cycles  
22 along with subsurface geochemistry. Overall, we found that electron acceptors, primarily sulfate (SO<sub>4</sub><sup>2-</sup>), were present  
23 at all tested depths and no CH<sub>4</sub> was detected, suggesting that electron acceptor availability was unlikely to be the  
24 primary limiting factor on microbially mediated CO<sub>2</sub> release; the availability of OC (concentration and composition)  
25 may rather act as a limiting factor. Following the addition of labile OC, CO<sub>2</sub> release in the pioneer marsh increased  
26 by up to 47.4 ± 36.4 % compared to the control, with a generally similar trend in the intertidal flat. The CO<sub>2</sub> release  
27 from the complex OC treatment was similar to the control. The results of our work improve understanding of  
28 minerogenic salt marsh OC dynamics in temperate zones and enable better prediction of future changes.

29

## 1 Introduction

30 Vegetated coastal wetlands, located at the interface between land and the open sea, occur along all continental  
31 coastal zones except Antarctica and comprise mangroves, seagrass, and salt marshes (Nellemann et al., 2009; Pendleton  
32 et al., 2012; Tan et al., 2025). Salt marshes, including the seaward adjoining intertidal flats, sequester high amounts of  
33 carbon primarily in the sediment (Mcleod et al., 2011; Nellemann et al., 2009; de Vlas et al., 2013). Globally, around  
34 60.4-70 Tg yr<sup>-1</sup> of carbon is buried in vegetated salt marshes (Duarte et al., 2005; Nellemann et al., 2009). The  
35 sequestration of carbon is disproportional in vegetated coastal areas, with around half of the total organic carbon in  
36 ocean sediment (often referred to as “blue carbon”) buried in these areas which only account for 0.2 % of the ocean  
37 surface (Duarte et al., 2013; Nellemann et al., 2009). As the rate of carbon input into the sediment exceeds its rate of  
38 decomposition (especially for allochthonous carbon), salt marshes are characterized by high carbon sequestration rates  
39 (Mueller et al., 2019; Temmink et al., 2022; Van de Broek et al., 2018). Simultaneously, salt marshes release  
40 greenhouse gases (GHGs) due to organic carbon (OC) decomposition: carbon dioxide (CO<sub>2</sub>) at 0.02-0.24 Pg CO<sub>2</sub> yr<sup>-1</sup>  
41 (Pendleton et al., 2012) and methane (CH<sub>4</sub>) at 0.142 ± 0.02 Mg carbon ha<sup>-1</sup> yr<sup>-1</sup> (Alongi, 2020). Therefore,  
42 understanding carbon turnover in coastal wetlands is crucial for predicting how these ecosystems will respond to  
43 climate change, such as temperature increase, sea level rise, and eutrophication of coastal waters. This is especially  
44 important given the annual 1-2 % loss of salt marshes due to land-use change and their vulnerability to climate impacts  
45 (Duarte et al., 2008).

46 In coastal wetlands, microbial respiration pathways couple OC as an electron donor with terminal electron  
47 acceptors (TEAs), especially oxygen (O<sub>2</sub>), ferric iron (Fe(III)) and sulfate (SO<sub>4</sub><sup>2-</sup>) (Tan et al., 2025; Tobias and  
48 Neubauer, 2019). Oxygen, the thermodynamically most favourable TEA, exhibits fluctuating penetration depth into  
49 the sediment due to tides, bioturbation or root-mediated O<sub>2</sub> transport (de Beer et al., 2005; Huettel et al., 2014; Maricle  
50 and Lee, 2002). In deeper sediment layers, where anoxic conditions can dominate, microorganisms utilize Fe(III), from  
51 iron minerals, or SO<sub>4</sub><sup>2-</sup>, which infiltrates the sediment through inundation of seawater, as alternative TEAs (Jørgensen  
52 et al., 2019; Tobias and Neubauer, 2019). Upon full depletion of TEAs, OC is further decomposed to CH<sub>4</sub> (Schlesinger  
53 and Bernhardt, 2013b). Microbial decomposition of OC may be further influenced by its chemical composition.  
54 Chemically simpler e.g., short chain aliphatic OC may be substantially favoured for decomposition compared to  
55 complex OC, such as natural organic matter (Gunina and Kuzyakov, 2022; Lipczynska-Kochany, 2018; Schlesinger  
56 and Bernhardt, 2013a).

57 The primary controls on GHG release in salt marshes, as interfaces between land and open ocean, are not  
58 fully understood. Specifically, it is unclear whether OC turnover is primarily controlled by the availability of the  
59 electron acceptors – as observed in organogenic marshes and consistent with studies in terrestrial wetlands (Schlesinger  
60 and Bernhardt, 2013b) – or by the organic matter itself, as suggested for marine sediment in general (Arndt et al.,  
61 2013). Past studies on OC dynamics (including GHG release) in salt marshes have largely concentrated on the eastern  
62 coast of the US (Capooci et al., 2024; Kostka et al., 2002b; Lowe et al., 2000; Seyfferth et al., 2020), which is dominated  
63 by organogenic peat marshes. Organogenic marshes are generally low energy, microtidal wetlands, characterized by a  
64 high organic matter deposition via autochthonous pathways that results in high TOC contents (Logemann et al., 2025).  
65 For example, Lowe et al. (2000) and Kostka et al. (2002a) observed that OC oxidation was controlled by SO<sub>4</sub><sup>2-</sup> and

66 Fe(III) reduction in salt marshes in Georgia, USA. Further, CH<sub>4</sub> fluxes were detected in salt marshes in Delaware,  
67 suggesting a co-occurrence of methanogenesis and SO<sub>4</sub><sup>2-</sup> reduction (Capooci et al., 2024; Seyfferth et al., 2020).  
68 European salt marshes, in contrast, are primarily minerogenic, i.e., contain high fractions of mineral sediment due to  
69 high sedimentation rates, resulting in comparably lower TOC content (Nolte et al., 2013). Studies conducted in  
70 European salt marshes have focused on the TEA turnover (e.g., SO<sub>4</sub><sup>2-</sup> respiration rates) and not GHG emissions (de  
71 Beer et al., 2005; Bosselmann et al., 2003; van Erk et al., 2023). These studies showed that O<sub>2</sub> penetrates down the  
72 sediment, Fe(III) is available and SO<sub>4</sub><sup>2-</sup> reduction occurs. Hence, these studies have provided indirect links between  
73 belowground biogeochemistry, especially in the context of available TEA, and the release of GHGs in minerogenic  
74 salt marshes; however, a direct investigation of the determining factor(s) of OC degradation from these ecosystems is  
75 missing. By understanding the controls on GHG release, we can better predict how climate impacts such as higher  
76 temperatures and sea level rise will affect OC turnover and thereby GHG release in minerogenic salt marshes.

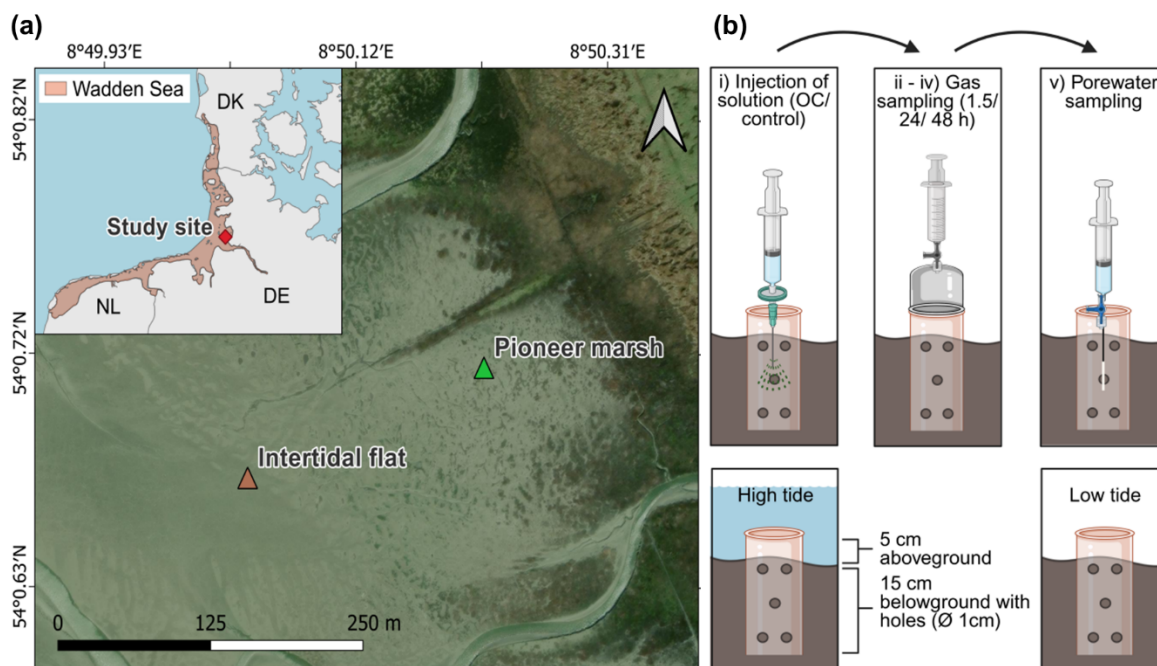
77 To investigate the in situ carbon dynamics in minerogenic salt marshes, we chose a representative field site  
78 at the Wadden Sea coast. Our goals were (i) to identify the key microbial processes (O<sub>2</sub>, Fe(III) and/or SO<sub>4</sub><sup>2-</sup> reduction)  
79 that control the release of OC as CO<sub>2</sub> and/or CH<sub>4</sub>, and (ii) to determine the role of OC (concentration and composition)  
80 in the release of GHGs. To this end, we first characterised the primary geochemical parameters from a minerogenic  
81 pioneer marsh and intertidal flat at the German Wadden Sea. Building on those results, we conducted an in situ  
82 manipulation experiment investigating the impact of two contrasting OC sources (acetate, humic acid) on GHG  
83 emissions. We hypothesized that (i) the high energy and sediment inputs in minerogenic salt marshes result in low  
84 TOC supply and high TEA availability. (ii) We further hypothesize that this leads to the likely limitation of electron  
85 donor and not acceptor on OC decomposition and (iii) the composition of OC plays a more important role than the  
86 concentration in CO<sub>2</sub> release from a minerogenic salt marsh. These hypotheses were tested in two successional zones  
87 of a salt marsh, a pioneer marsh with sparse pioneer vegetation and a non-vegetated intertidal flat.

## 88 2 Materials and Methods

### 89 2.1 Study site

90 This study was conducted at the Altfelder Koog by Friedrichskoog (54°01'02.4"N 08°51'17.09"E), an area  
91 that consists of a salt marsh with different successional zones in the Wadden Sea National Park (Schleswig-Holstein)  
92 in northern Germany at the mouth of the Elbe estuary (Fig. 1a). The Wadden Sea is a UNESCO World Heritage Site  
93 and the largest continuous salt marsh (including tidal flats) in Europe (Common Wadden Sea Secretariat, 2017). The  
94 tidal range at the study area is 3.59 m, defined as the difference between mean height of high water and approximately  
95 the lowest astronomical tide. The mean high tide is 1.56 m higher than the mean sea level (BSH, 2025).

96 At the Wadden Sea, different successional zones of salt marshes are developing as a result of the ongoing  
97 process of sediment transportation by waves and tides (Esselink et al., 2017; de Vlas et al., 2013). The two successional  
98 zones which are of interest in our study are the pioneer marsh and the intertidal flat (Fig. 1a). Pioneer species such as  
99 *Salicornia* spp. and *Spartina anglica* occur in the pioneer marsh, promoting further sediment trapping (Esselink et al.,  
100 2017; de Vlas et al., 2013). The intertidal flat (seaward of a pioneer marsh) is an area with no plants to buffer incoming  
101 waves and is therefore subject to a strong tidal influence (Esselink et al., 2017). In general, both the pioneer marsh and  
102 intertidal flat are inundated daily during high tide, with the pioneer marsh experiencing less and shorter inundation (<  
103 3 h fully inundated) compared to the intertidal flat (> 3 h fully inundated) (de Vlas et al., 2013). During a spring tide,  
104 which occurs twice a month, the magnitude of high and low tide is amplified leading to stronger exposure of the pioneer  
105 marsh to tides (Gao, 2019; Kvale, 2006).



106  
 107 **Figure 1. Study site at the Wadden Sea including the successional zones of a salt marsh and a schematic representation of**  
 108 **the in situ experimental design.** (a) Wadden Sea, in light red in the inset with a red marker indicating our study site in northern  
 109 Germany (Friedrichskoog, Elbe estuary). Gradient of salt marsh successional zones, beginning with the intertidal flat, followed by  
 110 the pioneer marsh and more developed successional zones extending further inland. Map information: Reference system WGS 1984,  
 111 UTM 32N, data imagery ESRI 2025. (b) Experimental design: experimental procedure (top) and cylinder setup in sediment (below).  
 112 Each sampling plot consisted of a 20 cm long cylinder (diameter 16 cm), drilled with 1 cm diameter holes along the length of the  
 113 cylinder. The cylinder was inserted 15 cm deep in the sediment to define the injection area. The top 5 cm was used to mount a gas  
 114 chamber during gas sampling. The cylinder stayed in the sediment over the course of the experiment including high and low tide.  
 115 Numbers i-v) indicate the experimental procedure: i) injection of solution (acetate or humic acid, only NaCl for control), ii) 1.5 h  
 116 after injection, the first gas measurement was done, iii) followed by the second gas measurement after 24 h of injection, and iv) the  
 117 final gas measurement after 48 h of injection, followed by the final step of v) porewater sampling. Each treatment (acetate, humic  
 118 acid) and the control consisted of spatial triplicates.

119 **2.2 Porewater and sediment sampling for general geochemistry**

120 In August 2022 and 2023, sediment cores were collected from the pioneer marsh and intertidal flat to analyse  
 121 the general geochemistry of the sediment and porewater. The sampling was performed during low tide. Push cores  
 122 were collected using core liners (UWITEC, polyvinyl chloride PVC) with an inner diameter of 8.6 cm (outer diameter  
 123 9 cm) and a length of 60 cm. To minimize compression, we used open push cores and only capped them when the core  
 124 liner was fully in the sediment. Furthermore, the inside wall of the cores was plain and clean to smoothly insert the  
 125 core liner in the sediment. To further minimize disturbance, the sampled cores were immediately closed, vertically  
 126 transported, and stored in the dark. At depth intervals of 5 cm, porewater samples (Rhizon sampler CSS, 0.12-0.18  $\mu\text{m}$   
 127 pore size, Rhizosphere Research, Netherlands) and sediment samples (using a cut-off syringe) were taken through  
 128 pre-drilled holes which had been covered with isolation tape during coring. We made sure to not take sediment or

129 porewater samples at the edges but rather from the middle of the cores, where the sediment is likely undisturbed.  
130 Porewater samples were analysed for dissolved organic carbon (DOC), iron speciation,  $\text{SO}_4^{2-}$ , and dissolved  $\text{CH}_4$ , and  
131 sediment samples for total organic carbon (TOC). Detailed method for dissolved  $\text{CH}_4$  sampling is given in Supplement,  
132 S1.1.

133 We collected further sediment cores for fine scale  $\text{O}_2$  profiles. For this, sediment push cores (inner diameter  
134 2.5 cm, length 10 cm) were collected and immediately sealed. Shortly after sampling,  $\text{O}_2$  profiles were taken with a  
135 depth resolution of 500  $\mu\text{m}$  using Clark-type  $\text{O}_2$  microsensors (Unisense, Denmark) with a 100  $\mu\text{m}$  tip, following  
136 Revsbech (1989). Before measurement, a two-point calibration was done using air-saturated seawater and 0.1 M  
137 sodium ascorbate in 0.1 M NaOH solution. Profiles were recorded with the Unisense software SensorTrace Suite  
138 (version 2.8.200.21688, Unisense, Denmark).

### 139 **2.3 Physicochemical characteristics of the sediment**

140 For a general physicochemical characterization, bulk sediment was collected from a depth up to 15-20 cm in  
141 sterile sample bags with puncture proof tabs (Nasco, Whirl-pak, USA), and stored at 4 °C in the dark. Stones and  
142 macrofauna were removed prior to further analysis. We determined grain density, bulk porosity, moisture content, and  
143 particle size (details in Supplement, S1.2).

### 144 **2.4 In situ experiment: Enhanced organic carbon input**

#### 145 **2.4.1 In situ experiment design**

146 An in situ OC addition experiment was conducted in August and September 2023 to test the response of  
147 pioneer marsh and intertidal flat systems to elevated inputs of OC with different compositions. We choose acetate, a  
148 chemically simple organic compound that has been detected at other salt marshes (Hyun et al., 2007; Kostka et al.,  
149 2002a) and at a site nearby (Llobet-Brossa et al., 2002), and humic acid (in the form of Pahokee Peat humic acid), a  
150 more complex OC source, as a proxy for natural organic matter. The two OC sources were chosen, knowing their  
151 thermodynamical difference from previous studies (Gunina and Kuzyakov, 2022), to present a fermentation product  
152 (acetate) and a proxy for terrestrial organic matter (in addition to the difference with respect to complexity). Studying  
153 both labile and complex OC additions is ecologically relevant as salt marshes receive OC from multiple sources  
154 (Howard et al., 2023; Temmink et al., 2022). Eutrophication of coastal waters and/or root exudates can supply readily  
155 degradable OC to salt marshes, while increased organic matter load in rivers can deliver more complex OC compounds  
156 to salt marshes. The applied OC compounds in our study, therefore, represent environmental scenarios and allows us  
157 to investigate how these OC sources influence GHG release under realistic conditions. The injection solutions were  
158 prepared in the laboratory prior to use in the field. Solutions of 1 g OC  $\text{L}^{-1}$  were prepared with either acetate or humic  
159 acid as a carbon source. For the preparation of the solutions, sodium acetate or Pahokee Peat humic acid (obtained  
160 from the International Humic Substances Society (IHSS), Table S1) were dissolved in deionized water (Barnstead MQ  
161 system, Thermo Fisher Scientific, Germany), the pH was adjusted to 7.07-7.81 and NaCl was added (20 g  $\text{L}^{-1}$ ). The  
162 solution for the control only contained NaCl. Additionally, 25 mM bromide ( $\text{Br}^-$ ) (in the form of NaBr) was added into

163 the carbon and control solutions as an inert tracer in the field. All solutions were purged with nitrogen and stored at 4  
164 °C in the dark until used in the field. Details of the preparation process are provided in Supplement, S1.3.

165 The in situ experiment was performed in the pioneer marsh (54°00'43.14"N 08°50'12.9"E) and intertidal flat  
166 (54°00'40.45"N 08°50'02.27"E) (Fig. 1a), with the same setup in both zones. The assigned plots in the field were  
167 selected as visually similar triplicates (spatial triplicates), at a distance of ~5 m between plots of the same treatment  
168 and ~10 m between different treatments and the control plots. In the pioneer marsh, plots were placed outside of  
169 vegetated areas, i.e., the actual plot area of injection and sampling were free of vegetation although vegetation was  
170 present in the vicinity (Figs. S1a/b). For the intertidal flat, no vegetation was present, neither in the surroundings nor  
171 inside of the plots (Figs. S1c/d). Each plot consisted of a 16 cm diameter PVC cylinder with both ends open which  
172 was pushed 15 cm deep into the sediment (Fig. 1b). Holes (diameter 1 cm) were drilled in the cylinder wall to allow  
173 underground water movement. A porewater sampler (Rhizon sampler CSS, 0.12-0.18 µm pore size, Rhizosphere  
174 Research, Netherlands) was inserted in the middle of each plot at a depth of 5-10 cm and remained in the sediment  
175 over the duration of the experiment. The cylinder reached 5 cm out of the sediment, allowing a gas flux chamber to be  
176 mounted gastight for gas measurements. During the experiment, the cylinder stayed in the field. To decrease the  
177 influence of disturbances due to the setup of the experiment, we waited at least three days between setting up and the  
178 first measurements. Apart from the incubation time for gas sampling, the sediment within the cylinder was exposed to  
179 the atmosphere (low tide) or covered with seawater (high tide) (Fig. 1b).

180 The experiment was conducted similarly in both zones, the pioneer marsh and intertidal flat, using spatial  
181 triplicates and comprising four injection cycles (Fig. 1b). One injection cycle consisted of i) the injection of the anoxic  
182 sterile solution (OC or control solution), followed by ii) the first gas sampling 1.5 h after the injection. Gas sampling  
183 was repeated iii) 24 h after the injection and iv) 48 h after the injection. After the 48 h gas sampling, v) porewater was  
184 collected. Injection of the solutions and sampling was done during low tide. The solution for the different treatments  
185 was slowly injected in step i) with a bent needle at a depth of approximately 5-10 cm in the middle of each plot into  
186 the sediment. The injected solution was filtered (PES filter, pore size 0.22 µm, pre-rinsed with double deionized water)  
187 during injection to ensure that the solutions were sterile.

188 In each injection cycle, the native OC was increased by 12.0 mg C L<sup>-1</sup> in the pioneer marsh and 12.6 mg C L<sup>-1</sup>  
189 in the intertidal flat, assuming an even distribution across the experimental cylinder (calculation Supplement, S1.4).  
190 After one cycle was completed, the system had three days to recover before the next injection. At the end of the four  
191 injection cycles, sediment samples were collected (details below). The applied approach allowed us to assess short-  
192 term OC process response in minerogenic salt marshes, rather than long-term responses.

## 193 **2.4.2 In situ experiment sampling**

### 194 **Gas sampling**

195 Gas sampling was conducted using an opaque, static, non-flow gas chamber made of polypropylene (chamber  
196 volume 3000 cm<sup>3</sup>). The gas chamber was placed on the cylinder and gas samples were collected at 20-minute intervals  
197 over an incubation period of 1 hour using a 50 mL gastight syringe with a three-way valve. For sampling, the chamber

198 gas was gently mixed by pumping the syringe plunger three times before withdrawing 35 mL gas. The first 5 ml were  
199 used to flush the attached needle, and the rest was transferred immediately into a pre-evacuated 12 mL Exetainer® vial  
200 (Labco, UK). The samples were measured with a Greenhouse GC equipped with two Pulsed Discharge Detector (PDD)  
201 (ThermoFisher Scientific TRACE™ 1310 GC-Analyzer, USA – custom designed by S+H-Analytik) and two column  
202 structure (first structure 30 m long, 0.53 mm ID TGBondQ column, second structure 30 m long, 0.53 mm ID Molsieve  
203 column (for CH<sub>4</sub>) and 30 m long 0.32 mm ID TGBondQ+ column (for CO<sub>2</sub>, N<sub>2</sub>O)). Calculation for the gas fluxes and  
204 cumulative CO<sub>2</sub> emissions are given in Supplement, S1.5.

## 205 **Porewater sampling**

206 Porewater samples were collected via the pre-installed porewater sampler. The pH (Mettler Toledo SevenGo,  
207 Germany) and salinity (refractometer) were measured in the field. The collected porewater was fixed for DOC  
208 (acidification with 2 M HCl), iron speciation (acidification with 1 M HCl), and total sulfide (S(II)<sub>tot</sub>) (alkalinization  
209 with zinc acetate). Dissolved inorganic carbon (DIC) samples were transferred into vials without headspace  
210 immediately after sampling and capped. The remaining porewater was anoxically stored in nitrogen flushed bottles in  
211 the dark at 4 °C for Br<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and chloride (Cl<sup>-</sup>) measurements.

## 212 **Sediment sampling**

213 At the end of the experiment, sediment samples were collected for geochemical analysis (TOC, solid iron  
214 speciation, sulfide species) and microbial analysis. For this, push cores (inner diameter of 2.5 cm, and a length 10 cm)  
215 were taken from the middle of each plot at the same positions as the porewater samples and immediately frozen until  
216 further analysis. Sediment samples for the molecular biology analysis were stored at -80 °C upon bringing them back  
217 to the laboratory.

## 218 **2.5 Geochemical analysis**

### 219 **2.5.1 Porewater analysis**

220 DOC (as non-purgeable OC) and DIC (as the difference of total carbon and OC) was determined by a TOC  
221 analyser (multi N/C 2100S, Analytik Jena GmbH, Germany). To analyse the iron speciation in the porewater, the  
222 ferrozine assay (Stookey, 1970) was used. The S(II)<sub>tot</sub> was quantified by the Cline assay (Cline, 1969). Sulfate, Br<sup>-</sup>,  
223 and Cl<sup>-</sup> were analysed by an ion chromatograph (Metrohm 930 Compact IC Flex, Switzerland).

### 224 **2.5.2 Sediment analysis**

225 For all sediment analyses, sampled cores were thawed in an anoxic glovebox to prevent oxidation (UNILab  
226 plus Glovebox, MBRAUN, Germany), sliced in two depths (0-5 and 5-10 cm), and each depth fraction was  
227 homogenized by hand.

### 228 **Iron extraction**

229 To target the poorly and higher crystalline iron phases in the sediment samples, parallel iron extractions were  
230 performed under anoxic conditions, adapted from Moeslundi et al. (1994) and Lueder et al. (2020). From each depth

231 (0-5 and 5-10 cm) ~0.2 g wet sediment sample (in triplicates) were added into an Eppendorf tube. To extract poorly  
232 crystalline iron minerals, we used an extraction with anoxic 0.5 M HCl (Heron et al., 1994). We expect that poorly  
233 crystalline iron (oxyhydr)oxides as well as ferrous iron (Fe(II)) phases such as carbonates and sulfides (e.g., FeCO<sub>3</sub> or  
234 FeS) would be extracted by this acidification. One mL of anoxic 0.5 M HCl was added to the sediment, vortexed, and  
235 incubated for 2 h in the dark at room temperature in the glovebox. For the extraction of iron minerals of higher  
236 crystallinity, targeting more crystalline Fe(II) (except pyrite) and Fe(III) phases (Cornwell and Morse, 1987; Heron et  
237 al., 1994), 1 mL of anoxic 6 M HCl was added to the sediment, and the sediment was vortexed and vertically rotated  
238 for 24 h under anoxic conditions at room temperature (30 rpm, dark). For both HCl extractions, the samples were then  
239 centrifuged (5 min, 13400 rpm), the supernatant was diluted with 1 M HCl, and iron speciation and concentration of  
240 the supernatant was determined using the ferrozine assay (Stookey, 1970). Total iron and Fe(II) concentrations of the  
241 supernatant were measured directly, and Fe(III) was determined by subtracting Fe(II) from total iron. To obtain the  
242 higher crystalline fraction separately, the poorly crystalline fraction (0.5 M HCl extract) was subtracted from the 6 M  
243 HCl fraction. We acknowledge that the weaker acid extraction extracted Fe(II) from carbonates and sulfides in addition  
244 to iron (oxyhydr)oxides. We therefore used this approach to determine the crystallinity of iron minerals and call it  
245 poorly (extracted by 0.5 M HCl) and higher (extracted by 6 M HCl) crystalline iron minerals (and not (oxyhydr)oxides).

#### 246 **Acid volatile sulfide**

247 To determine the mass of acid volatile sulfide (AVS) in the sediment similar to Burton et al. (2007), ~2 g of  
248 wet sediment was weighed in centrifuge tube in a glovebox. A smaller tube filled with anoxic 1 M zinc acetate + anoxic  
249 2 M NaOH (v/v 15:85) was placed into the sediment-filled centrifuge tube. To the sediment, 10 mL anoxic 6 M HCl  
250 + 2 mL anoxic 1 M L-ascorbic acid was added and immediately closed. The double tubes were placed in an ultrasonic  
251 bath for 30 seconds, followed by horizontal shaking overnight (150 rpm). The sulfide released from the sediment was  
252 captured in the zinc acetate solution and was analysed according to Cline (1969).

#### 253 **Total organic carbon**

254 To quantify sediment TOC, samples collected in 2023 were dried under anoxic conditions, while those from  
255 2022 were dried under oxic conditions, at room temperature until constant weight was reached. Sediments from both  
256 years were milled and analysed by a TOC analyser (SoliTOC Cube Elementar, Germany).

### 257 **2.6 Molecular biology analysis**

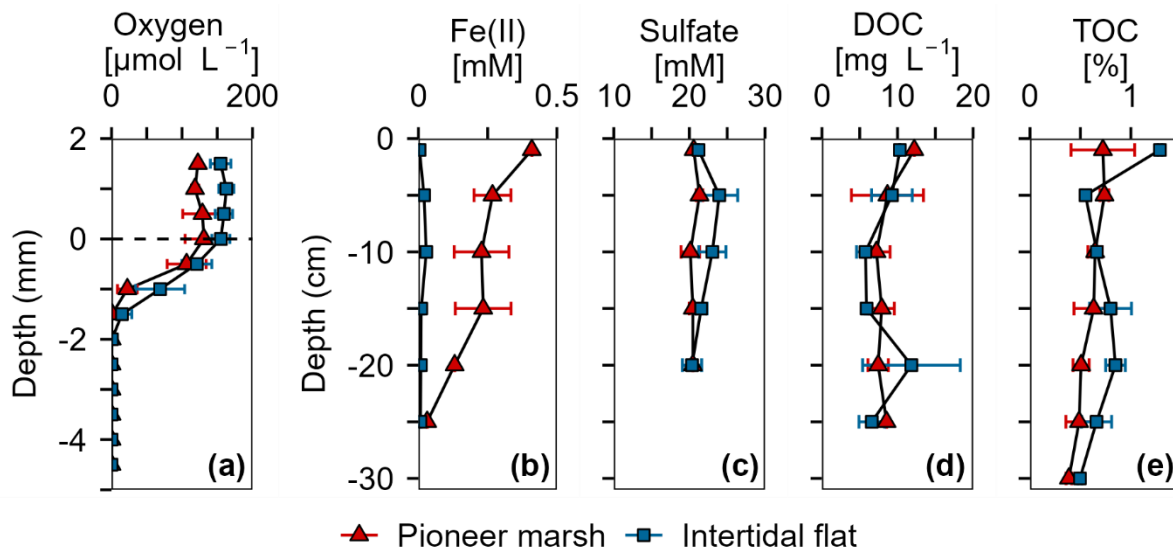
258 The co-extraction of DNA and RNA was performed according to Lueders et al. (2004). Quantitative  
259 polymerase chain reaction (qPCR) for DNA and complementary DNA (cDNA) was done to quantify total bacterial  
260 16S rRNA gene copies using the primer 341F and 797R. Functional genes were also targeted: *Geobacter* spp. (involved  
261 in Fe(III) reduction) using the primer Geo 577F and Geo 822R, and *dsrA* (involved in SO<sub>4</sub><sup>2-</sup> reduction) using the primer  
262 DSR\_1F and DSR\_1R. Quantitative polymerase chain reaction was done using SsoAdvanced SYBR Green Supermix  
263 (Bio-Rad) on the C1000 Touche Thermal Cycler (CFX96™ Real-Time System, Bio-Rad, Germany). Data analysis  
264 was performed by the software Bio-Rad CFX Maestro 1.1 (version 4.1.2433.1219). Further details are given in  
265 Supplement, S1.6 and Table S2.

## 266 2.7 Statistical analysis

267 For statistical analysis RStudio (R version R-4.4.3) was used (R Core Team, 2025). The significance level for  
268 all tests was set at  $p < 0.05$ . Normal distribution of the data and homogeneity of variances were tested by Shapiro-Wilk  
269 test and Levene test, respectively. Correlations between parameters was tested with the relevant tests (Pearson's  
270 correlation test or Spearman's rank correlation test depending on the normality of the data). Statistical differences  
271 between two groups were tested with a t-test and for more than two groups with a one-way Analysis of Variance  
272 (ANOVA) or Kruskal-Wallis rank sum test. For differences in the CO<sub>2</sub> release, a linear mixed model was applied.  
273 More details on the chosen tests and model are given in Supplement, S1.7. We reported the p-value in the text; further  
274 relevant statistical test results and parameters are shown in the corresponding sections in the SI. The variability of the  
275 geochemistry analysis is represented by the standard deviation of triplicates/duplicates. For the in situ experiment, the  
276 variability is reflected in the standard error of triplicates. For duplicate analyses, variability reflects the range of the  
277 two samples.

278 **3 Results**

279 **3.1 Geochemistry at the study site**



280  
 281 **Figure 2. Overview of porewater and sediment biogeochemistry in terms of electron acceptors ( $\text{O}_2$ ,  $\text{Fe(III)}$ ,  $\text{SO}_4^{2-}$ ) and**  
 282 **electron donor (DOC, TOC) from in situ push cores in the pioneer marsh (red triangles) and intertidal flat (blue squares).**  
 283 (a) Oxygen concentration profiles measured in intact cores using microsensors. Note that these cores were collected in 2022, separate  
 284 from the push cores used for analysis shown in (b-e). Two cores were collected from each zone and two to four profiles were taken  
 285 from each core, shortly (within hours) after sampling. (b) Ferrous iron in the porewater, as an indicator of  $\text{Fe(III)}$  reduction. (c)  
 286 Sulfate concentrations in the porewater. (d) Dissolved organic carbon in the porewater. (e) Total organic carbon in the sediment.  
 287 For (b-d), push cores were taken in triplicates in both zones to a depth of 25 cm in 2023. Duplicate push cores for (e) the TOC were  
 288 sampled in 2022. For all sub-figures, markers denote mean  $\pm$  standard deviation (due to limited sample mass, some depth values  
 289 only show mean and the range of two samples, or only a single value). All cores were sampled during low tide.

290 Porewater and solid phase measurements from the push and microsensor cores analysis show availability of  
 291 electron acceptors ( $\text{O}_2$ ,  $\text{Fe(III)}$ , and  $\text{SO}_4^{2-}$ ) over depth in both the pioneer marsh and intertidal flat (Fig. 2). In the pioneer  
 292 marsh,  $\text{O}_2$  decreased from  $131.02 \pm 26.49 \mu\text{mol L}^{-1}$  at the sediment-water interface to  $0.18 \pm 0.12 \mu\text{mol L}^{-1}$  over 2 mm  
 293 and was depleted beyond this depth. We observed a similar trend for the intertidal flat, with  $155.17 \pm 12.71 \mu\text{mol L}^{-1}$   
 294 at the sediment-water interface, and a decrease to  $0.62 \pm 1.10 \mu\text{mol L}^{-1}$  at 2 mm depth before it was fully depleted (Fig.  
 295 2a). Aqueous  $\text{Fe(II)}$  (as an indicator of  $\text{Fe(III)}$  reduction) showed a decreasing trend in both zones, with higher  
 296 concentration in the pioneer marsh of  $267.49 \pm 66.77 \mu\text{M}$  at 5 cm depth and  $31.41 \mu\text{M}$  at 25 cm, and  $19.93 \pm 16.15$   
 297  $\mu\text{M}$  at 5 cm decreasing to  $7.20 \pm 2.89 \mu\text{M}$  at 25 cm in the intertidal flat (Fig. 2b). Sulfate was detected in the porewater  
 298 at all sampled depths (1.5 to 20 cm) in both zones (Fig. 2c). In the pioneer marsh, it ranged in the upper 20 cm from a  
 299 minimum of  $20.12 \pm 1.23$  to a maximum of  $21.34 \pm 0.43$  mM and in the intertidal flat from  $20.35 \pm 1.27$  to  $23.95 \pm$   
 300  $2.44$  mM. We observed a slight decrease in  $\text{SO}_4^{2-}$  concentration over depth which was more pronounced in the intertidal  
 301 flat. This is further supported by the ratio of sulfate:chloride (Fig. S2a). The ratio remained constant in the pioneer  
 302 marsh, while a slight decrease was measured in the intertidal flat. We also measured  $\text{SO}_4^{2-}$  at lower depths (up to 50

303 cm) in cores taken in 2022 and observed similar  $\text{SO}_4^{2-}$  concentrations (Fig. S2b). To complement the porewater Fe(II),  
304 we measured the 0.5 M HCl extractable Fe(III) from the bulk sediment from a depth up to 15-20 cm:  $1.30 \pm 1.08 \mu\text{mol}$   
305 Fe(III)  $\text{g}^{-1}$  dry sediment in the pioneer marsh and  $1.00 \pm 0.51 \mu\text{mol}$  Fe(III)  $\text{g}^{-1}$  dry sediment in the intertidal flat. The  
306 resulting Fe(II) to total iron ratio was  $0.98 \pm 0.02$  and  $0.98 \pm 0.01$  respectively.

307 Organic carbon as the likely electron donor was measured in the porewater as non-purgeable organic carbon  
308 and in the sediment as TOC. The DOC and TOC decreased slightly over depth (Fig. 2d/e) in both zones. In the pioneer  
309 marsh, the DOC was  $12.21 \text{ mg C L}^{-1}$  at the top (1 cm deep) and decreased over depth to  $8.55 \text{ mg C L}^{-1}$  at 25 cm. For  
310 the intertidal flat, the DOC at the top (1 cm deep) was  $10.31 \text{ mg C L}^{-1}$  and decreased to  $6.60 \pm 1.69 \text{ mg C L}^{-1}$  at 25 cm.  
311 The TOC decreased from  $0.7 \pm 0.3 \%$  at the top to  $0.5 \pm 0.1 \%$  at a depth of 25 cm in the pioneer marsh and from  $1.3 \%$   
312 to  $0.7 \pm 0.2 \%$  in the intertidal flat (Fig. 2e). Concentrations at lower depths are shown in Supplement, Fig. S2c, and  
313 are in a similar range. In both the pioneer marsh and intertidal flat, no  $\text{CH}_4$  release, neither as fluxes or in the porewater  
314 up to a depth of 50 cm, was detected (detection limit: 0.28 and 0.53 ppm respectively; Table S3).

315 Particle size analysis indicated that sediment from the pioneer marsh was dominated by fine particles, whereas  
316 the intertidal flat sediment was coarser. In the sediment of the pioneer marsh, we determined  $41.7 \pm 9.1 \%$  sand,  
317  $38.7 \pm 2.5 \%$  silt, and  $19.7 \pm 8.1 \%$  clay. For the sediment of the intertidal flat, a higher sand fraction ( $61.5 \pm 0.5 \%$ ),  
318 less silt ( $29.0 \pm 5.0 \%$ ), and notably lower clay content ( $9.5 \pm 5.5 \%$ ) was measured. For more details on the size  
319 fractions, see Supplement, Table S4.

## 320 **3.2 In situ organic carbon manipulation experiment**

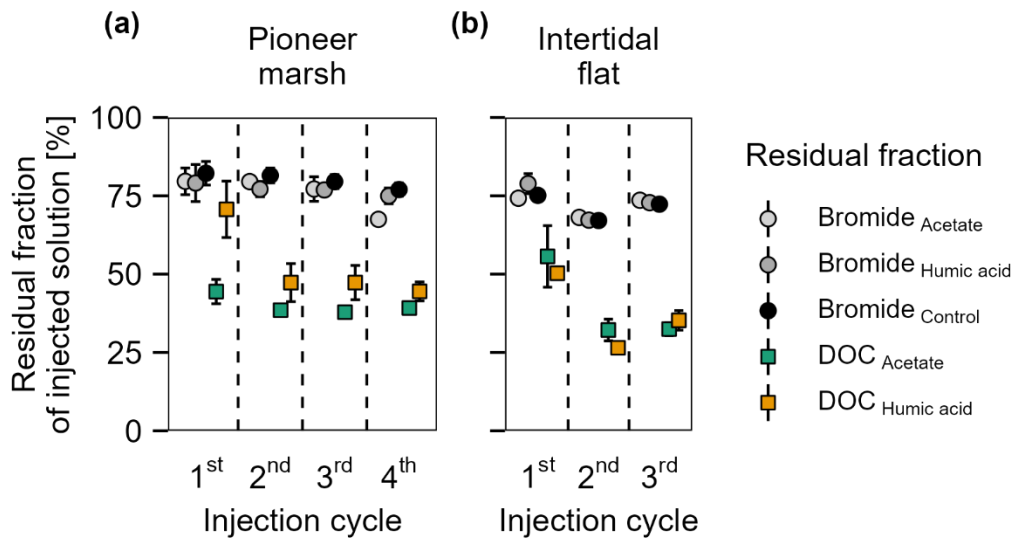
### 321 **3.2.1 Distribution of bromide tracer and dissolved organic carbon in the sediment**

322 Bromide was used in the in situ experiment as an inert tracer to test the washing out of the injection solution  
323 from the experimental plot over the sampling time of one injection cycle (48 h). The native  $\text{Br}^-$  concentration was  
324  $0.66 \pm 0.02 \text{ mM}$  in the pioneer marsh and  $0.63 \pm 0.01 \text{ mM}$  in the intertidal flat. Assuming an equal distribution of the  
325 injected solution in the experimental cylinder, we expected the  $\text{Br}^-$  concentration to increase by  $0.30 \text{ mM}$  to a final  
326 concentration of  $0.99 \text{ mM}$  in the plots of the pioneer marsh and by  $0.32 \text{ mM}$  to a final concentration of  $0.97 \text{ mM}$  for  
327 the plots in the intertidal flat (calculations Supplement, S1.4 – expected  $\text{Br}^-$  concentration). Throughout a test injection  
328 cycle with the same sampling intervals as the experimental injection cycles, the  $\text{Br}^-$  concentration remained above the  
329 background level with a gradual decrease over time in both zones (Figs. S3a/b). Overall, after 48 h (one injection  
330 cycle),  $\text{Br}^-$  levels in the porewater remained elevated in each cycle for both zones. In the pioneer marsh, an average of  
331  $77.5 \pm 5.9 \%$  of the expected level of  $\text{Br}^-$  remained in the porewater of the experimental cylinder. The intertidal flat  
332 had a slightly lower average residual fraction of  $72.1 \pm 4.4 \%$  of the expected  $\text{Br}^-$  level across all injection cycles (Fig.  
333 3). Here, residual fraction is defined as the ratio between the  $\text{Br}^-$  concentration measured in the porewater 48 h post  
334 injection and the expected total  $\text{Br}^-$  concentration in an experimental cylinder (Eq. (1); details in S1.4). The expected  
335 total  $\text{Br}^-$  concentration includes both the native  $\text{Br}^-$  and the added  $\text{Br}^-$  during the experiment (expected  $\text{Br}^-$ ) after  
336 accounting for dilution in the sediment. Details on the calculation of the  $\text{Br}^-$  residual fraction are provided in  
337 Supplement, S1.4.

338

$$\frac{\text{Br}^- \text{ concentration at the end of an injection cycle}}{\text{Br}^- \text{ expected}} = \text{residual fraction} \quad (1)$$

339 The residual fraction of DOC is defined in the same way as for Br<sup>-</sup>, representing the proportion of measured  
 340 DOC after 48 h to the expected DOC (native DOC + added acetate/humic acid) and was calculated analogously to Br<sup>-</sup>  
 341, with DOC concentrations used instead (Eq. (1) and S1.4). Comparing the average residual fraction of DOC and Br<sup>-</sup>  
 342 (Fig. 3) across all injection cycles, the DOC fraction was significantly lower in both the pioneer marsh and intertidal  
 343 flat (Br<sup>-</sup> vs. acetate and Br<sup>-</sup> vs. humic acid) ( $p \leq 0.001$ , Table S5). In the pioneer marsh,  $40.0 \pm 1.2 \%$  of the injected  
 344 DOC in the acetate treatment remained, on average across all injection cycles, while the corresponding value for the  
 345 humic acid treatment was  $52.9 \pm 4.5 \%$ . In the intertidal flat, relatively less carbon remained, with a smaller difference  
 346 between the carbon sources. Here, the mean residual fraction was  $38.2 \pm 4.8 \%$  for the acetate treatment and  $37.3 \pm 3.6$   
 347 % for the humic acid treatment.

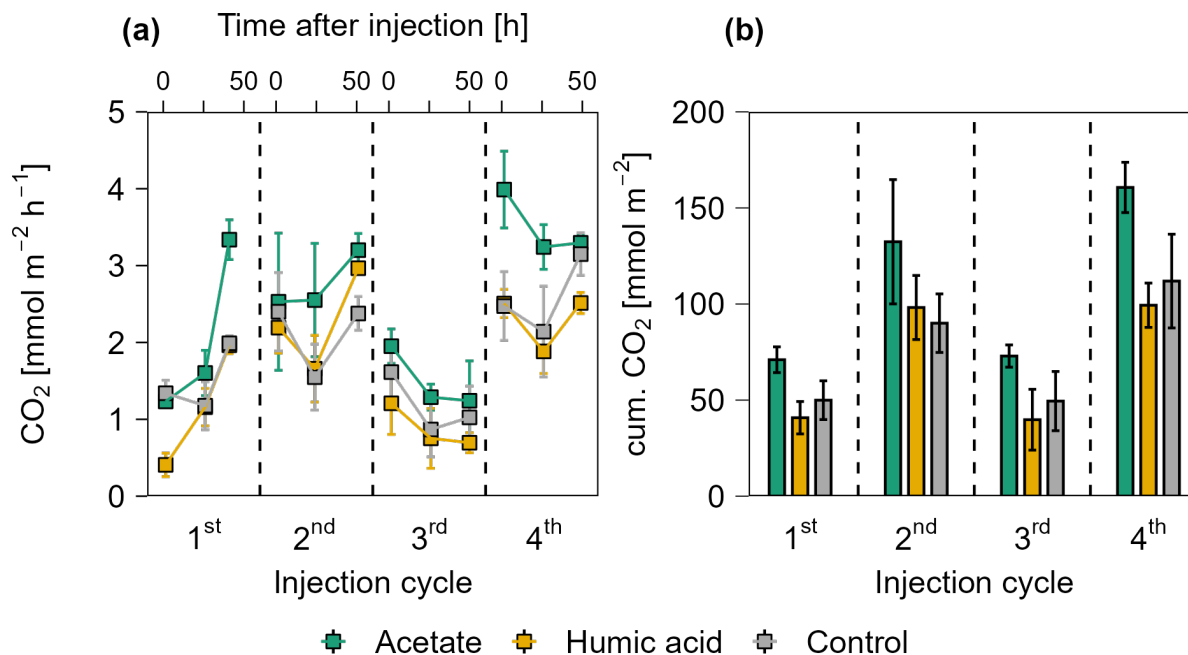


348

349 **Figure 3. Residual fraction of injected solutions ( $\text{Br}^-$  and DOC) in percentage after 48 h for treatments (acetate, humic acid)**  
350 **and control plots in the (a) pioneer zone (over four injection cycles) and (b) intertidal flat (over three injection cycles).**  
351 Coloured squares show the residual fraction of injected DOC (acetate in green and humic acid in orange). The grey shaded circles  
352 represent the residual of  $\text{Br}^-$  from the different treatments and the control. The values were calculated based on the ratio between  
353 the measured DOC or  $\text{Br}^-$  concentration (porewater concentration 48 h post injection) and the expected DOC or  $\text{Br}^-$  concentration  
354 (native + added). Markers represent the mean of the triplicates, with error bars indicating the corresponding standard error for  
355 treatments and control in both zones for DOC and  $\text{Br}^-$  across all injection cycles.

356 **3.2.2 Effect of organic carbon input in the pioneer marsh**

357 **Carbon dioxide release**



358  
 359 **Figure 4. CO<sub>2</sub> release over four OC injection cycles for the acetate, humic acid, and control plots in the pioneer marsh.** The  
 360 dashed lines separate the individual injection cycles. (a) presents individual measured CO<sub>2</sub> fluxes 1.5, 24, and 48 h  
 361 after injection in CO<sub>2</sub> mmol m<sup>-2</sup> h<sup>-1</sup>. Acetate (green), humic acid (orange), and NaCl for the control (grey) were injected into the sediment and  
 362 GHG fluxes were measured directly above the injection spot at the aforementioned time intervals. (b) shows the cumulative CO<sub>2</sub>  
 363 emissions in CO<sub>2</sub> mmol m<sup>-2</sup> over one injection cycle for each treatment and control. We note here that some variability in the fluxes  
 364 based on factors such as day/night could not be captured in our sampling approach; we therefore aimed to use a consistent approach  
 365 and report relative changes rather than emphasize absolute values. For (a/b), markers represent mean ± standard error of triplicates  
 366 for all treatments and the control across injection cycles. For the 1<sup>st</sup> and 3<sup>rd</sup> injection cycle for the acetate treatment (both 1.5 h  
 367 values) were based on duplicate measurements, which is thus also the case for the (b) cumulative CO<sub>2</sub> emission of these cycles.

368  
 369 Figure 4 presents the CO<sub>2</sub> release for each injection cycle with the individual CO<sub>2</sub> fluxes 1.5, 24, and 48 h  
 370 post injection (Fig. 4a) and the cumulative CO<sub>2</sub> emissions (Fig. 4b) in the pioneer marsh. For all four injection cycles,  
 371 the CO<sub>2</sub> fluxes of the acetate treated plots exceeded the CO<sub>2</sub> fluxes of the humic acid and control plots (Fig. 4a). For  
 372 the first injection cycle, the acetate treatment was significantly higher compared to the humic acid treatment ( $p < 0.05$ ,  
 373 Table S6) and slightly above the threshold for statistical significance ( $p = 0.08$ , Table S6) compared to the control. In  
 374 the following injection cycle, the CO<sub>2</sub> fluxes of the acetate treatment were also higher compared to the humic acid and  
 375 control plots but not significantly ( $p > 0.05$ ). Hence, the acetate treated plot consistently exhibited the highest fluxes.  
 376 The difference between the humic acid and control plots was statistically negligible ( $p > 0.05$ ). Similarly, the  
 cumulative CO<sub>2</sub> emissions from the acetate treated plots were the highest while the emissions from the humic acid and

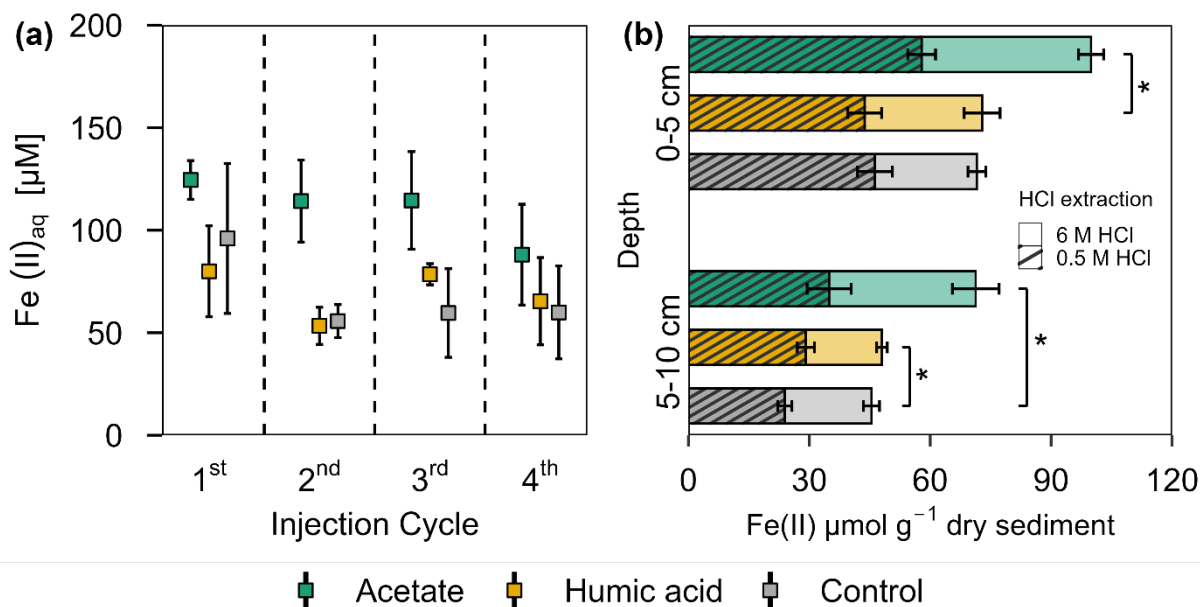
377 control plots were in a similar range for all four injection cycles (Fig. 4b). The CO<sub>2</sub> emitted from the acetate treated  
378 plots was up to  $83.2 \pm 53.7$  % higher than for the humic acid treated plots. Similarly, the emissions of the acetate plots  
379 were up to  $47.4 \pm 36.4$  % higher relative to the control plots. No statistical differences were measured between the  
380 cumulative CO<sub>2</sub> emission of the acetate treated plots and the control or humic acid treatment. Overall, these differences  
381 were smaller than those seen at individual CO<sub>2</sub> fluxes at specific time points (Fig. 4a), likely due to high variability in  
382 fluxes that resulted in variable cumulative CO<sub>2</sub> emissions. In all treatments and the control, no CH<sub>4</sub> as a flux was  
383 detected (lower than detection limit (0.28 ppm); Table S3).

384 The CO<sub>2</sub> fluxes showed a positive correlation with air temperature and a moderate positive correlation with  
385 the tidal cycle in the pioneer marsh (Table S7). Specifically, CO<sub>2</sub> fluxes were found to be higher as the spring tide  
386 receded. Lower CO<sub>2</sub> fluxes were measured during the first and third injection cycles, which occurred close to spring  
387 tides.

388 Further differences between the treatments and control were observed in the DOC concentrations (Fig. S4)  
389 and the residual fraction of DOC (Fig. 3a) in the pioneer marsh. Over all four injection cycles, the average DOC  
390 concentration in the acetate treated plots did not significantly differ from the control ( $p > 0.05$ ), while the DOC  
391 concentrations of the humic acid treated plots were significantly higher than the concentrations of acetate treated plots  
392 and the control plots ( $p < 0.05$ , Table S8). These differences are consistent with the residual fraction of DOC (Fig. 3a).  
393 Across all four injection cycles, the average residual fraction in the humic acid treatment was significantly higher  
394 compared to the acetate treatment but significantly lower than the Br<sup>-</sup> residual fraction ( $p < 0.002$ ,  $p < 0.001$   
395 respectively, Table S5). No difference in the TOC content was found between treatments and control in both depths.  
396 The content ranged from  $0.9 \pm 0.1$  % to  $1.2 \pm 0.1$  % in the upper 5 cm, with a slight decrease at lower depth (Table S9).

397 In addition to the gas fluxes, we also measured DIC and pH of the porewater for each treatment and control  
398 for each injection cycle (Fig. S5). As the differences in the CO<sub>2</sub> fluxes were more pronounced and our focus was on  
399 GHG release, we only present and later discuss these data.

400 **Effect of organic carbon input on the geochemistry of porewater and sediment**



401  
 402 **Figure 5. Ferrous iron in (a) porewater and (b) solid phase from acetate and humic acid treated plots and the control plots**  
 403 **in the pioneer marsh.** (a) Aqueous ferrous iron (Fe(II)<sub>aq</sub>) [µM] sampled after each injection cycle (cycles are separated by the  
 404 dashed line). Triplicates for each treatment and control for each injection cycle were collected and mean ± standard error is shown.  
 405 (b) HCl extractable Fe(II) content [µmol g<sup>-1</sup> dry sediment] at two different depths (0-5 and 5-10 cm) sampled at the end of all four  
 406 injection cycles. Different colour coding was used for contrasting treatments: acetate treatment (green), humic acid treatment  
 407 (orange), and control (grey). Striped bars represent poorly crystalline Fe(II) (0.5 M HCl extraction) and solid bars higher crystalline  
 408 Fe(II) (6 M HCl extraction). The 0.5 M HCl extract was subtracted from the 6 M HCl extracted fraction to separate poorly and  
 409 higher crystalline Fe(II). Significance is denoted for the 0.5 M HCl extraction. Statistical details are given in the SI (Table S11),  
 410 significance level  $p < 0.05$  \*. For each treatment and control, each spatial triplicate ( $n = 3$ ) was analyzed in triplicate (total  $n = 9$ )  
 411 for each depth (0-5 and 5-10 cm); results are presented as mean ± standard error.

412 In the pioneer marsh, acetate treated plots had significantly higher aqueous Fe(II) concentrations compared  
 413 to humic acid and control plots when considering the average concentration across all injection cycles (acetate vs.  
 414 humic acid  $p = 0.007$  and vs. control  $p = 0.002$ , Table S10). Although the differences were not always statistically  
 415 significant for the individual cycles, the Fe(II) concentration in the porewater of the acetate treated plots was  
 416 consistently higher (Fig. 5a): 1<sup>st</sup> cycle  $124.52 \pm 9.44$  µM, 2<sup>nd</sup> cycle  $114.20 \pm 19.98$  µM, 3<sup>rd</sup> cycle  $114.54 \pm 23.80$  µM,  
 417 and 4<sup>th</sup> cycle  $88.08 \pm 24.58$  µM. Humic acid treated plots and the control plots showed similar aqueous Fe(II)  
 418 concentrations. For humic acid treated plots the aqueous Fe(II) concentration ranged between  $53.36 \pm 9.05$  µM  
 419 (2<sup>nd</sup> cycle) and  $79.96 \pm 22.16$  µM (1<sup>st</sup> cycle), and for the control between  $55.69 \pm 8.04$  (2<sup>nd</sup> cycle) and  $96.01 \pm 36.61$   
 420 µM (1<sup>st</sup> cycle) (Fig. 5a).

421 A similar trend can be seen in the solid phase for the HCl extractable Fe(II), for both extractions approaches  
 422 (0.5 M and 6 M HCl) (Fig. 5b). Comparing the poorly crystalline Fe(II) fraction, the acetate treatment had the highest

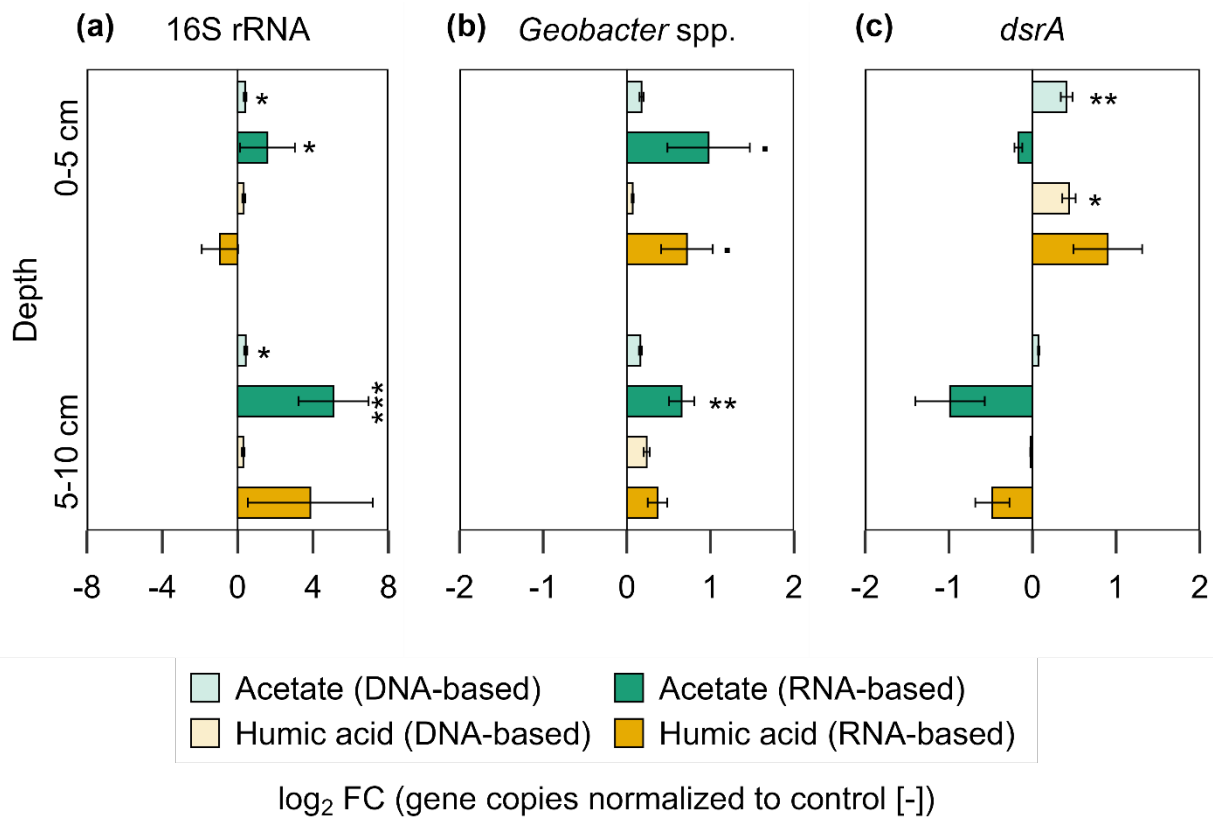
423 Fe(II) content compared to the humic acid treatment and the control at both depths. Acetate treated plots showed an  
424 Fe(II) content of  $57.87 \pm 3.44 \mu\text{mol g}^{-1}$  sediment in the upper 5 cm and  $34.91 \pm 5.45 \mu\text{mol g}^{-1}$  sediment from 5-10 cm.  
425 Humic acid and control plots had similar levels of Fe(II): for the humic acid plots, the content in the upper 5 cm was  
426  $43.74 \pm 4.18 \mu\text{mol g}^{-1}$  sediment and from 5-10 cm, it was  $29.13 \pm 2.12 \mu\text{mol g}^{-1}$  sediment. The control plots showed  
427  $46.28 \pm 4.32 \mu\text{mol g}^{-1}$  sediment in the upper 5 cm and  $23.93 \pm 1.75 \mu\text{mol g}^{-1}$  sediment between 5 to 10 cm. We observed  
428 the same trend for the higher crystalline Fe(II) content. The acetate treatment had the highest contents with  $42.04 \pm 3.12$   
429  $\mu\text{mol g}^{-1}$  sediment (0-5 cm) and  $36.38 \pm 5.79 \mu\text{mol g}^{-1}$  sediment compared with humic acid or control plots. For both  
430 depth and crystallinities, the acetate treatment showed significantly the highest content, in nearly all comparisons to  
431 the humic acid or control plots (Table S11). Except for poorly crystalline Fe(II) at 5-10 cm depth, humic acid and  
432 control plots did not differ significantly (Table S11).

433 No consistent difference was detected in  $S(\text{II})_{\text{tot}}$  in the porewater of the pioneer marsh (Fig. S6a). The  $S(\text{II})_{\text{tot}}$   
434 concentrations were in the same range: acetate from  $3.16 \pm 0.01 \mu\text{M}$  (4<sup>th</sup> cycle) to  $5.59 \pm 1.21 \mu\text{M}$  (1<sup>st</sup> cycle), humic  
435 acid from  $3.0 \pm 0.11 \mu\text{M}$  (4<sup>th</sup> cycle) to  $6.34 \pm 1.56 \mu\text{M}$  (1<sup>st</sup> cycle) and control from  $3.63 \pm 0.34 \mu\text{M}$  (1<sup>st</sup> cycle) to  
436  $4.39 \pm 1.13 \mu\text{M}$  (4<sup>th</sup> cycle). Also, statistical analysis did not reveal a difference between the different treatments and  
437 control  $S(\text{II})_{\text{tot}}$  averaged over all cycles ( $p > 0.05$ ). Similarly, AVS measurements of the solid sulfide species showed  
438 no difference between treatments and the control (Fig. S6b). In the upper 5 cm, contents were similar (acetate:  
439  $6.13 \pm 1.40$ , humic acid  $3.89 \pm 1.19$ , and control  $7.37 \pm 1.76 \mu\text{mol g}^{-1}$  sediment). Similar contents were measured at  
440 5-10 cm depth, with no coherent trend between the layers.

#### 441 **Effect of organic carbon input on microbial growth and metabolic activity**

442 The impact of the added OC on the bacterial community was analysed by qPCR. The analyses were based on  
443 DNA (microbial abundance) and RNA (metabolically active microorganisms). The results show the gene copies of  
444 both treatments normalized to the control as  $\log_2$  fold change ( $\log_2$  FC) (Fig. 6). Statistics are based on the absolute  
445 gene copy numbers (Fig. S7). For the acetate treated plots a significantly higher bacterial 16S rRNA gene copy number  
446 (DNA- and RNA-based) was measured compared to the control plots across all analysed depths (Fig. 6a;  $p < 0.05$ ). In  
447 comparison to the control, DNA-based bacterial 16S rRNA gene copies increased by a factor of  $0.4 \pm 0.07$  ( $\log_2$  FC)  
448 under acetate treatment and their potential activity, indicated by RNA, increased by  $1.58 \pm 1.46 \log_2$  FC in the upper 5  
449 cm. This remained similar at the depth of 5-10 cm, with an increase in DNA-based 16S rRNA gene copies by  $0.43 \pm$   
450  $0.09 \log_2$  FC and an increase in activity (RNA) by  $5.09 \pm 1.86 \log_2$  FC. For the comparison between plots amended  
451 with humic acid and the control, variations were observed but no significant differences were measured ( $p > 0.05$ ).  
452 Microbial activity (RNA) of *Geobacter* spp., were higher in the acetate and humic acid treatment compared to the  
453 control in the upper 5 cm, however, slightly over the significance criterion (Fig. 6b;  $p = 0.051$ ,  $p = 0.057$ , respectively).  
454 For the acetate treated plots, the activity (RNA-based) of *Geobacter* spp. was higher compared to the control by a  
455 factor of  $0.98 \pm 0.49$ . The humic acid treatment also had upregulated activity by a factor of  $0.72 \pm 0.31$ . The higher  
456 microbial activity of *Geobacter* spp. remained significantly enhanced ( $p = 0.008$ ) for the acetate treatment compared  
457 to the control at the lower depth (RNA-based:  $\log_2$  FC:  $0.66 \pm 0.15$ ), too. The addition of OC did not affect the microbial  
458 activity (RNA) of *dsrA* genes at both depths (Fig. 6c) in the pioneer marsh. However, the abundance (DNA) of *dsrA*

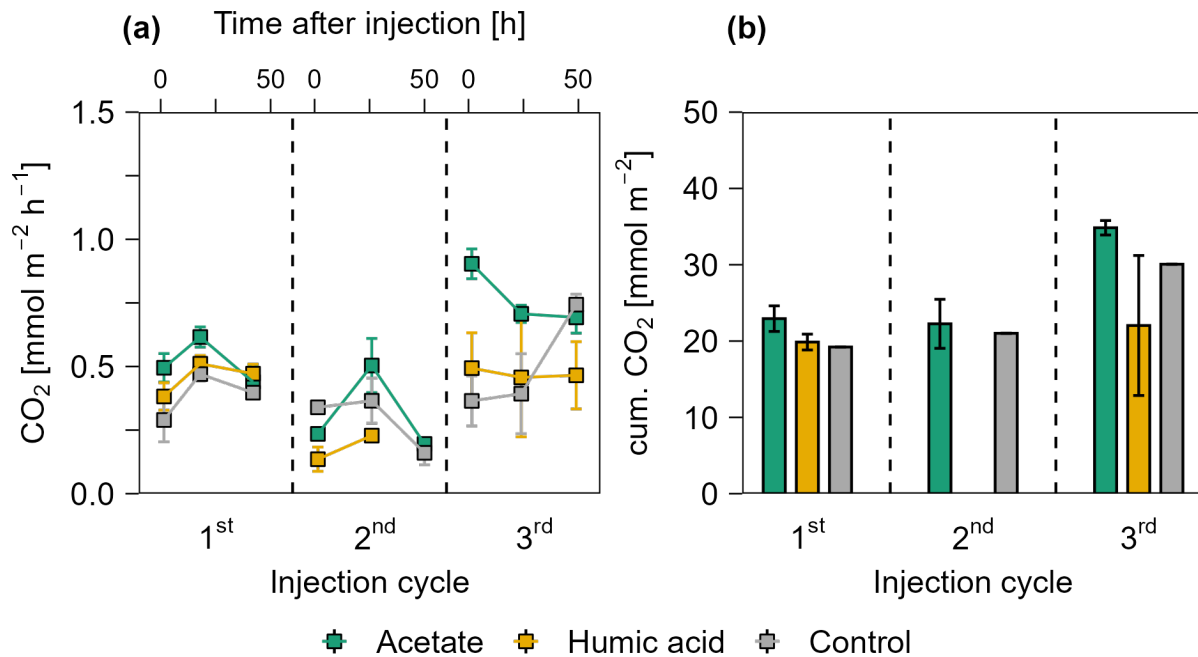
459 genes in the upper layer was significantly higher for both treatments (acetate  $p = 0.006$ , humic acid  $p = 0.015$ ). Absolute  
 460 gene copy numbers are given in Supplement, Fig. S7 and statistical details in Table S12.



461  
 462 **Figure 6. Bacterial gene copy numbers of (a) 16S rRNA (16S), (b) *Geobacter* spp., and (c) *dsrA* for acetate and humic acid**  
 463 **treatment normalized to the control in the pioneer marsh.** The values are represented as log<sub>2</sub> fold change (FC). Values > 0  
 464 indicate an upregulation while values < 0 indicate downregulation of the genes compared to the control (acetate in green, humic  
 465 acid in orange). DNA-based numbers are given in lighter colours and RNA-based in darker colours. Statistical differences in the  
 466 absolute gene copy numbers are indicated as stars in the figure: significant codes are  $p = 0.05$ .,  $p \leq 0.05$  \*,  $p \leq 0.01$  \*\*, and  
 467  $p \leq 0.001$  \*\*\*. Absolute gene copy numbers given in Supplement, Fig. S7. Sample sizes include triplicates of each treatment and  
 468 control at both depths, represented as mean  $\pm$  standard error (exception of duplicate measurements for 16s RNA-based humic  
 469 substances (5-10 cm) and 16s RNA-based control (0-5 cm)).

470 **3.2.3 Effect of organic carbon input in the intertidal flat**

471 **Carbon dioxide release**



472  
 473 **Figure 7. CO<sub>2</sub> release over three injection cycles for the acetate and humic acid treated plots and the control plots in the**  
 474 **intertidal flat.** (a) CO<sub>2</sub> fluxes after 1.5, 24, and 48 h after injection in CO<sub>2</sub> mmol m<sup>-2</sup> h<sup>-1</sup> over three injection cycles. The dashed  
 475 lines separate the individual injection cycles. In the 2<sup>nd</sup> injection cycle, fluxes in the humic acid treatment are only displayed at 1.5  
 476 and 24 h post injection due to missing data. Acetate (green), humic acid (orange), and NaCl for the control (grey) were injected into  
 477 the sediment and GHG fluxes were measured directly above the injection spot at the aforementioned time intervals. (b) presents the  
 478 cumulative CO<sub>2</sub> release in mmol CO<sub>2</sub> m<sup>-2</sup> over one injection cycle for each treatment and control. Due to missing values for humic  
 479 acid amended plots in the second injection cycle, cumulative emissions could not be calculated. For the same reason, standard errors  
 480 of the control plots are also not available. For (a/b), markers represent the mean ± standard error of triplicates for all treatments and  
 481 the control across injection cycles, except where missing values for CO<sub>2</sub> release occurred due to nonlinear CO<sub>2</sub> release during the  
 482 gas sampling incubation time. (a) duplicate measurements are reflected for the 1<sup>st</sup> injection cycle for the control (1.5 and 24 h), for  
 483 the 2<sup>nd</sup> injection cycle for the acetate treatment and control (48 h), and the 3<sup>rd</sup> injection cycle for the acetate treatment and control  
 484 (1.5, 24, and 48 h). Single measurement values are shown for the control in the 1<sup>st</sup> (48 h) and 2<sup>nd</sup> (1.5 h) injection cycle. For (b),  
 485 cumulative CO<sub>2</sub> emissions, the acetate treatment shows duplicate measurements for the 2<sup>nd</sup> and 3<sup>rd</sup> injection and for the control,  
 486 only single values are reflected.

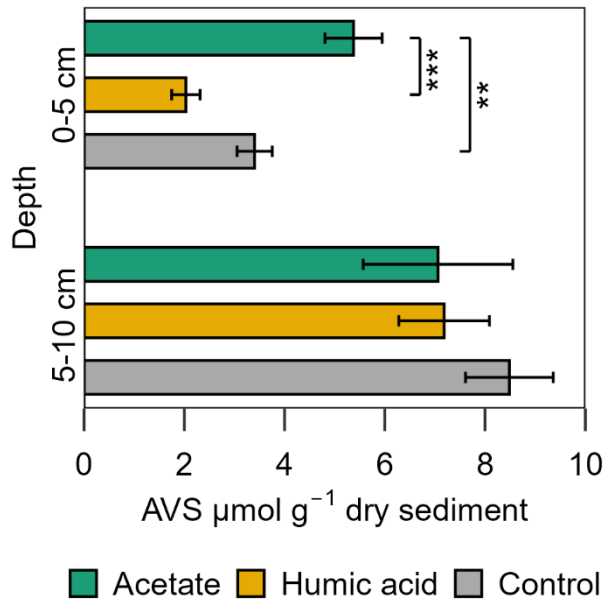
487 Figure 7a presents the CO<sub>2</sub> release from the intertidal flat over three injection cycles 1.5, 24, and 48 h post  
 488 injection. Acetate treated plots released the highest CO<sub>2</sub> in all three injection cycles compared to the humic acid and  
 489 the control plots. Similar to the pioneer marsh, no strong differences were observed between humic acid treated plots  
 490 and the control plots. Consistently, the maximum cumulative CO<sub>2</sub> emissions were observed in the acetate treated plots  
 491 (Fig. 7b). Due to nonlinearity of CO<sub>2</sub> release over the incubation time of gas sampling, some data points are missing;

492 therefore, statistical comparison of CO<sub>2</sub> release between treatments and the control was not done. Nevertheless, plots  
 493 amended with acetate consistently showed higher CO<sub>2</sub> releases across all injection cycles. Methane was not detected  
 494 in the fluxes of any treatment in the intertidal flat plots (lower than detection limit (0.28 ppm); Table S3). Similar to  
 495 the pioneer marsh, we focus here on CO<sub>2</sub> data although DIC and pH were measured (Fig. S8).

496 No difference in the DOC concentrations between the treatments and the control were measured (Fig. S9).  
 497 Similarly, no difference was measured between the residual fraction (recovery of injected DOC) between acetate and  
 498 humic acid treatments (Fig. 3b). The TOC content among the treatments and the control was also in the same range  
 499 (0.4-0.5 %) (Table S9).

### 500 Effect of organic carbon input on the geochemistry of porewater and sediment

501 In the intertidal flat, aqueous Fe(II) concentrations ranged from  $9.25 \pm 0.21$  to  $24.82 \pm 4.50$   $\mu\text{M}$  in both  
 502 treatments and the control, with no significant differences ( $p > 0.05$ ) (Fig. S10a). Additionally, no difference between  
 503 the treatments and the control was detected in the solid phase for both crystallinities (0.5 and 6 M HCl extraction) and  
 504 depths. In the upper 5 cm, the content of the poorly crystalline Fe(II) ranged from  $18.28 \pm 1.28$  to  $19.60 \pm 0.88$   $\mu\text{mol g}^{-1}$   
 505 sediment among all treatments and control, while in the deeper layer, the range was from  $18.11 \pm 0.71$  to  $24.59 \pm 1.22$   
 506  $\mu\text{mol g}^{-1}$  sediment. The content of the higher crystalline Fe(II) ranged from  $11.68 \pm 0.99$  to  $20.06 \pm 3.64$   $\mu\text{mol g}^{-1}$   
 507 sediment in the upper 5 cm and from  $12.98 \pm 1.03$  to  $17.50 \pm 2.75$   $\mu\text{mol g}^{-1}$  sediment at a depth of 5-10 cm (Fig. S10b).



508  
 509 **Figure 8. Acid volatile sulfide (AVS) in the solid phase sampled at the end of the experiment for the acetate and humic acid**  
 510 **treated plots and the control plots in the intertidal flat.** AVS [ $\mu\text{mol g}^{-1}$  dry sediment] content of the solid phase from the different  
 511 treatments (acetate in green, humic acid in orange) and control (grey). Significance is denoted for the upper sediment layer (0-5  
 512 cm), deeper layer no statistically significant difference occurred. Statistical details are given in the SI (Table S13), significance level

513  $p < 0.05$  \*,  $p < 0.01$  \*\*, and  $p < 0.001$  \*\*\*. Each spatial triplicate (n=3) was analyzed in triplicates (total n = 9) for each treatment  
514 and the control at both depths; results are presented as mean  $\pm$  standard error.

515 For porewater  $S(II)_{tot}$ , no large differences were measured between the treatments and control in the intertidal  
516 flat. The concentrations of both treatments and the control were in a similar range over all injection cycles,  $0.62 \pm 0.01$   
517 to  $1.73 \pm 0.67 \mu\text{M } S(II)_{tot}$  (Fig. S11). In contrast, the AVS in the solid phase exhibited a significant difference between  
518 the treatments and the control (Fig. 8). Higher AVS contents were measured in the acetate plots. This difference was  
519 strongly pronounced in the upper 5 cm in the acetate plots relative to the setups amended with humic acid and the  
520 control ( $p < 0.001$  and  $p = 0.007$ , respectively, Table S13). AVS content in the upper 5 cm was  $5.38 \pm 0.57 \mu\text{mol g}^{-1}$   
521 sediment from the acetate plots,  $2.03 \pm 0.28 \mu\text{mol g}^{-1}$  sediment from the humic acid plots, and  $3.40 \pm 0.35 \mu\text{mol g}^{-1}$   
522 sediment from the control. In the deeper layer (5-10 cm), the differences between treatments and control were  
523 statistically negligible ( $p > 0.05$ ).

#### 524 **Effect of organic carbon input on microbial growth and metabolic activity**

525 In the intertidal flat, an increase in DNA- and RNA-based gene copy numbers of the bacterial 16S rRNA gene  
526 was detected in the acetate treatment compared to the control at both depths (0-5 and 5-10 cm) (Fig. S12a). This  
527 increase was significant for DNA and RNA in the upper layer and remained significant for RNA in the lower layer ( $p$   
528 = 0.008,  $p = 0.01$ , and  $p = 0.008$ , respectively). The acetate treatment showed a  $3.62 \pm 2.41 \log_2$  FC increase in the  
529 metabolic activity (RNA) of the total microbial community compared to the control in the upper layer and an increase  
530 of  $2.73 \pm 1.41 \log_2$  FC from 5-10 cm. For *Geobacter* spp. (Fig. S12b) the RNA-based gene copies were significantly  
531 higher compared to the control ( $p < 0.001$ ) by a factor of  $0.6 \pm 0.10$  in the upper 5 cm. No significant increase in the  
532 RNA-based copy numbers of *dsrA* genes in both depths (Fig. S12c) were observed; however, we detected slightly  
533 higher RNA-based *dsrA* gene copies in the acetate treatments ( $0.33 \pm 0.06 \log_2$  FC) compared to the control in the  
534 upper layer. Absolute gene copy numbers are presented in Fig. S13 and statistical details in Table S14.

## 535 4 Discussion

### 536 4.1 Geochemistry at the study site

537 Porewater and solid phase measurements from the push cores showed availability of electron acceptors ( $O_2$ ,  
538  $Fe(III)$ , and  $SO_4^{2-}$ ) at different depths in both the pioneer marsh and intertidal flat. Based on microsensor measurements  
539 during low tide, we observed  $O_2$  concentrations in the top 2 mm decreasing with depth, from  $131.02 \pm 26.49$  to  $0.18 \pm$   
540  $0.12 \mu\text{mol L}^{-1}$  in the pioneer marsh, and in the intertidal flat from  $155.17 \pm 12.71$  to  $0.62 \pm 1.10 \mu\text{mol L}^{-1}$ , reaching 0  
541  $\mu\text{M}$  below that depth. This finding directly affects which biogeochemical processes occur below this depth. Other  
542 studies conducted in comparable ecosystems have indicated that during high tide and/or daytime,  $O_2$  penetrates deeper  
543 into the sediment (de Beer et al., 2005; Bosselmann et al., 2003), but reducing conditions may prevail underneath and  
544 that the depth of  $O_2$  penetration might be influenced by sediment grain size. Both zones in our study showed a high  
545 proportion of fine particles (silt:  $29.0 \pm 5.0$  to  $38.7 \pm 2.5$  % and clay:  $9.5 \pm 5.5$  to  $19.7 \pm 8.1$  %). Such a size distribution  
546 retains more water (Novák and Hlaváčiková, 2019), resulting in water-filled pore spaces even during low tide, which  
547 limits gas exchange. We suggest that the lack of  $O_2$  penetration beyond 2 mm at our study site results from the presence  
548 of fine particles. Despite differences in the duration and magnitude of inundation between the zones, the depth of  $O_2$   
549 penetration remained similar, indicating that these factors do not influence  $O_2$  penetration depth and that reducing  
550 conditions prevail beyond the upper millimetres during both tidal conditions. We do not exclude that the presence of  
551 sparse vegetation in the pioneer marsh compared to no vegetation in the intertidal flat may cause differences in the  
552 intrusion of  $O_2$  into the sediment (Koop-Jakobsen et al., 2017; Maricle and Lee, 2002). However, we did not detect  
553 this difference in our  $O_2$  measurements. In addition to plants, benthic organisms such as worms may introduce  $O_2$  into  
554 the sediment and influence the biogeochemical cycling in the sediment (Huettel et al., 2014). As worms were present  
555 in both zones, it is likely that they play a role in  $O_2$  penetration and re-oxidizing of reduced  $Fe(II)$  or sulfide species  
556 (Figs. S14a-d). We expect that this effect is not substantially different for the two zones, as no large qualitative  
557 difference in the presence of worms was observed visually.

558 Below the oxic zone, alternative electron acceptors were present. We used  $Fe(II)$  porewater data as an  
559 indicator of  $Fe(III)$  reduction. A decrease in the aqueous  $Fe(II)$  from  $267.49 \pm 66.77$  to  $31.41 \mu\text{M}$   $Fe(II)$  in the pioneer  
560 marsh and from  $19.93 \pm 16.15$  to  $7.20 \pm 2.89 \mu\text{M}$   $Fe(II)$  in the intertidal flat was measured over 25 cm. Based on the  
561 presence of aqueous  $Fe(II)$ , we assumed that  $Fe(III)$  reduction is likely occurring in both zones, which is less  
562 pronounced in the intertidal flat. The observed decreasing trend over depth has been commonly seen in other studies  
563 of coastal sediment (Moeslund et al., 1994; Lowe et al., 2000). It suggests a depletion of bioavailable  $Fe(III)$  with depth  
564 and/or removal of aqueous  $Fe(II)$ . Aqueous  $Fe(II)$  can precipitate with sulfide, which forms through  $SO_4^{2-}$  reduction  
565 deeper in the sediment when more thermodynamically favourable electron acceptors are exhausted (Jørgensen et al.,  
566 2019). The  $Fe(II)$  porewater concentrations are in the range of other studies from salt marshes, especially for the pioneer  
567 marsh (0-800  $\mu\text{M}$ ) (Kostka et al., 2002b; Seyfferth et al., 2020). Concentrations of the intertidal flat are on the lower  
568 end of the studies mentioned above. Ferrous iron was the predominant iron species in the solid fraction extracted by  
569 0.5 M HCl in both zones. Manganese(IV) as an electron acceptor was not further considered as the total manganese  
570 concentration from the study site is  $5 \mu\text{mol g}^{-1}$  sediment (Kubeneck et al., 2025), and thus relatively low in comparison  
571 to the total iron concentration.

572 Sulfate has a major role in the oxidation of OC as an important electron acceptor in coastal wetlands due to  
573 its frequent supply via the incoming seawater. We observed a slight decrease in  $\text{SO}_4^{2-}$  over a depth of 20 cm which  
574 was more distinct in the intertidal flat, as seen in the sulfate to chloride ratio (Fig. S2a). This suggests some  $\text{SO}_4^{2-}$   
575 reduction in the upper 20 cm. A similar pattern was observed at a comparable site where Fe(II) predominates over total  
576 iron and porewater  $\text{SO}_4^{2-}$  concentration decreases with depth, albeit with slightly higher  $\text{SO}_4^{2-}$  concentrations (Kostka  
577 et al., 2002b). The relatively high levels of  $\text{SO}_4^{2-}$  at all tested depths (>50 cm), supported the absence of detectable  
578  $\text{CH}_4$  dissolved in the porewater or as an efflux. This is consistent with past studies such as Martens and Berner (1974)  
579 who stated that if more than ~10 % of seawater  $\text{SO}_4^{2-}$  is still present,  $\text{CH}_4$  is not produced, as a thermodynamically  
580 more favourable electron acceptor is available (Schlesinger and Bernhardt, 2013b). We examined different possible  
581 explanations for the lack of detected  $\text{CH}_4$  as we could not entirely exclude that  $\text{CH}_4$  was produced further down in the  
582 sediment and oxidized via anaerobic methane oxidation (AOM), as observed in some coastal wetlands (Capooci et al.,  
583 2024; La et al., 2022; Wang et al., 2019), or by lateral transport to surrounding tidal channels (Trifunovic et al., 2020).  
584 We did not measure any  $\text{CH}_4$  as a efflux or in the porewater over multiple field campaigns, similar to a study conducted  
585 at the same study site by Kubeneck et al. (2025). We considered the sensitivity of detection: the detection limit for  
586 porewater  $\text{CH}_4$  was 0.53 ppm (Table S3) which corresponds to 1.13  $\mu\text{mol/L}$  based on our sampling method. We would  
587 expect that methane, if produced within the depths examined here, would be above this concentration as porewater  
588 concentrations of  $\text{CH}_4$  in wetlands slightly inland within the Elbe estuary were much higher (0.16 to 2.46 mmol/L,  
589 Kubeneck et al., 2025). It is possible that trace amounts of  $\text{CH}_4$  (ppb) were present below the detection limit. The few  
590 other studies that have detected  $\text{CH}_4$  in the Wadden Sea were at depths where  $\text{SO}_4^{2-}$  was largely depleted (Røy et al.,  
591 2008; Wu et al., 2015), which is not the case in our study. Furthermore, the absence of an observed decrease in  $\text{SO}_4^{2-}$   
592 concentration, particularly in the pioneer marsh, suggest a lack of AOM until 50 cm, as  $\text{CH}_4$  and  $\text{SO}_4^{2-}$  are consumed  
593 in a 1:1 stoichiometric ratio during sulfate AOM. Thus, our results indicate that  $\text{CH}_4$  production and consumption are  
594 unlikely until 50 cm. Below these depths, these processes may be occurring. Further analysis of the microbial  
595 community and/or  $\text{CH}_4$  injection experiments would help to determine if methanogenesis and AOM occur at lower  
596 depths. Based on the high concentrations of  $\text{SO}_4^{2-}$  with relatively low changes with depth as well as the lack of  
597 detectable  $\text{CH}_4$ , we suggest that electron acceptors may not be limiting the microbial turnover of OC and release of  
598  $\text{CO}_2$  in our study. To our knowledge, this is rarely reported for coastal wetlands and not commonly expected for  
599 terrestrial ecosystems. Here, we caution that further measurements of rates of electron acceptor turnover and/or  
600 incubation experiments are needed to unambiguously exclude an electron acceptor limitation.

601 We also considered the OC sources in the system: porewater DOC and solid phase TOC. The TOC content  
602 was ~1 % and decreased with depth in both zones. A decreasing trend over depth was also seen in the DOC  
603 concentrations. The decrease of OC with depth indicates decomposition and has been commonly observed in other  
604 studies (Hansen et al., 2017; Mueller et al., 2019). The range in TOC and DOC concentrations are at the lower end of  
605 comparable ecosystems with the main differences in the upper centimetres (Gribsholt and Kristensen, 2003; Hansen et  
606 al., 2017; Mueller et al., 2023).

## 607 **4.2 In situ organic carbon manipulation experiment**

#### 608 4.2.1 Validation of the experimental setup

609 Bromide, as an inert tracer, was injected along with the OC/control solution into each experimental cylinder  
610 for each injection cycle. This allowed us to follow the distribution and retention time of the injected solution over one  
611 injection cycle. The Br<sup>-</sup> concentration over each injection cycle was higher than the background Br<sup>-</sup> concentration (Fig.  
612 3/S3a/b), indicating that the injected solution was partially retained within the experimental cylinder over one injection  
613 cycle. The observed decrease in Br<sup>-</sup> concentration over one injection cycle, more pronounced in the intertidal flat (Fig.  
614 S3b), was likely due to flushing out by tidal water and belowground water movement. We observed a slightly lower  
615 retention of Br<sup>-</sup> in the intertidal flats compared to the pioneer zone. We attribute this difference to the higher sand  
616 fraction in the intertidal flats, which likely increased permeability and led to stronger tidal flushing of the injected  
617 solution as well as subject to greater tidal inundation.

618 As the Br<sup>-</sup> concentrations and the respective calculated residual fractions were similar for each cycle (Fig. 3),  
619 we infer that there was no residue of Br<sup>-</sup> and thus no injected OC was carried over between cycles. Furthermore, the  
620 retained Br<sup>-</sup> was similar between the plots of a treatment within one zone, indicating similar belowground conditions  
621 within one zone and thereby validating the experimental setup. By placing the experimental plots outside of vegetated  
622 areas in the pioneer marsh, we tried to avoid geochemical influence on the sediment by plants. However, it is possible  
623 that benthic organisms such as worms may have influenced the biogeochemistry in both the pioneer marsh and  
624 intertidal flat, causing some variability.

#### 625 4.2.2 Effect of organic carbon input in the pioneer marsh

##### 626 Carbon dioxide fluxes

627 To test our hypothesis that that microbially mediated CO<sub>2</sub> release is OC limited in the pioneer marsh, we  
628 injected two different OC sources into the sediment and monitored the subsequent release of CO<sub>2</sub> 1.5, 24, and 48 h post  
629 injection. We observed that acetate treated plots emitted the highest CO<sub>2</sub> throughout the experiment (Fig. 4). No  
630 difference in the CO<sub>2</sub> release was measured between the humic acid treatment and the control despite the additional  
631 availability of OC. This is supported by the work of Gunina and Kuzyakov (2022) who showed that reduced and  
632 complex organics in soils are predominantly thermodynamically preserved due to insufficient energy yield upon  
633 decomposition. Humic acid, as complex OC, may be thus preserved in our study, as reflected in higher DOC  
634 concentrations. In contrast, acetate, with a simpler chemical structure, is favourable for microbial decomposition even  
635 under reducing conditions (Boye et al., 2017; LaRowe and Van Cappellen, 2011) and thus could be readily utilized  
636 and oxidized to CO<sub>2</sub>. Notably, plots treated with humic acid received the same OC concentrations as the acetate plots,  
637 indicating that OC composition is crucial for the CO<sub>2</sub> release from minerogenic pioneer marshes. Based on the  
638 geochemistry at the field site, which suggested that the ecosystem is limited by the availability of OC, the results from  
639 the in situ experiment further support our hypothesis, while simultaneously highlighting the importance of OC  
640 composition. This is contrasting to other terrestrial wetlands, which are characterized by a depletion of TEAs  
641 (Schlesinger and Bernhardt, 2013b).

642 The increased turnover of acetate to CO<sub>2</sub> relative to humic acid is also evidenced in the DOC concentrations  
643 (Fig. S4) and the retention fraction of both DOC sources (Fig. 3a). Although the same mass of OC was added to both  
644 treatments, the DOC concentrations in the acetate plots were significantly lower than that in the humic acid plots,  
645 suggesting that more acetate was utilized, reflected in higher CO<sub>2</sub> release. However, this result does not explain the  
646 lower retention of DOC relative to the retention of Br<sup>-</sup> from the humic acid plots (Fig. 3a). This suggests that in addition  
647 to flushing out, adsorption likely occurred. Previous studies have shown that minerals within the subsurface adsorb  
648 organic compounds (Kahle et al., 2003; Kleber et al., 2021). This adsorption may be preferential, favouring more  
649 aromatic and high molecular weight compounds, particularly when metal (oxyhydr)oxides and clay minerals are  
650 present (Kaiser and Guggenberger, 2000; Lv et al., 2016; Voggenreiter et al., 2024). Based on the results of our study  
651 and a previous study conducted at the same site (Kubeneck et al., 2024), both iron(oxyhydr)oxides and clay minerals  
652 are present. As adsorption suppresses the decomposition of OC (Kleber et al., 2021), we speculate that the lower  
653 retention fraction of humic acid compared to Br<sup>-</sup> was primarily due to adsorption onto the sediment rather than  
654 decomposition. This is consistent with the CO<sub>2</sub> fluxes: humic acid treated plots showed lower retention fractions  
655 compared to the Br<sup>-</sup> retention fractions, however, the CO<sub>2</sub> fluxes were comparable to the control. This suggests that  
656 little to no decomposition occurred and that adsorption was the dominant process. It is worth noting that anoxic  
657 decomposition of humic acid is generally possible but the turnover time would have exceeded the duration of the  
658 experiment (Lipczynska-Kochany, 2018). These results highlight that it is not only the presence of OC that affects  
659 short-term OC release from coastal wetlands; the composition of OC is the primary determining factor.

660 Furthermore, it is important to note that the OC concentrations used in this experiment are higher than those  
661 expected for naturally occurring OC inputs, such as root exudates, which are typically released at lower concentrations  
662 with a continuous input. Thus, upscaling the enhanced CO<sub>2</sub> fluxes measured in our study might result in overestimation  
663 of CO<sub>2</sub> release from minerogenic salt marshes. Our findings rather reveal, on a process level, that the addition of labile  
664 OC stimulates microbially mediated CO<sub>2</sub> release. Enhanced CO<sub>2</sub> release from the acetate amended plots was measured  
665 at nearly all sampling time points (1.5, 24, and 48 h) without a clear trend, while the concentration of the inert tracer  
666 showed a slight decrease over the same period (Fig. S3) – indicating slight dilution and flushing of the injected OC.  
667 This suggest that the elevated CO<sub>2</sub> release was driven by enhanced availability of labile OC independently of its  
668 concentration. These findings allow us to generalize that the system is likely limited by labile OC availability,  
669 regardless of the concentration; however, further work should quantify how the magnitude of CO<sub>2</sub> promotion  
670 corresponds to OC concentration, particularly under low, naturally sustained OC input rates. In conclusion, we can  
671 reliably predict the direction of increased OC inputs to minerogenic salt marshes, but further studies are needed to  
672 predict the specific long-term magnitude of changes in the carbon cycle in these ecosystems.

### 673 **Enhanced microbial Fe(III) reduction leads to higher CO<sub>2</sub> release**

674 This section combines the observed effect of OC input on the geochemistry of the porewater and sediment  
675 with the microbial growth and metabolic activity and links them to the CO<sub>2</sub> release from the pioneer marsh. The  
676 bacterial 16S rRNA gene copy number, an indicator of the total bacterial abundance, was significantly higher in the  
677 acetate treatment compared to the control for both DNA and RNA at both depths. This suggests greater bacterial  
678 abundance and metabolic activity, which likely led to higher CO<sub>2</sub> fluxes from these plots. No significant difference

679 was noticeable in the 16S rRNA gene copy number between plots amended with humic acid and the control. Overall,  
680 the 16S rRNA gene copy numbers (DNA) are in the range of other studies from coastal wetlands and marine sediment  
681 (Petro et al., 2019; Zhou et al., 2017).

682 The enhanced metabolic activity in the acetate treated plots is further reflected in the elevated aqueous and  
683 solid phase Fe(II). The acetate treatment showed higher aqueous Fe(II) concentrations in all four injection cycles, while  
684 no significant difference was observed between the humic acid and control plots. In the solid phase, the Fe(II) content  
685 was the highest in the acetate treatment. Thus, the higher expression of *Geobacter* spp. in the acetate treated plots  
686 corresponds well to our geochemical observations. *Geobacter* spp. have been shown to use acetate as a carbon source  
687 to gain energy (Coates et al., 1996). The higher Fe(II) levels observed in both aqueous and solid phase of acetate treated  
688 plots along with elevated *Geobacter* spp. gene copies indicate that Fe(III) reduction was stimulated by increased  
689 availability of labile OC.

690 Ferric iron and  $\text{SO}_4^{2-}$  reduction have been reported as OC decomposition processes in salt marshes (Hyun et  
691 al., 2007; Kostka et al., 2002a; Lowe et al., 2000). Sulfide concentrations in the porewater as well as in the solid phase  
692 gave evidence that  $\text{SO}_4^{2-}$  reduction occurred; however, no differences between the treatments and controls were seen.  
693 The functional gene analysis provided further evidence for this, as sulfate-reducing bacteria (SRB) were present  
694 (absolute gene copy numbers in Supplement, Fig. S7); however, none of the treatments led to an increase in their  
695 metabolic activity compared to the control (Fig. 6). Thus, we speculate that the higher  $\text{CO}_2$  release from the acetate  
696 treatment was mainly driven by the enhanced Fe(III) reduction and not by  $\text{SO}_4^{2-}$  reduction. Our finding that acetate is  
697 utilized follows the conventional thermodynamic sequence of iron reduction being more favorable than  $\text{SO}_4^{2-}$  reduction  
698 (Schlesinger and Bernhardt, 2013b) – even if the concentrations and availability of  $\text{SO}_4^{2-}$  were much higher.  
699

### 700 4.2.3 Effect of organic carbon input in the intertidal flat

#### 701 Carbon dioxide fluxes

702 Adding OC to the intertidal flat, a zone more influenced by tides than the pioneer marsh, resulted in CO<sub>2</sub>  
703 trends similar to the pioneer marsh. Acetate addition led to a noticeable increase in CO<sub>2</sub> fluxes. In contrast, the CO<sub>2</sub>  
704 fluxes from the humic acid and control plots were similar. This supports our hypothesis that the electron donor limits  
705 CO<sub>2</sub> release from the ecosystem. Moreover, it highlights that irrespective of tidal influence, the system is limited by  
706 the availability and composition of OC.

#### 707 Enhanced microbial activity leads to higher CO<sub>2</sub> release

708 Total microbial 16S gene copies were significantly higher in the acetate treated intertidal flat plots compared  
709 to the control at both depths (RNA-based), whereas plots amended with humic acid showed no significant difference  
710 from the control plots (Fig. S12a). In contrast to the significant increase in *Geobacter* spp. gene copies, no difference  
711 in the aqueous Fe(II) or in the Fe(II) content in the upper sediment layer (0-5 cm) was measured for the acetate  
712 treatment, except for a higher Fe(II) content in the deeper sediment layer. Conversely, we measured higher AVS  
713 contents in the upper layer for the acetate treatment, but this is not reflected in higher *drrA* copies numbers. Based on  
714 these mixed results, we consider two hypotheses: (i) acetate promoted increased Fe(III) reduction, which is supported  
715 by higher gene copies of *Geobacter* spp.. However, this is not clearly reflected in the Fe(II) data. Furthermore, with  
716 increased Fe(III) reduction and a constant SO<sub>4</sub><sup>2-</sup> reduction rate, we would have expected a depletion of S(II)<sub>tot</sub> in the  
717 porewater of the acetate treatment due to iron-sulfur mineral formation; however, this was not observed. Thus, we  
718 consider a second hypothesis that (ii) acetate promoted SO<sub>4</sub><sup>2-</sup> reduction, supported by increased AVS content in the  
719 acetate treatment in the upper sediment layer. In contrast, the number of *drrA* gene copies was not higher in the acetate  
720 treatment. Although a small increase (RNA-based) in the gene copies of *drrA* was observed in the upper layer, this  
721 was not statistically significant. Additionally, no differences were observed in the S(II)<sub>tot</sub> concentrations, which were  
722 generally low and should therefore be interpreted with caution. Based on our data, we cannot clearly reject either  
723 hypothesis. We therefore suggest Fe(III) and SO<sub>4</sub><sup>2-</sup> reduction both lead to higher CO<sub>2</sub> release, stimulated by higher  
724 supply of labile OC in the intertidal flat.

## 725 **5 Conclusion and Implications**

726 Our study demonstrated that the composition in combination with the concentration of OC can drive the CO<sub>2</sub>  
727 release from minerogenic salt marshes typical of the Wadden Sea. Initial porewater and sediment geochemical  
728 characterization suggested that microbially mediated CO<sub>2</sub> release is likely not limited by the availability of electron  
729 acceptors in both the pioneer marsh and intertidal flat, contrary to what is generally observed in terrestrial wetlands.  
730 Overall, our results indicate that the OC composition, rather than the concentration alone, influenced CO<sub>2</sub> release in  
731 both succession zones. This suggests that OC composition likely plays a limiting role in microbially mediated CO<sub>2</sub>  
732 release from minerogenic salt marshes. We caution here that we did not directly measure TEA reduction rates. Future  
733 studies should investigate turnover rates, potentially utilizing isotopes to confirm our findings. The higher CO<sub>2</sub> release  
734 observed in the acetate treated plots within the pioneer marsh was accompanied by higher levels of reduced iron. This  
735 pattern also corresponded with greater activity of Fe(III)-reducing bacteria in these plots, indicating that microbially  
736 mediated CO<sub>2</sub> release resulted from Fe(III) reduction driven by increased labile OC input. The addition of the complex  
737 OC (humic acid) did not exceed the CO<sub>2</sub> release of the control, showing that complex OC was not decomposed. Similar  
738 trends in CO<sub>2</sub> release were measured for the intertidal flat, further indicating that OC (both in terms of composition  
739 and concentration) is a key driver of microbial decomposition of OC to CO<sub>2</sub> for salt marsh systems. We expect that  
740 this is particularly relevant in salt marshes similar to ours with a high proportion of fine particles (muddy marshes)  
741 relative to marshes with larger particles (sandy marshes).

742 The results of this in situ study contribute to our understanding of short-term carbon dynamics in minerogenic  
743 temperate salt marshes. Labile OC inputs such as root exudates may enhance CO<sub>2</sub> release from minerogenic salt  
744 marshes, while complex OC inputs, such as plant fragments, might be sequestered in the sediment rather than degraded  
745 and released as CO<sub>2</sub>. The controls on OC turnover observed here should be considered when accounting for these  
746 ecosystems as carbon sinks and stocks. Also, our results show that the link between OC composition and the release  
747 of CO<sub>2</sub>, independent of electron acceptor concentrations, is crucial and should be included in process-based modelling  
748 of carbon fluxes in these ecosystems (Brown, 2025; Regnier et al., 2013). This will contribute to more accurate  
749 predictions of the response of salt marshes to climate change. Further, the in situ experiment simulated a potential  
750 increase of short-term OC inputs to the ecosystem, reflecting scenarios associated with climate change such as  
751 inundation of previously unflooded areas due to sea level rise and storm surges or eutrophication (van Beusekom,  
752 2005; Esselink et al., 2017; Woth et al., 2006). For example, eutrophication may result in an input of organic matter  
753 into the Wadden Sea that is eventually washed onto the coastal sediment. Our study thus provides valuable insight into  
754 the consequences of such short-term scenarios for GHG release and highlights that the input of labile OC (e.g., primary  
755 production during eutrophication, root exudates) into the sediment of a minerogenic salt marsh results in higher CO<sub>2</sub>  
756 releases.

757 **CRedit authorship contribution statement**

758 **NK:** Investigation, Methodology, Formal Analysis, Visualization, Writing – Original Draft Preparation,  
759 Conceptualization. **FR:** Investigation, Writing – Review & Editing. **LJK:** Methodology, Writing – Review & Editing.  
760 **RK:** Methodology, Writing – Review & Editing. **AK:** Writing – Review & Editing, Funding Acquisition. **PJ:**  
761 Conceptualization, Funding Acquisition, Supervision, Project Administration, Writing – Review & Editing.

762 **Competing interests**

763 The authors declare that they have no conflict of interest.

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778 **Data availability statement**

779 Data are publicly available at Zenodo via [doi.org/10.5281/zenodo.19032950](https://doi.org/10.5281/zenodo.19032950) (Kainz et al., 2025)

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