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# Elevated sedimentary removal of Fe, Mn, and trace elements following a transient oxygenation event in the Eastern Gotland Basin, central Baltic Sea

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1 **ABSTRACT**

2 Iron, manganese, and trace elements play an important role in the marine carbon cycle as  
3 they are limiting nutrients for marine primary productivity. Water column concentrations of  
4 these bio-essential elements are controlled by the balance between input and removal, with  
5 burial in marine sediments being the main sink. The efficiency of this burial sink is dependent  
6 on the redox state of the water column, with sediments underlying a sulphidic (euxinic) water  
7 column being the most efficient sinks for Fe, but also Mn and trace elements (Co, Cd, Ni, Mo,  
8 As, W, V, and U). Transient changes in ocean redox state can hence affect trace element burial,  
9 and correspondingly, the ocean's trace element inventory, but the impact of transient  
10 oxygenation events on trace element cycling is currently not well understood.

11 Here, we investigate the impact of a natural oxygenation event on trace element release and  
12 burial in sediments of the Eastern Gotland Basin (EGB), a sub-basin of the Baltic Sea. After  
13 being anoxic ( $< 0.5 \mu\text{M O}_2$ ) for ~10 years, the deep waters of the EGB experienced a natural  
14 oxygenation event (Major Baltic Inflow, MBI) in 2015. Following this oxygenation event, we  
15 deployed benthic chamber landers along a depth transect in the EGB in April 2016, 2017 and  
16 2018. We complemented these *in situ* flux measurements with analyses of water column, solid  
17 phase and pore water chemistry. Overall, the event increased the benthic effluxes of dissolved  
18 trace elements, though particular responses were element-specific and were caused by different  
19 mechanisms. Enhanced fluxes of Cd and U were caused by oxidative remobilisation, while Ni  
20 showed little response to the inflow of oxygen. In contrast, enhanced release of Co, Mo, As, W,  
21 and V was caused by the enhanced transient input of Mn oxides into the sediment, whereas Fe  
22 oxides were of minor importance. Following the dissolution of the oxides in the sediment, Mn  
23 and W were nearly completely recycled back to the water column, while fractions of Fe, Co,  
24 Mo, As, and V were retained in the sediment. Our results suggest that transient oxygenation  
25 events in euxinic basins may decrease the water column inventory of certain trace elements (Fe,  
26 Co, Mo, As, and V), thus potentially affecting global marine primary productivity on longer  
27 timescales.

28

## 29 1. INTRODUCTION

30 The biogeochemical cycling of iron (Fe), manganese (Mn), and trace elements plays a vital  
31 role in marine ecosystems and the global carbon cycle (GEOTRACES, 2006). Most trace  
32 elements are essential nutrients and despite their abundance in the Earth's crust, they are  
33 limiting nutrients for primary production (McLennan, 2001; Morel and Price, 2003; Mahowald  
34 et al., 2018; Baeyens et al., 2018). This apparent paradox is caused by the restricted supply of  
35 dissolved trace elements to the ocean. Aerosol deposition has typically been considered the  
36 dominant source for trace elements into the open ocean (Jickells, 2005), though other  
37 mechanisms are also increasingly considered. Fluvial and hydrothermal pathways can be  
38 significant in certain regions of the ocean (Buck et al., 2007; Jones et al., 2011; Fitzsimmons et  
39 al., 2017), while shelf-to-basin shuttling is thought to be an important source of Fe for pelagic  
40 primary production in the open ocean (Elrod et al., 2004; Severmann et al., 2010; Dale et al.,  
41 2015; Klar et al., 2017). In the ocean, these sources are counterbalanced by burial in sediments,  
42 which represents a permanent sink for Fe, Mn and trace elements. The efficiency of sediment  
43 burial controls the water column concentrations and depends largely on the redox state of the  
44 overlying water column.

45 Under oxic conditions, Fe and Mn form insoluble oxides (Thamdrup, 2000), while they exist  
46 as dissolved  $Mn^{2+}$  and  $Fe^{2+}$  or form reduced minerals under anoxic ( $< 0.5 \mu M O_2$ ) conditions.  
47 Sediments deposited under an oxygenated water column generally lose a fraction of their  
48 particulate Fe and Mn (oxyhydr)oxides as a dissolved benthic flux to the overlying water  
49 column (Elrod et al., 2004; Lyons and Severmann, 2006). These benthic effluxes are stimulated  
50 by bioturbation, in particular by the activity of bio-irrigating macrofauna that flush their burrow  
51 systems (van de Velde and Meysman, 2016; Thibault de Chanvalon et al., 2017; Lenstra et al.,  
52 2018). In contrast, sediments underlying anoxic waters with free hydrogen sulphide (euxinia)  
53 act as permanent sinks for Fe through precipitation of FeS minerals in the water column and  
54 subsequent burial in the sediment (Anderson and Raiswell, 2004; Lyons and Severmann, 2006).  
55 This redox behaviour is important for local Fe transport, so called 'shelf-to-basin shuttling'.  
56 Iron that is reduced in deeper, anoxic parts of coastal shelf sediments and is released to an oxic  
57 water column can be transported further offshore in dissolved form, before it is oxidised and  
58 forms particulate Fe. The Fe oxides can aggregate and sink to the sediment again, and by this  
59 mechanism Fe may undergo several oxidation-reduction cycles as it is "shuttled" further  
60 offshore. Manganese also exhibits a similar shuttling behaviour (Lyons and Severmann, 2006;

61 Jilbert and Slomp, 2013; Scholz et al., 2013; Dijkstra et al., 2016), while physical transport via  
62 deposition-resuspension cycles is important for shelf sediments with a relatively low organic  
63 matter input (Lenstra et al., 2018).

64 Trace elements can respond directly or indirectly to redox changes and their behaviour  
65 depends primarily on their physico-chemical properties. **Cobalt (Co), Cadmium (Cd) and**  
66 **Nickel (Ni)** belong to the category of divalent cations that are unlikely to undergo redox  
67 reactions but are particle-reactive. All three elements form complexes with organic ligands or  
68 dissolved anions and can be scavenged by particles (organic matter, Fe and Mn oxides). In the  
69 presence of dissolved sulphide, they can form insoluble sulphide minerals and become  
70 incorporated in pyrite (Huerta-diaz and Morse, 1992; Morford and Emerson, 1999; Saito and  
71 Moffett, 2001; Piper and Perkins, 2004; Tribovillard et al., 2006). Note that  $\text{Co}^{2+}$  has been  
72 shown to oxidise to  $\text{Co}^{3+}$  in the presence of Mn oxides (Lee and Tebo, 1994; Moffett and Ho,  
73 1996; Murray et al., 2007), but the presence of organic or inorganic ligands in natural water  
74 stabilises the reduced  $\text{Co}^{2+}$  form (Saito and Moffett, 2001). **Molybdenum (Mo), Arsenic (As)**  
75 **and Tungsten (W)** are a group of metalloids that form oxyanions under oxic conditions, and  
76 which efficiently adsorb onto Fe and Mn oxides (Bertine, 1972; Gustafsson, 2003; Giménez et  
77 al., 2007). The oxygen atoms in the oxyanion complex can be replaced by dissolved sulphide,  
78 which leads to the formation of thio-complexes and concomitant changes in adsorption  
79 properties. While thio-molybdate is highly particle-reactive (Tribovillard et al., 2004; Vorlicek  
80 et al., 2004; Tribovillard et al., 2006), the thio-complexes of both As and W are less prone to  
81 particle scavenging (Kirk et al., 2010; Cui and Johannesson, 2017), although As does co-  
82 precipitate with pyrite (Huerta-diaz and Morse, 1992). **Vanadium (V) and Uranium (U)**  
83 belong to a category of trace elements that are somewhat particle reactive in their oxidised  
84 forms and can adsorb onto Fe and Mn oxides (Wehrli and Stumm, 1989a; Waite et al., 1994;  
85 Hastings et al., 1996; Wang et al., 2013). In their reduced form, these elements precipitate as  
86 solid oxide or hydroxide phases (Klinkhammer and Palmer, 1991; Wanty and Goldhaber, 1992;  
87 Morford and Emerson, 1999; Cumberland et al., 2016).

88 Changes in the oxygenation state of the water column will likely affect the availability of  
89 Fe, Mn and trace elements in the ocean. In the coming decades, oceanic oxygen concentrations  
90 are expected to decrease, whereas anoxic and euxinic zones are expected to increase in size  
91 (Keeling et al., 2010). The extent of an oxygen minimum zone (OMZ) is not fixed in time and  
92 space (Scholz et al., 2011), and the anoxic or euxinic conditions within the most pronounced of

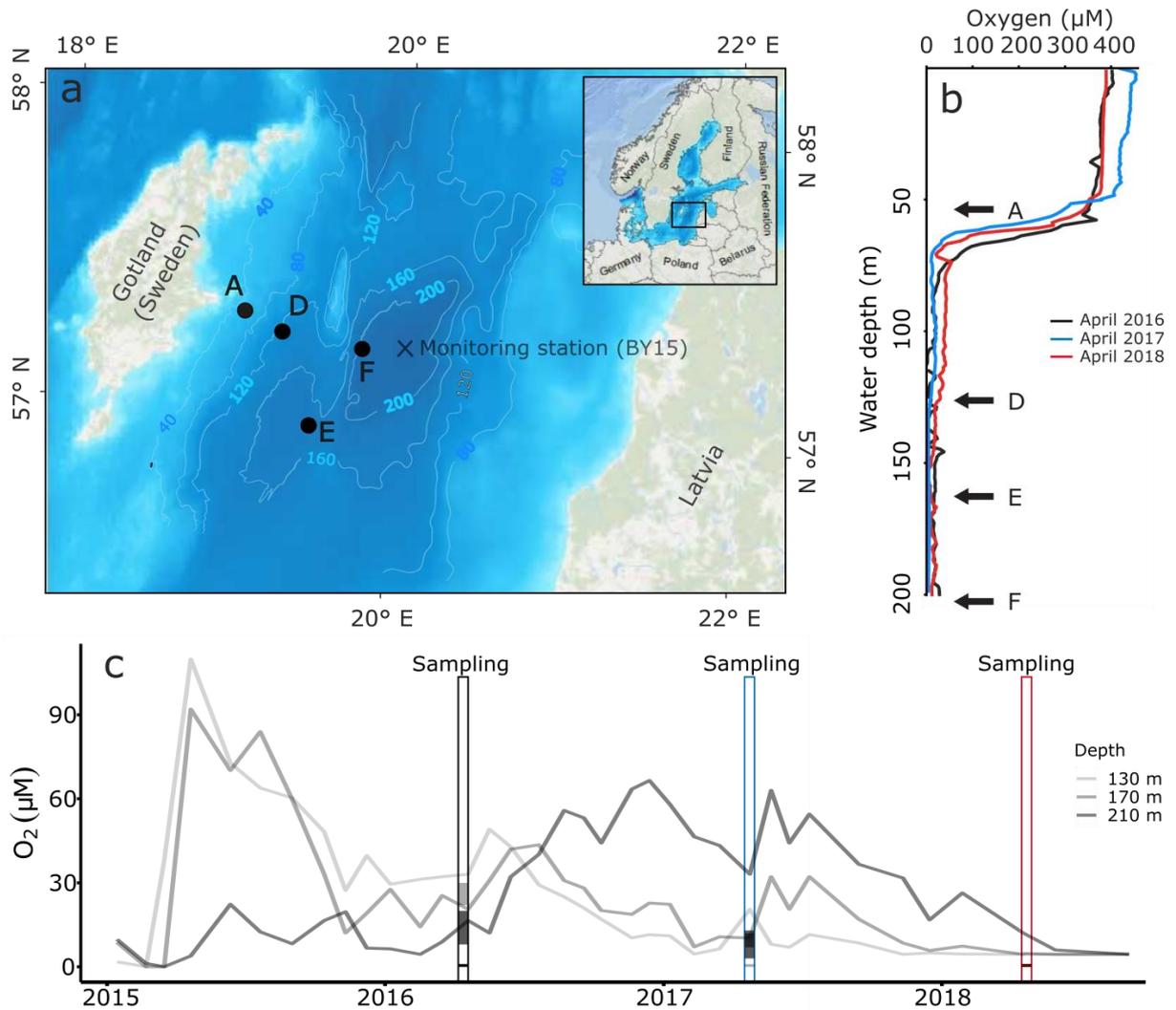
93 these OMZs (e.g. offshore Mexico and Peru; Scholz et al., 2014) will thus experience transient  
94 reoxygenation events. This will affect the sink/source behaviour of marine sediments, and  
95 consequently the trace element inventory in the ocean (Scholz et al., 2014). However, detailed  
96 studies of the impact of transient bottom-water reoxygenation of euxinic bottom waters on the  
97 sedimentary release of trace elements are rare. The available studies remain generally restricted  
98 to Fe, Mn (Hermans et al., 2019) and paleo-proxies (V, Mo and U; Scholz et al., 2011; Scholz  
99 et al., 2018), with no *in situ* quantification of trace element release using benthic landers.

100 Here, our aim was to investigate the impact of a natural transient reoxygenation event in the  
101 long-term euxinic Eastern Gotland Basin (EGB), a sub-basin of the central Baltic Sea, on the  
102 sedimentary release and retention of Fe, Mn and trace elements (As, Cd, Co, Mo, Ni, U, V, W).  
103 These elements have importance for biology or as paleo-proxies, represent different physico-  
104 chemical groups, and sedimentary effluxes can be measured with sufficient accuracy using the  
105 methods we employed. We followed the evolution of Fe, Mn and trace element diagenesis after  
106 the transient re-oxygenation during campaigns in three consecutive years, using a combination  
107 of *in situ* measured benthic fluxes, water column, and pore water sampling and solid phase  
108 analysis.

## 109 **2. MATERIALS & METHODS**

### 110 **2.1 Field site**

111 The EGB is situated in the central part of the Baltic Sea, between Latvia and the island of  
112 Gotland (Sweden) (Fig. 1). It is the largest sub-basin of the Baltic Proper (the central part of the  
113 Baltic Sea), with a maximum water depth of 249 m and a strong and permanent halocline at  
114 approximately 60-80 m depth. The EGB is heavily affected by eutrophication, which in  
115 combination with a strong stratification of the water column has led to prolonged periods of  
116 anoxia ( $[O_2] < 0.5 \mu M$ ) below the halocline. The sediments above the halocline (< 80 m depth)  
117 are strongly affected by waves and bottom currents and are generally classified as erosion-  
118 transport bottoms. These shallow sediments show no net long-term sediment accumulation and  
119 consist of coarser sand since finer material is rapidly eroded and transported to the deeper basin  
120 (Carman and Cederwall, 2001; Nilsson et al., 2018). Below the halocline (> 80 m depth), fine  
121 sediment accumulates at a rate of  $\sim 0.1 \text{ cm yr}^{-1}$  (Hille et al., 2006).



122  
 123 **Figure 1:** (a) Map of the Eastern Gotland Basin with the locations of the sampling stations (A, D, E and F), as well as the  
 124 position of the monitoring station where the oxygen time series of panel c was recorded (BY15). (b) Oxygen depth profiles  
 125 recorded in April 2016, 2017 and 2018. Arrows indicate water depth of the stations. Bathymetry was taken from the Baltic Sea  
 126 Bathymetry Database (BSBD; <http://data.bshc.pro>). (c) Variability of oxygen concentrations through time at the following  
 127 water depths: 130 m, 170 m, and 210 m obtained from the Swedish Meteorological and Hydrological Institute website  
 128 (<https://sharkweb.smhi.se/>) at station BY15. These water depths correspond to the bottom depth of our sediment sampling sites.  
 129 Coloured bars indicate sampling periods; greyscale on bars indicate oxygen concentrations recorded by our benthic landers at  
 130 each station. During the 2018 sampling, all measured oxygen concentrations were below LOD (<0.5 µM).

131  
 132 In 2014, a large inflow of dense and oxygenated water from the North Sea, a so called major  
 133 Baltic inflow (MBI), entered the Baltic Sea (Mohrholz et al., 2015). This MBI reached the EGB  
 134 in March 2015 and temporarily re-oxygenated the waters below 140 m depth, after 10 years of  
 135 preceding anoxia (Fig. 1c ; Hall et al., 2017; Liblik et al., 2018). The newly brought oxygen  
 136 was consumed by October 2015, but the bottom water oxygen levels increased again in March

137 2016, when a smaller inflow reached the EGB. However, by March 2017, the oxygen had  
138 mostly disappeared again (Fig. 1c; Liblik et al., 2018). Over the period 2015-2018, several  
139 smaller inflows were recorded at ~120 m depth in the EGB (Fig. 1c; Liblik et al., 2018).

## 140 **2.2 Benthic lander deployments and *in situ* water measurements**

141 The EGB was visited during separate sampling campaigns aboard the R/V Skagerak in three  
142 consecutive years (April 2016, 2017 and 2018; Fig 1c). Benthic chamber landers were deployed  
143 at stations A (60 m water depth), D (130 m water depth), E (170 m water depth) and F (210 m  
144 water depth) (Fig. 1a,b). Landers were deployed twice per location during each campaign, with  
145 a few exceptions due to ship time scheduling or weather constraints (Table 1). Before each  
146 lander deployment, water column depth profiles of temperature, salinity and oxygen were  
147 recorded using a CTD instrument (SBE 911, Sea-Bird Scientific) equipped with a high-  
148 accuracy oxygen sensor (SBE 43, Sea-Bird Scientific).

149 Water column samples were collected using 5 L NISKIN bottles attached to a CTD carousel  
150 during one deployment in 2017 at the deepest station (F; 210 m water depth). Water samples  
151 were collected at discrete depths (5 m, 15 m, 30 m, 40 m, 60 m, 80 m, 100 m, 120 m, 140 m,  
152 160 m, 180 m and 200 m). One litre of bottom water per sampled depth was filtered through  
153 pre-weighed polyethersulphone (PES) filters (0.45  $\mu\text{m}$  pore size, Supor, PALL) by pressure  
154 filtration using 50 mL syringes (PP). Filtrate was collected in two different 500 mL acid-cleaned  
155 LDPE bottles (Nalgene<sup>TM</sup>) per sample depth.

156 Solute fluxes across the sediment-water interface were measured by collecting water samples  
157 *in situ* using the autonomous Gothenburg benthic lander (Tengberg et al., 2004; Almroth et al.,  
158 2009; Kononets et al., *subm.*). This lander carried four benthic chambers, each incubating a  
159 sediment surface area of  $A_{\text{chamber}} = 400 \text{ cm}^2$ . The overlying water was stirred with a horizontal  
160 paddle wheel to prevent the build-up of concentration gradients in the chamber. Nine syringes  
161 (PP) allowed sampling of the overlying water in each chamber at pre-set times. The syringes  
162 were cleaned with milli-Q before deployment, as previous tests indicated that acid-washing  
163 syringes led to random contamination effects. Blank incubations (lander incubations without  
164 sediment) using syringes that were rinsed using milli-Q water showed that trace elements did  
165 not leach from the materials used in the lander (Supplementary Fig. 1, Appendix 2). Ambient  
166 bottom water entered the chamber through a small stainless-steel loop as samples were  
167 withdrawn. Sensors mounted inside and outside of the chambers monitored the oxygen

168 concentration (Oxygen Optode 3830; Aanderaa Data Instruments), turbidity (Turbidity Sensor  
169 Model 3612A; Aanderaa Data Instruments), conductivity, and temperature (Sensor 3919;  
170 Aanderaa Data Instruments). The volume ( $V_{\text{chamber}}$ ) of overlying water in each chamber was  
171 calculated from the decrease in salinity following the injection of a known volume of milli-Q  
172 water ( $V_{\text{injection}}$ ) corresponding to 0.5-1 % of the total chamber volume (Kononets et al., subm.):

$$173 \quad V_{\text{chamber}} = V_{\text{injection}} \frac{S_{\text{before}}}{S_{\text{before}} - S_{\text{after}}} \quad [1]$$

174 where  $S_{\text{before}}$  and  $S_{\text{after}}$  are the salinities before and after the injection, respectively. The chamber  
175 water height (necessary to calculate the benthic flux) was calculated as  $H = V_{\text{chamber}}/A_{\text{chamber}}$ ,  
176 where  $A$  is the incubated surface area (relative uncertainty: 6-12%). This procedure has been  
177 tested at a salinity of  $\sim 2.5$ , at which the freshening of chamber water is still measurable  
178 (Kononets et al., subm.).

179 Before the start of each incubation, the lander frame was left hanging for 2 hours at a depth  
180 of  $\sim 1$  m above the seafloor with open chambers that were actively stirred. During that time, a 5  
181 L NISKIN flask attached to the frame was used to sample bottom water before the deployment  
182 of the lander. After this 2h waiting period, the lander frame was slowly lowered to the seafloor  
183 and the chambers were inserted into the sediment with the chamber lid open and continuous  
184 stirring for another 2 hours. These pre-incubation steps ensured that ambient bottom water was  
185 incubated and that any oxygen contained in the polycarbonate chamber walls equilibrated with  
186 the surrounding environment. After the chamber lid was closed, sediment and water were  
187 incubated for 37 hours at station A and 14 hours at stations D, E and F. Immediately after lander  
188 recovery, syringe samples were filtered in open air through pre-rinsed cellulose acetate filters  
189 (Sartorius, 0.45  $\mu\text{m}$  pore size). Bottom water collected by the NISKIN flask was processed as  
190 described before for the water column samples.

191 Benthic fluxes of dissolved trace elements were calculated from their concentration change  
192 in the chamber water over time. Concentrations were corrected for the small dilution that took  
193 place when new bottom water entered the chamber during syringe sampling. A linear or  
194 quadratic least-square regression line was fitted to concentration data versus time (selected  
195 based on highest adjusted  $R^2$  value, which was adjusted for the number of predictors in the  
196 model; see below). When a quadratic fit was selected, the flux was calculated only for the first  
197 time point, which gives the flux at the start of the deployment. Data points with high leverage  
198 were identified through the calculation of Studentized Deleted Residual Index (SDRI) and

199 Cook's distance values (Belsley et al. 1980; Cook and Weisberg 1982; Williams 1987). Points  
200 with a SDRI higher than 2 and Cook's distance higher than  $4/(n-2)$ , where  $n$  is the number of  
201 data points were considered outliers and were removed. Diagnostic graphs of residuals were  
202 used to verify that the assumptions of the regression were fulfilled (e.g. random distribution of  
203 residuals, distribution of residuals has a constant variance). All analysis was done in the open  
204 source software R using the 'lm' and 'nls' functions from the built-in CRAN:stats package (R  
205 Core Team, 2017). The flux across the sediment-water interface was calculated by multiplying  
206 the chamber water height with the initial slope of the regression line. Fluxes with  $p$ -values  $<$   
207 0.05 were considered to differ significantly from a zero flux. For a detailed discussion of the  
208 flux evaluation method, see Hylén et al. (subm.).

### 209 **2.3 Sediment sampling**

210 Sediment was retrieved during each sampling campaign at all stations using a modified box  
211 corer (Blomqvist et al., 2015). Six subcores were manually collected from several box cores  
212 using transparent PVC core liners (inner diameter 60 mm; length 30 cm). Sediment cores were  
213 closed with a rubber stopper from the bottom and were temporarily stored with an open top in  
214 an incubation tank filled with bottom water collected from the sampling site. The tank was  
215 equipped with a temperature controller that kept the water at *in situ* temperature. Oxygen  
216 concentrations were continuously monitored by an optic sensor (Oxygen Optode 3830;  
217 Aanderaa Data Instruments). To keep the *in situ*  $O_2$  concentration, the water was bubbled with  
218 a  $N_2/CO_2$  mixture at an intensity that was manually adjusted to keep the correct  $O_2$   
219 concentration.

220 After a ~6 hours transit back to the harbour, sample processing started onboard. Two cores  
221 from each station were sectioned immediately for pore water extraction under  $N_2$  atmosphere  
222 in a portable glove bag (Captair Pyramid, Erlab, France). Oxygen concentrations in the glove  
223 bag were continuously monitored (Portable Oxygen Analyzer Model 3110; Teledyne  
224 Analytical Instruments). Sediment slicing was performed at 0.5 cm resolution from 0 to 3 cm  
225 depth, at 1 cm resolution between 3 and 10 cm depth, and in 2 cm slices from 10 to 14 cm depth.  
226 Sediment sections were collected in 50 mL centrifuge tubes (polypropylene; Techno Plastic  
227 Products, Switzerland) and pore water was extracted by two different methods depending on  
228 the campaign. In the first campaign (April 2016), the 50 mL tubes were centrifuged at 2500 g  
229 for 10 min (Sigma 3-16L, Sigma Laborzentrifugen GmbH, Germany). Subsequently, the

230 centrifuge tubes were opened in the anoxic glove bag and overlying pore water was transferred  
231 into suitable sample containers after filtration through 0.45  $\mu\text{m}$  pore size cellulose acetate filters  
232 (CHROMAFIL Xtra; MACHERY-NAGEL, Germany). During the subsequent campaigns  
233 (April 2017 and April 2018), pore water was extracted from the centrifuge tubes by Rhizon  
234 samplers (pore size  $\sim 0.15 \mu\text{m}$ ; Rhizosphere Research Products, The Netherlands), which  
235 allowed us to extract more pore water than the centrifugation method. In the glove bag, Rhizons  
236 were manually inserted into the tubes until the porous part was completely covered by sediment.  
237 Syringes attached to the Rhizons were drawn back and fixed in this position, creating a vacuum  
238 which extracted the pore water. Afterwards, sample volume was distributed into sample  
239 containers without filtration.

#### 240 **2.4 Sediment physical parameters**

241 Individual sediment cores were collected with a custom-made multi-corer for the  
242 determination of porosity depth profiles at all stations in each sampling campaign. The cores  
243 (inner diameter 9.9 cm) were sliced at 0.5 cm resolution between 0 and 2 cm depth, at 1 cm  
244 resolution between 2 and 6 cm depth and 2 cm between 6 and 10 cm depth. The water content  
245 of each sediment section was obtained from the weight loss after drying the samples at 70  $^{\circ}\text{C}$   
246 until constant weight (at least 48 h). The solid-phase density was determined by recording the  
247 mass difference between a 25 mL volumetric flask filled with only milli-Q water ( $m_{MQ}$ ) and  
248 the same flask with a known mass of homogenised freeze-dried sediment ( $m_{sed}$ ) and filled with  
249 milli-Q water to the same volume ( $m_{MQ+sed}$ ). The volume of the added sediment was then  
250 calculated as

$$251 \quad V_{sed} = \frac{[m_{MQ} - (m_{MQ+sed} - m_{sed})]}{\rho_{H_2O}} \quad [1]$$

252 where  $\rho_{H_2O}$  is the density of water. The sediment density was subsequently calculated as  
253  $\rho_{sed} = m_{sed} / V_{sed}$ . Sediment porosity (volume of pore water per volume of bulk sediment) was  
254 determined from water content and solid-phase density, accounting for the salt content of the  
255 pore water.

## 256 **2.5 Water column, chamber water and pore water analysis**

257 Water samples for determination of dissolved elemental composition (As, Co, Cd, Fe, Mn,  
258 Mo, Ni, U, V, W) were stabilised with 50  $\mu\text{L}/\text{mL}$  bidistilled  $\text{HNO}_3$  (65%, Suprapure, Merck;  
259 final  $\text{HNO}_3$  concentration was  $\sim 3\%$ ) and stored at  $4^\circ\text{C}$ . In 2016, the acid to sample ratio for the  
260 pore water samples was 100  $\mu\text{L}/\text{mL}$ , which we decreased to 50  $\mu\text{L}/\text{mL}$  in the subsequent years.  
261 In 2016, the samples were diluted 20 times with a 1% aqueous  $\text{HNO}_3$  solution prior to analysis.  
262 In the subsequent years, the dilution factor was reduced to 10 times, which increased the  
263 performance of our method (Supplementary Table 3, Appendix 1). The analysis was done by  
264 High Resolution Inductively Coupled Plasma Mass Spectrometry (HR-ICP-MS; Element 2,  
265 ThermoFisher Scientific). Indium (2.5 ppb) containing 2%  $\text{HNO}_3$  was injected simultaneously  
266 with the samples as an internal standard (the detection and quantification limits for each metal  
267 are shown in Supplementary Table 1, Appendix 1). Before each run, certified reference material  
268 (SLEW-3, estuarine water, National Research Council Canada; SLRS-6, river water, National  
269 Research Council Canada; NIST 1640a, natural water, National Institute for Standards and  
270 Technology, USA) was diluted in the same fashion as the samples and analysed to monitor the  
271 precision and accuracy of the method (Supplementary Table 3; Appendix 1). It should be noted  
272 that HR-ICP-MS analysis provides total elemental concentrations. In this paper, we use the  
273 operational term ‘dissolved’, referring to the fraction that either passed through a  $0.45\ \mu\text{m}$  filter  
274 (2016 campaign) or a Rhizon sampler with pore size  $\sim 0.15\ \mu\text{m}$  (2017/2018 campaigns).

## 275 **2.6 Solid-phase and filter analysis**

276 In the 2016 campaign, the solid phase that remained after centrifugation was freeze-dried  
277 and stored in aluminium bags under  $\text{N}_2$  atmosphere for later analysis. Only 2016 samples were  
278 used, as we did not expect to see any change in total trace element contents between samplings.  
279 Total contents of (trace) elements (Al, As, Cd, Co, Fe, Mn, Mo, Ni, Ti, U, V, and W) were  
280 determined by total digestion. Freeze-dried subsamples (300 mg) were homogenised and  
281 dissolved by microwave-assisted digestion (CEM Mars 5) using 12 mL of an acid mixture  
282 ( $\text{HF}/\text{HCl}/\text{HNO}_3$  in a 2:1:3 ratio), followed by a second neutralising step using 30 mL  $\text{H}_3\text{BO}_3$   
283 (US EPA method 3052). Certified Reference Material (MESS-3: Marine Sediment, National  
284 Research Council Canada) and method blanks were included in every digestion run to monitor  
285 precision and accuracy of the extractions (Supplementary Tables 2 and 3; Appendix 1).  
286 Subsequently, total digests were analysed for Al, Ti and Fe by Inductively Coupled Plasma

287 Optical Emission Spectrometry (Iris Advantage ICP-OES, Thermo Scientific) after 100-fold  
 288 dilution and using 0.2 ppm gold and ytterbium as internal standards. The precision of the  
 289 method was < 10% (all precisions are calculated as one relative standard deviation), accuracy  
 290 for each element is reported in Supplementary Table 3 (Appendix 1). For trace elements (As,  
 291 Cd, Co, Mn, Mo, Ni, U, V, W) the total digests were analysed by HR-ICP-MS as described in  
 292 section 2.5. In 2017, the material remaining on the filter after filtration of water column samples  
 293 was oven-dried to constant weight (70°C) and digested following an identical method as  
 294 described for the solid phase samples.

295 Freeze-dried samples from the 2016 campaign were also analysed for particulate organic  
 296 carbon (POC) by a Thermo1112 Flash elemental analyser. Samples were acidified before each  
 297 analysis with 0.1N HCl to remove the inorganic carbon (Nieuwenhuize et al., 1994). The POC  
 298 values are expressed as mass % of dry weight of the sediment sample. The precision was < 5%  
 299 for the POC measurements.

300 **Table 1:** Summary of bottom water data. Salinity (S), temperature (T, °C) and oxygen (O<sub>2</sub>, μM) as measured by sensors on the  
 301 benthic chamber lander less than 0.5 m above seafloor. The range of recorded values is given over the deployment period.  
 302 Limit of Detection (LOD) for oxygen = 0.5 μM. D1= first deployment, D2 = second deployment; missing values indicate that  
 303 only one deployment was done that year. Values in italics are CTD values replacing lander values, due to issues with  
 304 conductivity/salinity sensor on the lander during deployment.

Station	Coordinates	Depth	Year	Salinity		Temperature (°C)		O <sub>2</sub> concentration (μM)	
				D1	D2	D1	D2	D1	D2
A	N 57°23.11'	60m	2016	7.25-7.35	-	3.60-3.90	-	330-350	-
	E 19°04.95'		2017	<i>7.7</i>	<i>8.9</i>	4.00-5.00	<i>5.0</i>	100-120	<i>300</i>
			2018	7.42-7.50	<i>7.5</i>	2.70-3.00	2.60-3.00	330-355	325-350
D	N 57°19.67'	130m	2016	12.5-12.70	12.55-12.65	6.50-6.60	6.50-6.60	<0.5	<0.5
	E 19°19.41'		2017	<i>12.7</i>	<i>12.7</i>	6.72-6.76	<i>6.7</i>	8-13	<i>9</i>
			2018	12.50-12.55	12.40-12.50	6.65-6.85	6.60-6.80	<0.5	<0.5
E	N 57°01.52'	170m	2016	12.96-12.99	12.90-13.10	6.75-6.85	6.75-6.85	8-20	7-10
	E 19°30.45'		2017	<i>13.1</i>	<i>13.1</i>	6.91-6.95	7.00-7.20	6-13	3-8
			2018	13.05-13.15	-	6.80-7.10	-	<0.5	-
F	N 57°17.22'	210m	2016	13.82-13.86	13.75-13.85	7.38-7.43	7.34-7.38	22-30	23-27
	E 19°48.04'		2017	<i>13.5</i>	-	7.20-7.40	-	<0.5	-
			2018	13.12-13.18	13.24-13.29	6.90-7.05	6.90-7.05	<0.5	<0.5

### 305 **3. RESULTS**

#### 306 **3.1 Bottom water conditions**

307 We visited four stations in the EGB (Fig. 1a) during three annual sampling campaigns in  
308 April 2016, 2017, and 2018 (Table 1). Station A was situated just above the halocline and had  
309 oxygenated bottom waters on all occasions. In 2017, a storm caused the redoxcline to shift  
310 downward between lander deployments which were three days apart, causing a large difference  
311 in oxygen concentrations between deployments 1 and 2 (Table 1; Supplementary Fig. 2,  
312 Appendix 2). Stations D, E, and F were situated at depths below the halocline at all times (Fig.  
313 1b). In 2016, bottom waters at the deeper stations E and F had O<sub>2</sub> concentrations of 7-30 μM,  
314 indicative of a recent MBI. In the two subsequent years, oxygen levels dropped and bottom  
315 waters were anoxic (<0.5 μM; the detection limit of the oxygen optodes attached to the lander)  
316 at station E in 2018 and station F in both 2017 and 2018. Station D (located closer to the  
317 halocline) was anoxic in 2016 and 2018 but had an O<sub>2</sub> concentration of ~8 μM in 2017 (Table  
318 1). Note that the concentrations measured by the oxygen optodes on the lander are consistently  
319 lower than the values measured in the water column (Fig. 1c). This likely reflects spatial  
320 differences between concentrations in the water column at station BY15 and concentrations  
321 measured near the seabed.

#### 322 **3.2 Sediment parameters**

323 Solid-phase density showed no trend with sediment depth at any of the four sites, so values  
324 are reported as depth-averaged values. The shallow site (A) had a slightly higher solid-phase  
325 density ( $2.2 \pm 0.4 \text{ g cm}^{-3}$ ), compared to the deeper stations (D:  $1.9 \pm 0.4 \text{ g cm}^{-3}$ ; E:  $2.0 \pm 0.3 \text{ g}$   
326  $\text{cm}^{-3}$ ; F:  $1.9 \pm 0.5 \text{ g cm}^{-3}$ ). The solid-phase density recorded at the deeper stations is lower than  
327 that of typical siliclastic marine sediments (~2.6 g cm<sup>-3</sup>; Burdige, 2006), and this is partially  
328 explained by the high organic matter content (see below), which has a solid-phase density close  
329 to 1.0 g cm<sup>-3</sup>.

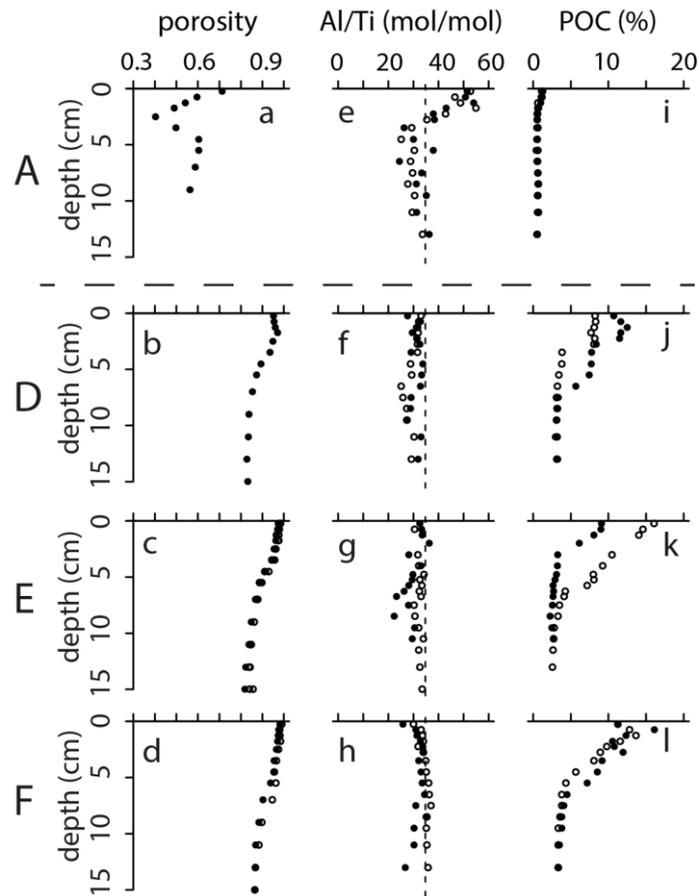
330 Porosity at station A had a distinct minimum (~0.4) at 2.5 cm depth before increasing again  
331 with depth (Fig. 2a). This profile suggests that at station A, a shallow layer (3-4 cm) of recent  
332 sediment overlies an old, consolidated clay layer. The recent sediment contains more sandy  
333 particles, which explains the lower porosity in the upper 4 cm. The porosity depth profiles at  
334 the three deeper sites (D, E, and F) were similar, with high values (> 0.9) in the upper three  
335 centimetres (Fig. 2b-d), gradually declining to ~0.8 in the deeper sediment layers. The apparent

336 constant porosity in the upper 3 cm of the sediment is most likely due to mixing of the fluffy  
337 upper layer during core sampling. The exponential decrease of porosity with depth is consistent  
338 with what is often encountered in coastal and shelf sediments (Boudreau et al., 1998).

339 At the shallowest station (A), the Al/Ti molar ratio (a proxy for the input of detrital material)  
340 of the sediment layers below 4 cm reflected the Al/Ti ratio of the average upper crust (34.8  
341 mol/mol; McLennan, 2001) (Fig. 2e). However, above 4 cm, the Al/Ti ratio was markedly  
342 higher. Since Ti associates mainly with organic matter (Kryc et al., 2003), the elevated Al/Ti  
343 ratio of the upper sediment layer at station A is consistent with the selective removal of fine-  
344 grained organic-rich particles from erosion-transport bottoms. At the deeper sites (D, E, and F),  
345 Al/Ti molar ratios were close to the average ratio of the upper continental crust (McLennan,  
346 2001) and did not show variation with depth or across sites. As parent soils or rocks are typically  
347 characterized by specific Al/Ti fingerprints, the consistency in Al/Ti ratio between stations D,  
348 E and F (Fig. 2f-h) suggests that these sites receive a similar type of detrital input.

349 The POC content was markedly higher in the deeper stations (D, E, and F) than in the shallow  
350 shelf station (A) (Fig. 2i-l). This is consistent with station A being an erosion-transport bottom,  
351 where most of the fine-grained POC particles are washed away, to finally accumulate in the  
352 deeper stations (Carman and Cederwall, 2001; Nilsson et al., 2018).

353



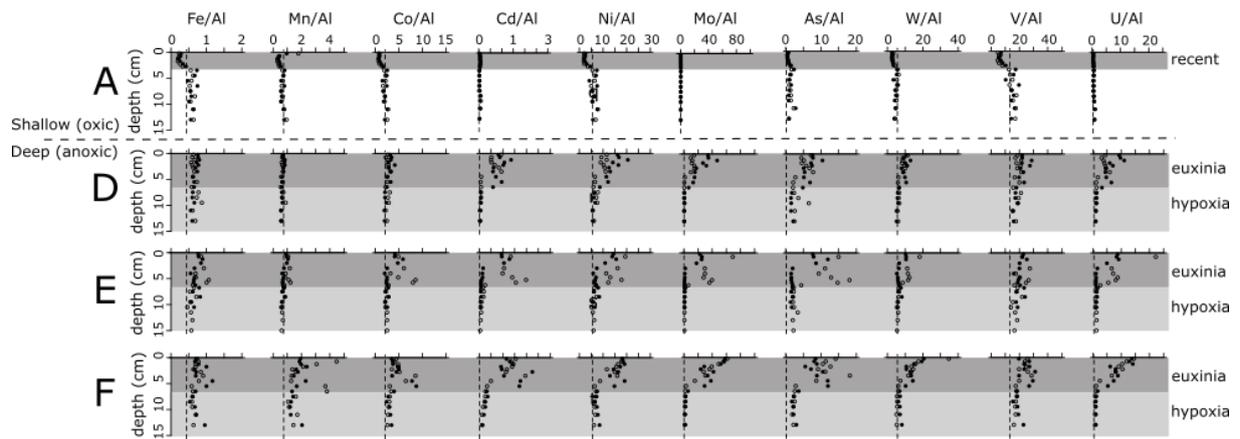
354

355 **Figure 2:** General sediment characterisation at the four sites (A, D, E, F). (a)-(d) Porosity depth profiles. Closed symbols are  
 356 porosity values from April 2016 (this study), empty symbols are from 2015 (Hall et al., 2017). (e)-(h) Solid phase Al/Ti molar  
 357 ratios at all sites recorded in April 2016. Open and closed symbols represent duplicate cores. The dashed line represents the  
 358 average molar Al/Ti ratio of the upper continental crust (McLennan, 2001). (i)-(l) Particulate organic carbon (POC)  
 359 concentrations in the sediment in April 2016. Open and closed symbols represent duplicate cores.  
 360

### 361 3.3 Solid-phase chemistry

362 Elemental concentrations (X) were normalized to Al, thus correcting for variations in the  
 363 magnitude of detrital input (Fig. 3). The X/Al ratios in the upper 4 cm of the shallow station  
 364 (A) were depleted (apart from Cd and U) relative to the sediment layers deeper than 4 cm, and  
 365 generally lower than the average crustal value. Tungsten was consistently offset compared to  
 366 the average crustal value, so we defined a local baseline (defined as the W/Al value of the  
 367 sediment layers below 4 cm depth of station A; Fig. 3). At stations D, E and F, the X/Al ratios  
 368 tended to be higher than the average crustal value, suggesting an enrichment in the deeper  
 369 stations relative to the detrital input. Fe was enriched above the average crustal value over the

370 whole core depth at all deep stations (Fe/Al ~ 1.7 times the average crust), while Mn showed  
 371 only a strong enrichment at the deepest station F (Mn/Al ~ 2.7 times the average crustal value).  
 372 All trace elements examined (Co, Cd, Ni, Mo, As, W, V, and U) showed a stronger enrichment  
 373 in the top 6 cm compared to the deeper sediment layers of the same core. Tungsten showed the  
 374 strongest enrichment at the deepest station (F). The average sediment accumulation rate for the  
 375 deep basin of the EGB is ~0.1 cm yr<sup>-1</sup> (Hille et al., 2006), and so the 6 cm depth horizon appears  
 376 to correspond to the onset of persistent anoxia and euxinia in the area in 1955-1974 (Carstensen  
 377 et al., 2014).



378  
 379 **Figure 3:** Depth profiles of X/Al ratios in sediments. Units are g/g for Fe/Al, 10<sup>-2</sup> g/g for Mn/Al and 10<sup>-4</sup> g/g for Co/Al, Cd/Al,  
 380 Ni/Al, Mo/Al, As/Al, W/Al, V/Al, and U/Al. The dashed line represents the X/Al ratio of the average upper crust (McLennan,  
 381 2001), apart for Tungsten, where we defined a local baseline (W/Al=7 10<sup>-4</sup> g/g). Dark gray shading in station A panels  
 382 represents the recent sediment (station A is an erosion-transport bottom and accumulates very little material). The dark gray  
 383 shading in stations D, E and F corresponds to sediments accumulated since the onset of deep-water euxinia in the deeper Baltic  
 384 Proper (~1955-1974), while light gray shading represents the anteceding period of deep-water hypoxia ([O<sub>2</sub>] < 62.5 μM; from  
 385 ~1906) (Carstensen et al., 2014). Open and closed symbols represent duplicate cores.

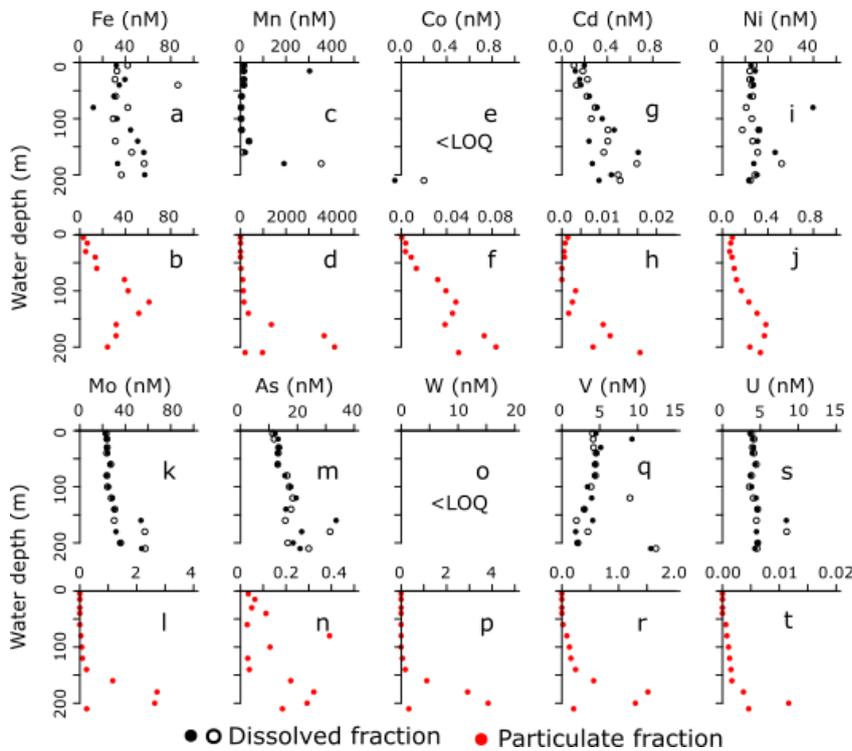
386

### 387 3.4 Water-column chemistry

388 Water column depth profiles of dissolved and suspended fractions were recorded in 2017.  
 389 Dissolved Fe, Ni, and U (dFe, dNi and dU) showed little variation with depth (Fig. 4a,i,s).  
 390 Consistent with previous observations (Hermans et al., 2019), concentrations of dMn were  
 391 elevated near the seafloor (Fig. 4c). Concentrations of dCd, dMo and dAs were relatively  
 392 constant over the first 50 m of the water column, below which concentrations gradually  
 393 increased (Fig. 4g,k,m). Dissolved V gradually decreased with depth (Fig. 4q). The particulate  
 394 fraction of Fe showed a peak at ~130 m water depth (Fig. 4b). In contrast, the particulate

395 fraction of Mn and trace elements showed a higher concentration at greater depth (Fig.  
 396 4d,f,h,j,l,n,p,r,t).

397



398

399 **Figure 4:** Water column depth profiles of dissolved ( $< 0.45 \mu\text{m}$ ) and particulate ( $> 0.45 \mu\text{m}$ ) fractions of (a),(b) Fe; (c),(d) Mn;  
 400 (e),(f) Co; (g),(h) Cd; (i),(j) Ni; (k),(l) Mo; (m),(n) As; (o),(p) W; (q),(r) V; (s),(t) U. Samples were collected at site F (water  
 401 depth = 210 m) in April 2017. Closed and open symbols represent duplicate samples for the dissolved fraction. Dissolved  
 402 concentrations of Mo, U, V and W have been normalised to salinity. Concentrations for elements below the Limit of  
 403 Quantification are marked as <LOQ.

404

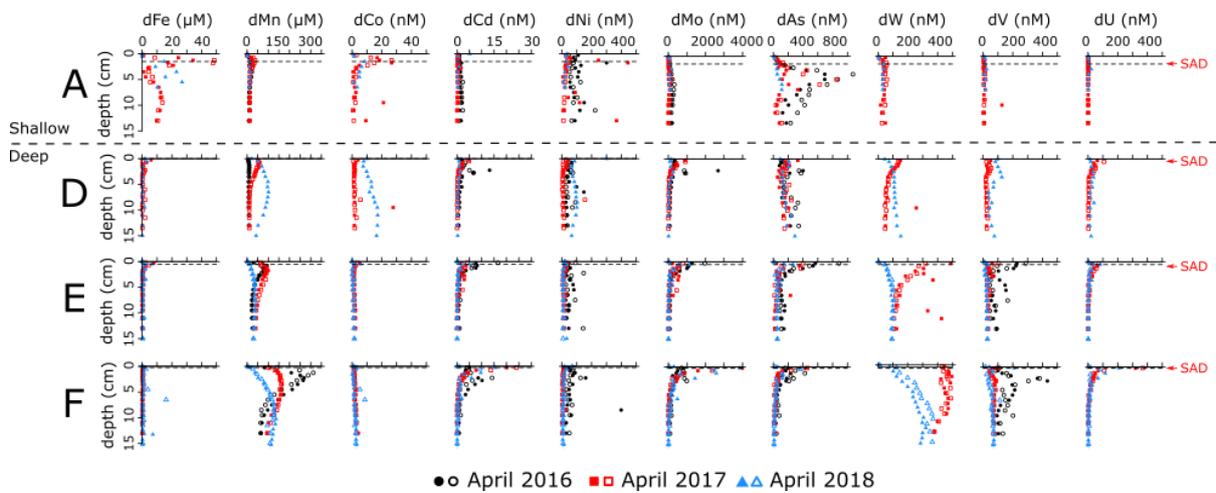
### 405 3.5 Pore water chemistry

406 Both dFe and dMn showed elevated concentrations in the upper 3-4 cm of the shallow station  
 407 (A) (Fig. 5), consistent with Fe and Mn cycles sustained by sediment mixing by burrowing  
 408 fauna and oxygenated overlying water (Aller, 1990; Thamdrup et al., 1994a; van de Velde and  
 409 Meysman, 2016). Note that in 2016, dFe was undetectable in the pore water at station A, though  
 410 this was likely due to the methodological problem. At the deeper stations, dFe was only present  
 411 in low concentrations near the sediment-water interface, and undetectable below the sulphide  
 412 appearance depth (the dashed line in Fig. 5; data taken from Marzocchi et al., 2018). In contrast,  
 413 dMn accumulated in the pore water of all stations after the inflow of oxygenated water (2017

414 for D, 2016 for E and F; Fig. 1c). The concentrations decreased with time, indicating that dMn  
 415 was either redistributed through the sediment column and/or removed via precipitation (Fig. 5).

416 At station A, the pore water concentration of dCo correlated with dFe (Fig. 5), while dCd  
 417 showed no trend with depth (Fig. 5). In the deeper stations, dCo and dCd only accumulated near  
 418 the sediment-water interface, except for dCo in 2018 at station D. (Fig. 5). The dCd  
 419 concentrations at the sediment-water interface increased with water depth (Fig. 5). Pore water  
 420 profiles of dNi did not show any trend with sediment depth in any of the stations (Fig. 5). In  
 421 2018, the concentrations of dCo and dNi were highest at station D, similar to dMn (Fig. 5).

422 The pore water concentrations of dMo and dAs peaked at ~4 cm in the shallow station A,  
 423 below the depth of Fe and Mn oxide reduction (Fig. 5). In the deeper stations, dAs and dMo  
 424 were enriched near the sediment-water interface, and decreased with sediment depth (Fig. 5).  
 425 Dissolved W, dV and dU did not accumulate in the pore water of station A (Fig. 5). In the  
 426 deeper stations, dW and dV appeared to respond to the oxygenation events in the same way as  
 427 dMn (Fig. 5). In contrast, dU concentrations showed increasing trends with station water depth,  
 428 similar to dCd (Fig. 5).



429  
 430 **Figure 5:** Pore water depth profiles recorded at stations A (water depth = 60 m, top row), D (water depth = 130 m, second  
 431 row), E (water depth = 170 m, third row) and F (water depth = 210 m, bottom row) in April 2016, April 2017 and April 2018.  
 432 Depth profiles from two replicate cores are shown (closed and open symbols). Black dashed line indicates depth where  
 433 dissolved sulphide started accumulating (Sulphide Appearance Depth; SAD) in 2016 (depths were identical in 2017, except for  
 434 station D where it was ~0.1 cm; Marzocchi et al., 2018).

435

### 436 3.6 Benthic fluxes

437 Sedimentary effluxes are reported as positive fluxes while sedimentary uptake are reported  
 438 as a negative flux. Benthic fluxes from the shallow station A, which had a fully oxygenated  
 439 water column, did not vary between sampling times for any of the redox-sensitive elements  
 440 (Table 2). Fluxes of dFe and dMn measured at this station fell within the range of previously *in*  
 441 *situ* measured fluxes of dFe and dMn in continental margin sediments underlying fully  
 442 oxygenated bottom waters (Table 2). The fluxes of the other trace elements were a few orders  
 443 of magnitude lower than the fluxes of dFe and dMn, and were found to be in the same range as  
 444 previously measured fluxes in the a range of sediments, although dAs fluxes were slightly  
 445 elevated compared to previously reported values from the Venice Lagoon (Table 2).

446 **Table 2:** Recorded range of significant fluxes at the oxic station (A) compared to fluxes found in the literature. All  
 447 significant fluxes are reported in Supplementary Table 4. BW = bottom water.

Year	BW O <sub>2</sub> (μM)	Flux range (μmol m <sup>-2</sup> d <sup>-1</sup> )				
		Fe	Mn	Co	Cd	Ni
2016	340	+80	+26 – +28	-	-	+1.1 – +1.2
2017	110	+18	+12 – +35	-	-0.06 – +0.02	+1.1
	300	-	+14 – +34	-	-0.02	-2.6
2018	340	-	+50 – +110	-	-	+0.4 – +1.3
	340	+17	+6 – +112	-	-	+0.7 – +3.0
<i>Literature range</i>		<i>-0.2 – +568<sup>1-6</sup></i>	<i>+3 – +1300<sup>2,3,7,8</sup></i>	-	<i>+0.013 – +0.05<sup>9,10</sup></i>	<i>+0.209<sup>10</sup></i>

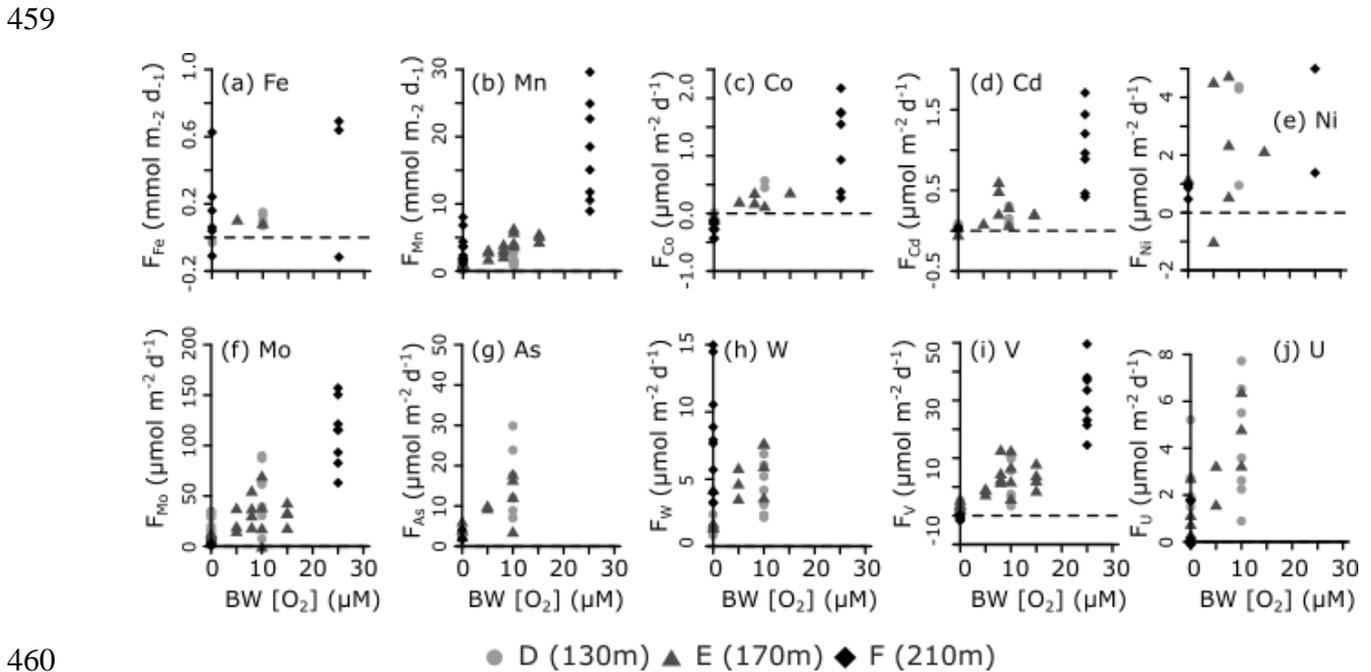
  

Year	BW O <sub>2</sub> (μM)	Flux range (μmol m <sup>-2</sup> d <sup>-1</sup> )				
		Mo	As	W	V	U
2016	340	+0.8 - +2	-	-	+0.2 – +0.4	-
2017	110	-	+1.5	-	+0.3 – +0.7	-0.03
	300	-	-	-0.55	-	-
2018	340	-	+0.3 – +0.5	+0.8	+0.2 – +0.3	+0.03 – +0.04
	340	+0.2 - +2	-	+0.2 – +0.5	+0.4 – +0.5	+0.2
<i>Literature range</i>		<i>-1.66 – +1.22<sup>9</sup></i>	<i>-0.04 – +0.06<sup>9</sup></i>	-	<i>-2.0 – +0.31<sup>9</sup></i>	<i>-7.5 – +20.4<sup>11</sup></i>

448 <sup>1</sup>(Elrod et al., 2004), <sup>2</sup>(Pakhomova et al., 2007), <sup>3</sup>(Almroth et al., 2009), <sup>4</sup>(Severmann et al., 2010), <sup>5</sup>(Noffke et al., 2012),  
 449 <sup>6</sup>(Lenstra et al., 2018), <sup>7</sup>(Thamdrup et al., 1994b), <sup>8</sup>(Berelson et al., 2003), <sup>9</sup>Venice Lagoon (Turetta et al., 2005),  
 450 <sup>10</sup>Gullmarsfjorden (Sundby et al., 1986; Westerlund et al., 1986), <sup>11</sup>(Point et al., 2007).

451  
 452 In the deeper stations (D-F), dFe, dMn, dV, dMo, dU, dCo, dCd, and dAs responded in a  
 453 consistent way to the transient oxygenation event. The highest benthic effluxes were measured  
 454 when the bottom water oxygen concentrations were the highest, and lower fluxes were  
 455 measured during the anoxic periods (Fig. 6). Notable exceptions are the dMn and dW fluxes  
 456 which remained relatively elevated at station F after return to anoxia. The fluxes of dFe and

457 dNi furthermore showed substantial variability, although higher fluxes of dNi were generally  
 458 found at intermediate oxygen concentrations.



461 **Figure 6:** *In situ* measured trace element fluxes at the deeper stations (D, E, F) versus *in situ* measured bottom water O<sub>2</sub>  
 462 concentration (as reported in Table 1). Note that duplicate lander deployments have now been split up (bottom water O<sub>2</sub>  
 463 concentrations varied between deployments). Only statistically significant fluxes are shown (see section 2.2). All significant  
 464 fluxes are reported in Supplementary Table 4.

465

#### 466 4. DISCUSSION

467 The deeper stations (D-F) of the EGB are long-term anoxic, but experienced a transient  
 468 oxygenation in 2015 (stations E and F) and 2016 (station D) (Fig. 1c). Following these  
 469 oxygenation events, trace element effluxes were generally higher than during bottom water  
 470 anoxia (Fig. 6). The exposure of long-term anoxic sediments to oxygenated bottom water can  
 471 lead to an increase in benthic effluxes via two mechanisms (see e.g. Scholz et al., 2011). Firstly,  
 472 oxygenation of the bottom water can lead to the formation of metal (hydr)oxide minerals in the  
 473 water column, which sink out and settle onto the sediment surface. Within the sediment, these  
 474 metal (hydr)oxides become subsequently reduced, thus leading to a transient increase in the  
 475 benthic release. Secondly, penetration of oxygen into the sediment can lead to oxidation and  
 476 dissolution of authigenic minerals previously formed under anoxic bottom water conditions. In

477 the first case, the increased efflux is caused by the *reduction of oxidised minerals*, following an  
478 increase in trace element supply to the sediment, leading to enhanced sedimentary recycling of  
479 the element (this typically occurs at the sediment-water interface). In contrast, in the second  
480 case, the increased benthic efflux is caused by *oxidation of reduced minerals* in the sediment,  
481 and in this way, elements that would be otherwise buried are now remobilised. Therefore, we  
482 propose to name the first mechanism (reduction in the sediment) ‘**enhanced elemental**  
483 **recycling**’. For the second mechanism (oxidation in the sediment) we propose ‘**oxidative**  
484 **remobilisation**’. Whether a particular element shows a higher benthic efflux due to enhanced  
485 elemental recycling or oxidative remobilisation depends on its redox and adsorption properties.

486 It is difficult to distinguish between the two mechanisms based on benthic flux data alone,  
487 as both mechanisms will lead to higher effluxes after the inflow of oxygen. Additionally, they  
488 will both lead to accumulation of solutes in the pore water after dissolution of either the Fe or  
489 Mn oxide carrier or the authigenic mineral. To distinguish between the mechanisms, we can  
490 compare the element-to-aluminum ratio (X/Al) of the suspended particles in the water column  
491 with the X/Al ratio of the upper few centimetres of the sediment column. If the X/Al ratio in  
492 the water column is higher than the X/Al ratio of the sediment, the particulate input to the  
493 sediment of the element in question is higher after the inflow compared to before the inflow.  
494 The higher input to the sediment is then likely the consequence of the inflow of oxygenated  
495 water and suggests enhanced elemental recycling. In the case of oxidative remobilisation, one  
496 would expect a decrease in X/Al ratio of the sediment (since authigenic minerals in the sediment  
497 are being dissolved), with the X/Al ratio of the detrital input being the minimum value.  
498 However, the X/Al ratio in the water column would also be lower, since no new reduced  
499 authigenic minerals are formed in the water column. The X/Al composition of the water column  
500 would then be expected to reflect the ratio of the detrital input. Thus, if the X/Al ratio of the  
501 water column is comparable to or lower than the X/Al of the sediment, the enhanced benthic  
502 release is likely related to oxidative remobilisation. This approach assumes that there was no  
503 significant recycling in the sediment after deposition under anoxic conditions because the X/Al  
504 ratio in the water column would then always be higher than in the sediment. Since the EGB was  
505 euxinic before the inflow (Sommer et al., 2017), one expects a limited recycling of elements  
506 that form sulphides (i.e. Fe, Co, Cd, Ni) or of elements that are retained under euxinic conditions  
507 (Mo, As, W, V, U). We therefore believe that the comparison of metal-to-aluminum ratios can  
508 give us some insight into the exact source of the measured flux.

509

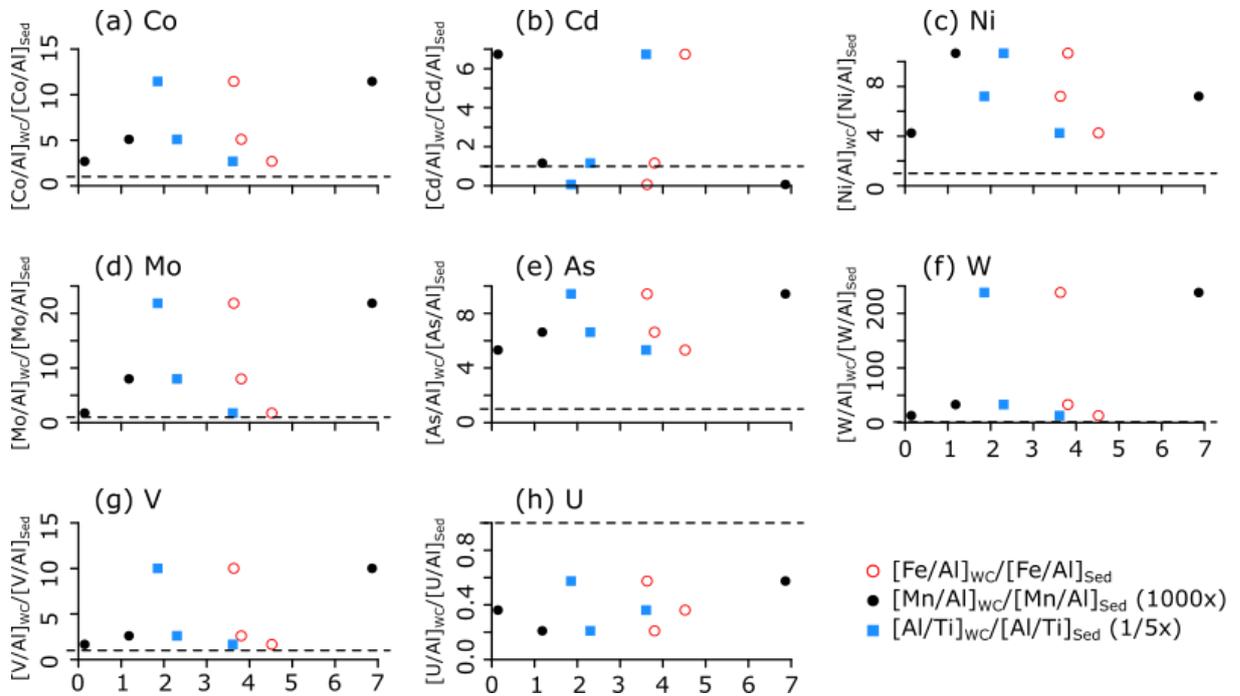
#### 510 **4.1 Major carrier phases: Fe and Mn**

511 During an inflow of oxygenated water, Fe and Mn are expected to form oxides in the water  
512 column, sink to the sediment, experience reduction and be released back to the water column  
513 as soluble  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$ . These reduced species are then re-oxidised again, leading to higher  
514 X/Al ratios in the water column (Sulu-gambari et al., 2017; Hermans et al., 2019). Indeed, both  
515 Fe and Mn had a higher X/Al ratio in the water column than in the sediment (Fig. 7). For Fe  
516 however, the higher ratios in the water column also persisted after the water column had turned  
517 anoxic again at station F in 2017, indicating the ventilation was muted in the deepest part of the  
518 basin. This is consistent with the observed dFe fluxes, which are of a similar magnitude for  
519 sediments underlying anoxic and hypoxic water columns (Fig. 6a). Iron did show higher benthic  
520 fluxes after the inflow (Fig. 6a), but the increase was limited to  $\sim +0.6 \text{ mmol m}^{-2} \text{ d}^{-1}$ , which is  
521 comparable to dFe fluxes observed in San Pedro basin sediments underlying low-oxygen  
522 bottom waters ( $\sim +0.6 \text{ mmol m}^{-2} \text{ d}^{-1}$ ; Severmann et al., 2010).

523 In contrast, Mn showed much higher water column X/Al ratios at stations D and E (hypoxic  
524 in 2017), and the dMn fluxes had increased to  $+30 \text{ mmol m}^{-2} \text{ d}^{-1}$  (Fig. 6b), which was three  
525 orders of magnitude higher than those before the MBI ( $+7.1 - +8.2 \mu\text{mol m}^{-2} \text{ d}^{-1}$ ; Neretin et al.,  
526 2003). Generally, distinct Mn carbonates sedimentary layers in Baltic Sea sediments have been  
527 found to correspond to (long-lasting) inflows of oxygenated water (Huckriede and Meischner,  
528 1996; Neumann et al., 1997; Sternbeck and Sohlenius, 1997; Neumann et al., 2002; Scholz et  
529 al., 2013). During short-lived inflow events, however, Mn carbonate formation is limited  
530 (Heiser et al., 2001). Indeed, we found that dMn accumulated in the pore water after the inflow  
531 of oxygenated water (Fig. 5), indicating that very little Mn was retained in the sediment as e.g.  
532 Mn-rich carbonate minerals. This is consistent with the limited solid-phase enrichments (Fig.  
533 3) and previous observations from the 2015 inflow event (Scholz et al., 2018; Dellwig et al.,  
534 2018). Our results support the hypothesis of Hermans et al. (2019), who suggested that high  
535 concentrations of suspended Mn oxides observed in the deep waters of the basin could be  
536 caused by enhanced Mn recycling due to the absence of an efficient sink in the sediments of the  
537 western flank of the EGB.

538 Before the MBI event, the dFe concentrations in the water column were 10 to 15 times lower  
539 than the dMn concentrations (Fig. 4a-d; Hermans et al., 2019), and so it was expected that the

540 dFe efflux would be smaller than the dMn efflux after the inflow. Indeed, just after the inflow  
 541 (in 2016), the measured dMn flux at station F was 30 times higher than that of dFe (Fig. 6a,b).  
 542 The release of dFe to the water column was likely further limited by the formation of insoluble  
 543 FeS in the sediment. Iron sulphide formation is supported by the pore water profiles of dFe,  
 544 which show no accumulation in any of the deep stations (Fig. 5). Based on the bottom water  
 545 concentration ratio between dMn and dFe, the enhanced release of dFe (without any trapping)  
 546 should be 10-15 times smaller than the dMn flux, i.e.  $+1.2 - +1.8 \text{ mmol m}^{-2} \text{ d}^{-1}$ . However, only  
 547  $+0.6 \text{ mmol m}^{-2} \text{ d}^{-1}$  was released, which indicates that 50-70% of the dFe was trapped as FeS.  
 548 This highlights the role of free sulphide as a very efficient Fe trap, consistent with the close  
 549 correlation between Fe and S in the solid phase of the EGB and other deep basins in the Baltic  
 550 Sea (Suess, 1979; Sternbeck and Sohlenius, 1997; Scholz et al., 2013; Dijkstra et al., 2016).



552 **Figure 7:** Correlation between water column enrichments relative to sediment enrichments (calculated as the metal-to-  
 553 aluminum ratio of the water column relative to the metal-to-aluminum ratio of the sediment;  $[X/Al]_{wc}/[X/Al]_{sed}$ ) of each of the  
 554 trace elements studied versus the water column enrichments of Fe (hollow red circles), Mn (filled black circles) and Ti (filled  
 555 blue squares) for stations D, E and F. The dashed line indicates 1, values plotted below this value show depletion in the water  
 556 column, values above this line are enriched in the water column.

## 557 4.2 Divalent cations (Co, Cd and Ni)

558 The divalent cations (Co, Cd and Ni) can adsorb onto Fe or Mn oxides (Gendron et al., 1986;  
 559 Kay et al., 2001), but are also particle-reactive and hence can adsorb on other carrier phases as  
 560 well, like organic matter or clays (O'Connor and Kester, 1975; Sheng et al., 2004;  
 561 Vijayaraghavan et al., 2005). Dissolved Co and dCd showed higher fluxes right after the inflow

562 (Fig. 6c,d), whereas this trend was less obvious for dNi due to high scatter in the data (Fig. 6e).  
563 The water column enrichment of Co correlated positively with that of Mn (Fig. 7a), indicating  
564 that Co adsorption to, or incorporation of Co in Mn oxides (Lee and Tebo, 1994; Moffett and  
565 Ho, 1996), drove the input of Co to the sediment. The enhanced release of dCo after the inflow  
566 was thus likely caused by the enhanced input of Mn oxide minerals to the sediment and the  
567 subsequent reductive dissolution of the carrier phase. After the inflow, dCo did not accumulate  
568 in the pore water (apart from one observation at station D in 2018; Fig. 5), indicating that some  
569 of the Co was retained in the sediment, likely due to incorporation in FeS minerals (Wallmann,  
570 1992; Saito and Moffett, 2002). When the water column returned to anoxia, Co was taken up  
571 by the sediment (Fig. 6c), probably due to co-precipitation with sulphide minerals (Wallmann,  
572 1992).

573 Water column enrichments of Cd showed an inverse correlation with Mn and seemed to  
574 correlate better with Fe or Ti (indicative of detrital material) (Fig. 7b). This could suggest that  
575 Cd preferentially adsorbs on Fe oxides rather than on Mn oxides, although it is known to adsorb  
576 on both (Gadde and Laitinen, 1974). Alternatively, it could indicate that Cd transport to the  
577 sediment was preferentially controlled by detrital input and potential adsorption on clay (Suraj  
578 et al., 1998), rather than on Fe or Mn (hydr)oxides. The Cd/Al ratio in the water column was  
579 generally lower than or similar to the Cd/Al ratio in the sediment of the stations that were  
580 hypoxic in 2017 (D and E) (Fig. 7b). This similarity suggests that Cd likely experienced  
581 oxidative remobilisation, rather than an enhanced input and recycling. Cadmium is indeed  
582 known to be susceptible to remobilisation following re-exposure to oxygen (Westerlund et al.,  
583 1986; Tribovillard et al., 2006). Interestingly, the dCd pore water profile in 2016 at station F  
584 showed a peak well below the sulphide appearance depth, which could be caused by dCd release  
585 following the dissolution of an oxide carrier phase (Fig. 5). At this station, the Cd/Al  
586 enrichments in the water column were also higher than in the sediment (Fig. 7b). Dissolved Cd  
587 concentrations in the water column increased with water depth, which could lead to differences  
588 in adsorption capacity. Overall, the response of Cd to re-oxygenation seems to differ between  
589 stations and is likely very dependent on local conditions.

590 Benthic dNi fluxes did not show a clear trend with oxygen concentration (Fig. 6e), nor did  
591 the water column enrichment seem to correlate with Fe, Mn or Ti (Fig. 7c). Potentially, Ni  
592 transport is predominantly controlled by adsorption on organic compounds, rather than on Fe  
593 or Mn oxides (Vijayaraghavan et al., 2005). Additionally, Ni is less likely to experience

594 oxidative remobilisation and should therefore serve as a good indicator of primary production,  
595 as previously reported (Tribovillard et al., 2006; Böning et al., 2015). Overall, our data suggest  
596 that Ni was not very sensitive to the transient re-oxygenation event.

### 597 **4.3 Metalloids (Mo, As and W)**

598 All three metalloids (Mo, As and W) showed higher benthic effluxes when the water column  
599 was oxygenated (Fig. 6f,g,h). After the return to anoxia, however, dMo and dAs fluxes rapidly  
600 decreased, while dW fluxes remained high (Fig. 6h). This indicates that all three elements have  
601 a similar response to oxygenation, but show a divergent response when anoxia returns.

602 Molybdenum enrichments in the water column correlated well with Mn enrichments (Fig.  
603 7d), consistent with previous observations of the relation between formation of Mn oxides in  
604 the water column and the delivery of Mo to the sediment (Berrang and Grill, 1974; Scholz et  
605 al., 2013; Sulu-Gambari et al., 2017). However, the benthic dMo fluxes rapidly decreased when  
606 the water column returned to anoxia (Fig. 6f), while dMn fluxes remained high (Fig. 6b).  
607 Additionally, Mo did not accumulate much in the pore water (Fig. 5). These factors indicate  
608 that a fraction of the Mo was retained in the sediment, potentially sequestered by organic matter  
609 within the sulfidic zone (Scholz et al., 2018). Our observations hence agree with a recent study  
610 by Scholz et al. (2018) on the impact of the MBI on Mo cycling in the Gotland Basin.

611 Overall, the As cycle was highly similar to that of Mo following the transient re-oxygenation.  
612 Water column enrichments correlated closely with Mn (Fig. 7e), fluxes rapidly decreased after  
613 the return to anoxia (Fig. 6e) and accumulation in the pore water was limited to the sediment-  
614 water interface (Fig. 5). This again suggests an enhanced delivery to the sediment via adsorption  
615 on oxide minerals, followed by retention of a fraction of the As in the euxinic sediment, likely  
616 sequestered in iron-sulphide minerals (Huerta-Diaz and Morse, 1992).

617 Immediately following the transient oxygenation, W responded similarly to Mo and As.  
618 Water column enrichments correlated with Mn enrichments (Fig. 7f), consistent with the  
619 adsorption of W on Mn oxides (Gustafsson, 2003; Dellwig et al., 2019). However, after the  
620 dissolution of the oxides in the sediment, W accumulated in the pore water (Fig. 5) and benthic  
621 fluxes remained high after return to anoxic conditions (Fig. 6h). The lack of efficient trapping  
622 in anoxic conditions, and the lack of a downward flux in the pore water (Fig. 5) suggests that  
623 very little – if any – W was retained in the sediment. The latter could be caused by the formation

624 of thioesters in the sulphidic pore water, which reduce the adsorption capacity of the W  
625 complex (Cui and Johannesson, 2017).

#### 626 **4.4 Vanadium**

627 In oxygenated conditions, V is particle reactive and can adsorb onto Fe or Mn oxides (Wehrli  
628 and Stumm, 1989b), which is evident from the correlation between the water column  
629 enrichment of V and Mn (Fig. 7g). The enhanced benthic fluxes of V after the inflow event  
630 (Fig. 6i) are thus likely related to an enhanced sedimentary deposition of V associated with Mn  
631 oxides, which has been proposed earlier by Scholz et al. (2013). Pore water accumulation of V  
632 was limited (Fig. 5), and V fluxes rapidly decreased when the bottom waters returned to anoxia  
633 (Fig. 6i). This indicates that at least a fraction of the V that entered the sediment adsorbed on  
634 oxide minerals was retained (Scholz et al., 2013). The retention of V is driven by the reduction  
635 from its V(V) form to its V(IV) or V(III) forms under reducing conditions. The reduced forms  
636 of V can either form insoluble oxide or hydroxide phases, or adsorb on particles (Emerson and  
637 Husted, 1991; Wanty and Goldhaber, 1992).

#### 638 **4.5 Uranium**

639 In its oxidised form, U can adsorb on Fe or Mn oxides (Waite et al., 1994; Wang et al., 2013).  
640 However, the U/Al ratios in the water column were consistently lower than in the sediment, and  
641 there was no correlation with Fe, Mn, or Ti (Fig. 7h). The lack of enrichment in the water  
642 column indicates that the enhanced benthic fluxes after the oxygenation event (Fig. 6j) were  
643 most likely related to oxidative remobilisation. Pore water profiles of dU showed a  
644 concentration peak at the sediment-water interface (Fig. 5), which suggests that dU was released  
645 due to the oxidative dissolution of authigenic U minerals. Uranium is known to be susceptible  
646 to remobilisation following re-exposure to oxygen (Anderson et al., 1989; Barnes and Cochran,  
647 1990).

648 The source for U is authigenic minerals that had been formed in the upper 3 mm of the  
649 sediment of stations D, E, and F before the MBI. Most likely, the measured fluxes represent a  
650 combination of dissolution of authigenic minerals and elements released during the  
651 mineralisation of organic matter. Nevertheless, the measured dU fluxes were consistently  
652 higher after the inflow of oxygenated water, suggesting that authigenic minerals were being  
653 dissolved. In contrast to Zheng et al. (2002), who reported a threshold oxygen level of 15  $\mu\text{M}$   
654 above which U remobilisation occurs, our results show that even a limited transient increase of

655 oxygen can lead to measurable losses of U from the sediment. For instance, in 2017, the bottom  
656 water oxygen concentration at station E was  $< 10 \mu\text{M}$ , while the benthic dU flux reached  $\sim +4$   
657  $\mu\text{mol m}^{-2} \text{d}^{-1}$ . This is more than twice the flux measured when station E returned to anoxia in  
658 2018 (Fig. 6j).

#### 659 **4.6 Wider implications for oxygenation and trace nutrient fertilisation**

660 Primary productivity is limited by the availability of Fe and other trace elements in large  
661 regions of the ocean (Mahowald et al., 2018; Baeyens et al., 2018). Sediments underlying an  
662 oxic water column generally release a fraction of the reactive Fe, Mn and trace elements that  
663 are deposited in solid forms (as shown by the predominantly positive fluxes in Table 2), and  
664 are thus likely a significant source of these elements (Elrod et al., 2004; Severmann et al., 2010;  
665 Dale et al., 2015). In contrast, sediments underlying a euxinic water column release a much  
666 smaller fraction (if any) of the trace element input they receive, in particular for elements that  
667 form sulphide minerals or get incorporated in FeS minerals, and thus act as permanent sinks for  
668 Fe and other trace elements. Changes in the oxygenation state of the water column can therefore  
669 have important consequences for the ocean's trace element inventory.

670 A clear example of this is the oxygen minimum zone in the Peru upwelling system. Over the  
671 past 140,000 years, iron limitation has been shown to limit denitrification during times when  
672 the oxygen minimum zone has been larger, due to efficient sedimentary retention of Fe under  
673 more strongly reducing conditions (Scholz et al., 2014). As a result of increasing climate  
674 change, oxygen minimum zones are expected to expand in the coming decades (Keeling et al.,  
675 2010). It is thus plausible that the euxinic sink for Fe and other trace elements will increase over  
676 time (Scholz et al., 2014). Our results here indicate that the transient re-oxygenation of a euxinic  
677 system leads to enhanced delivery of Fe, Mn, and trace elements to the sediment. After re-  
678 establishment of anoxia, Mn and W are readily recycled to the water column, but at least  
679 fractions of Fe, Co, Mo, As, and V are retained in the sediment. Hence, while expanding the  
680 euxinic sink will lead to less recycling back to the water column, transient re-oxygenation of  
681 these euxinic systems will promote the long-term burial of Fe and other trace elements. This  
682 would decrease the ocean's trace element inventory even more, potentially further constraining  
683 primary productivity in regions where trace elements are limiting.

684 **5. SUMMARY AND CONCLUSIONS**

685 We have conducted *in situ* measurements of benthic dissolved element fluxes following  
686 transient oxygenation of long-term (~10 year) anoxic sediments. Our results indicate that the  
687 oxygenation event caused by an Major Baltic Inflow in the Eastern Gotland Basin increased the  
688 benthic effluxes of Fe, Mn, V, Mo, Co, W, and As via ‘enhanced elemental recycling’ – the  
689 sedimentary reduction of metal oxides formed in the water column. Uranium was released due  
690 to ‘oxidative remobilisation’ – the re-oxygenation of previously anoxic sediments, which leads  
691 to dissolution of authigenic minerals. The sedimentary release of Cd was strongly dependent  
692 on local conditions, and was found to be a result of both mechanisms. Nickel showed limited  
693 response to the transient oxygenation.

694 Our results suggest that the oxygenation event led to a transiently enhanced input of Fe, Mn,  
695 Co, Mo, As, W, and V into the sediment, predominantly modulated by the formation of Mn  
696 oxides in the water column. Iron oxides were less important as a carrier phase, most likely due  
697 to the limited presence of dFe in the water column before the inflow. Cadmium, Ni, and U were  
698 less strongly affected by water column oxide formation, and Cd and U were likely lost from the  
699 sediment because of oxidative dissolution of reduced minerals. After the transient input of Fe,  
700 Mn Co, Mo, As, W, and V, the oxides dissolved in the sediment. This lead to almost quantitative  
701 recycling of Mn and W to the water column. In contrast, a fraction of the Fe, Co, Mo, As, and  
702 V that entered the sediment were converted to sulphide minerals or formed insoluble reduced  
703 minerals, which lead to enhanced retention of these elements in the sediment after the re-  
704 establishment of anoxia.

705 Overall, our results suggest that transient re-oxygenation of a previously euxinic water  
706 column only has a transient effect on Mn or W, but promotes the burial of Fe, Co, Mo, As, and  
707 V. A climate change driven increase in the spatial extent of regions underlying euxinic water  
708 columns, in combination with transient re-oxygenation events, could potentially lead to more  
709 frequent transient re-oxygenation events. Over longer time scales, the resulting enhanced  
710 removal of Fe and other bio-essential trace elements from the water column via burial in the  
711 sediments could potentially lead to trace element limitation of primary production in regions  
712 where these euxinic zones develop.

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- 1081

1082 **Appendix to Elevated sedimentary removal of Fe, Mn, and**  
 1083 **trace elements following a transient oxygenation event in**  
 1084 **the Eastern Gotland Basin, central Baltic Sea – by van de**  
 1085 **Velde et al.**

1086

1087 **Appendix 1 – Supplementary Tables**

1088

1089 **Supplementary Table 1:** Limit of Detection (determined as 3 times the standard deviation of five replicate acidified blank  
 1090 samples) and Limit of Quantification (determined as 10 times the standard deviation of five replicate acidified blank samples)  
 1091 for the HR-ICP-MS measurements of water samples.

	Limit of Detection		Limit of Quantification	
	$\mu\text{g L}^{-1}$	nM	$\mu\text{g L}^{-1}$	nM
Fe	0.09	2	0.3	5
Mn	0.02	0.4	0.07	1
Co	0.01	0.2	0.05	0.8
Cd	0.004	0.03	0.01	0.1
Ni	0.05	0.8	0.2	3
Mo	0.01	0.1	0.04	0.4
As	0.04	0.5	0.1	2
W	0.1	0.6	0.4	2
V	0.02	0.5	0.08	2
U	0.0004	0.002	0.001	0.005

1092

1093 **Supplementary Table 2:** Limit of Detection (determined as 3 times the standard deviation of five replicate acidified blank  
 1094 samples) and Limit of Quantification (determined as 10 times the standard deviation of five replicate acidified blank samples)  
 1095 for the total digestion of solid samples.

	Limit of Detection		Limit of Quantification	
	$\mu\text{g g}^{-1}$	$\text{nmol g}^{-1}$	$\mu\text{g g}^{-1}$	$\text{nmol g}^{-1}$
Al	50	2000	200	6000
Ti	1	20	4	70
Fe	10	200	30	600
Mn	0.06	1	0.2	4
Co	0.003	0.05	0.01	0.2
Cd	0.006	0.05	0.02	0.2
Ni	0.01	0.2	0.04	0.6
Mo	0.02	0.2	0.06	0.6
As	0.2	2	0.5	7
W	0.1	0.6	0.3	2
V	0.04	0.8	0.1	3
U	0.01	0.05	0.04	0.2

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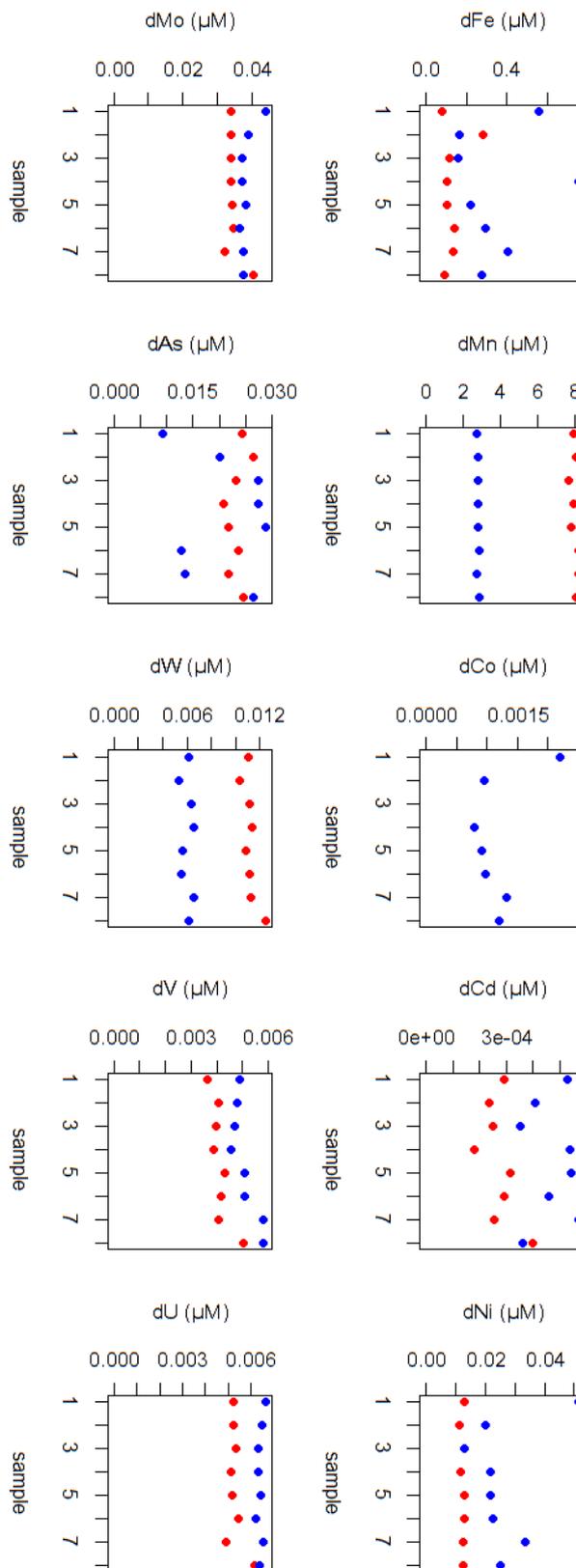
**Supplementary Table 3:** Measured concentrations of the reference material and certified concentrations. No CRM for tungsten is yet available, but values reported by Dellwig et al. (2019) for SLRS-6 ( $0.01 \mu\text{g L}^{-1}$ ) were below our LOQ and LOD for tungsten (Supplementary Table 1). SLEW-3 reference material was measured during the first campaign (2016), we adapted the sampling protocol for 2017 and 2018 (less acid per volume sample and 10 times dilution), which increased the performance of our method and is likely the reason why measurements of Fe and Cd deviate from the certified concentration of the SLEW-3 CRM.

MESS - 3					Water CRMs					
	This study (n=12)	Certified	Accuracy %	Precision %			This study	Certified	Accuracy %	Precision %
Al (wt %)	$7.6 \pm 0.7$	$8.59 \pm 0.23$	-12	9.2	<b>CRM</b>					
Ti (wt %)	$0.39 \pm 0.01$	$0.44 \pm 0.06$	-11	2.6	Fe ( $\mu\text{g L}^{-1}$ )	SLEW- 3	<b><math>3 \pm 2</math> (n=4)</b>	$0.561 \pm 0.058$	<b>+435</b>	<b>67</b>
Fe (wt %)	$4.01 \pm 0.39$	$4.34 \pm 0.11$	-7.6	9.7		SLRS-6	$79 \pm 2$ (n=3)	$84.5 \pm 3.6$	-6.5	2.5
Mn (ppm)	$284 \pm 30$	$324 \pm 12$	-12	11		1640	$37.1 \pm 0.4$ (n=3)	$36.5 \pm 1.7$	+1.6	1.1
Co (ppm)	$12.9 \pm 1.3$	$14.4 \pm 2.0$	-10	10	Mn ( $\mu\text{g L}^{-1}$ )	SLEW- 3	$1.9 \pm 0.3$ (n=4)	$1.59 \pm 0.22$	+19	16
Cd (ppm)	$0.27 \pm 0.03$	$0.24 \pm 0.01$	+12	11		SLRS-6	$2.0 \pm 0.2$ (n=3)	$2.12 \pm 0.10$	-5.6	10
Ni (ppm)	$43 \pm 5$	$46.9 \pm 2.2$	-8.3	12		1640	$37 \pm 4$ (n=3)	$40.07 \pm 0.35$	-7.7	11
Mo (ppm)	$2.56 \pm 0.13$	$2.78 \pm 0.07$	-7.9	5.1	Co ( $\mu\text{g L}^{-1}$ )	SLEW- 3	$0.05 \pm 0.01$ (n=4)	$0.040 \pm 0.010$	+25	20
As (ppm)	$22.6 \pm 4$	$21.2 \pm 1.1$	+6.6	18		SLRS-6	$0.055 \pm 0.001$ (n=3)	$0.053 \pm 0.012$	+3.8	1.8
W (ppm)	$38 \pm 1$	-	-	-		1640	$19.3 \pm 0.2$ (n=3)	$20.08 \pm 0.24$	-3.9	1.0
V (ppm)	$236 \pm 23$	$243 \pm 10$	-2.9	9.7	Cd ( $\mu\text{g L}^{-1}$ )	SLEW- 3	<b><math>0.09 \pm 0.01</math> (n=4)</b>	$0.047 \pm 0.004$	<b>+91</b>	<b>11</b>
U (ppm)	$3.76 \pm 0.15$	4*	-6.0	4.0		SLRS-6	<LOQ	$0.0063 \pm 0.0014$	-	-
						1640	$3.8 \pm 0.2$ (n=3)	$3.961 \pm 0.072$	-4.1	5.3
					Ni ( $\mu\text{g L}^{-1}$ )	SLEW- 3	$1.31 \pm 0.08$ (n=4)	$1.21 \pm 0.07$	+8.3	6.1
						SLRS-6	$0.62 \pm 0.02$ (n=3)	$0.617 \pm 0.022$	+0.5	3.2
						1640	$24.6 \pm 0.4$ (n=3)	$25.12 \pm 0.12$	-2.1	1.6
					Mo ( $\mu\text{g L}^{-1}$ )	SLEW- 3	$5.5 \pm 0.8$ (n=4)	5.1*	7.8	15
						SLRS-6	$0.17 \pm 0.02$ (n=3)	$0.215 \pm 0.018$	-21	17
						1640	$45 \pm 2$ (n=3)	$45.24 \pm 0.59$	-0.5	4.4
					As ( $\mu\text{g L}^{-1}$ )	SLEW- 3	$1.8 \pm 0.4$ (n=4)	$1.36 \pm 0.09$	+32	22
						SLRS-6	$0.584 \pm 0.005$ (n=3)	$0.57 \pm 0.08$	+2.5	0.9
						1640	$8.07 \pm 0.1$ (n=3)	$8.010 \pm 0.067$	+0.7	1.2
					W ( $\mu\text{g L}^{-1}$ )	SLEW- 3	-	-	-	-
						SLRS-6	< LOQ	-	-	-
						1640	< LOQ	-	-	-
					V ( $\mu\text{g L}^{-1}$ )	SLEW- 3	$3.3 \pm 0.2$ (n=4)	$2.54 \pm 0.31$	+30	6.1
						SLRS-6	$0.367 \pm 0.005$ (n=3)	$0.352 \pm 0.006$	+4.3	1.4
						1640	$14.8 \pm 0.2$ (n=3)	$14.93 \pm 0.21$	-0.9	1.4
					U ( $\mu\text{g L}^{-1}$ )	SLEW- 3	-	1.8*	-	-
						SLRS-6	$0.058 \pm 0.004$ (n=3)	$0.0699 \pm 0.0034$	-17	6.9
						1640	$27 \pm 2$ (n=3)	$25.15 \pm 0.26$	+7.4	7.4

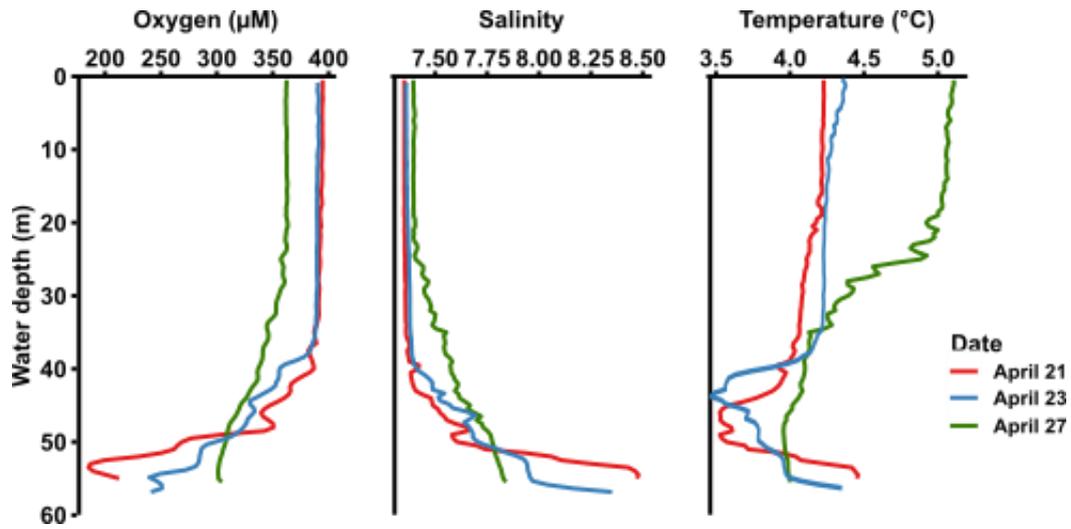
\* information value only

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**Supplementary Figure 1:** Evolution of element concentrations in the chambers of the benthic landers during a dummy incubation (the lander was deployed with a dummy bottom, which allowed to incubate bottom water, without sediment). None of the analysed elements shows a clear increase with deployment time, which indicates that metal leaching/contamination from the lander parts was negligible. Concentrations of dCo during one of the incubations were below the detection limit.



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1107 **Supplementary Figure 2:** Oxygen, salinity and temperature depth profiles recorded at station A during the 2017 sampling.  
1108 Profiles recorded at different days show significant variation, indicating that the halocline was shifting vertically during the  
1109 sampling.

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