

1 **Pelagic molybdenum concentration anomalies and the impact of sediment resuspension**
2 **on the molybdenum budget in two tidal systems of the North Sea**

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22
23 **Abstract**

24 The seasonal dynamics of molybdenum (Mo) were studied in the water column of two
25 tidal basins of the German Wadden Sea (Sylt-Rømø and Spiekeroog) between 2007 and 2011.
26 In contrast to its conservative behaviour in the open ocean, both, losses of more than 50% of
27 the usual concentration level of Mo in seawater and enrichments up to 20% were observed
28 repeatedly in the water column of the study areas. During early summer, Mo removal by
29 adsorption on algae-derived organic matter (e.g. after *Phaeocystis* blooms) is postulated to be
30 a possible mechanism. Mo bound to organic aggregates is likely transferred to the surface
31 sediment where microbial decomposition enriches Mo in the pore water. First $\delta^{98/95}\text{Mo}$ data
32 of the study area disclose residual Mo in the open water column being isotopically heavier
33 than MOMo (Mean Ocean Molybdenum) during a negative Mo concentration anomaly,
34 whereas suspended particulate matter shows distinctly lighter values. Based on field

35 observations a Mo isotope enrichment factor of $\epsilon = -0.3\text{‰}$ has been determined which was
36 used to argue against sorption on metal oxide surfaces. It is suggested here that isotope
37 fractionation is caused by biological activity and association to organic matter.

38 Pelagic Mo concentration anomalies exceeding the theoretical salinity-based
39 concentration level, on the other hand, cannot be explained by replenishment via North Sea
40 waters alone and require a supply of excess Mo. Laboratory experiments with natural anoxic
41 tidal flat sediments and modelled sediment displacement during storm events suggest fast and
42 effective Mo release during the resuspension of anoxic sediments in oxic seawater as an
43 important process for a recycling of sedimentary sulphide bound Mo into the water column.

44

45 **Keywords**

46 Molybdenum, Mo isotopes, *Phaeocystis* sp., sediment resuspension, storm events, tidal flats,
47 German Wadden Sea, North Sea

48

49 **1. Introduction**

50 Molybdenum (Mo) is a redox-sensitive trace metal occurring as dissolved molybdate
51 (MoO_4^{2-}) in the oxygenated ocean with a concentration of about 110 nM (Morris, 1975;
52 Collier, 1985). Although Mo is involved in biological cycles, its behaviour is generally
53 considered to be conservative (e.g. Howard and Cole, 1985; Cole, 1993). An increasing
54 number of recent studies, however, demonstrate temporal deviations from conservative
55 behaviour in different aquatic ecosystems. Mo removal from oxic seawater can be caused by
56 various processes, e.g., scavenging by freshly formed manganese oxides, Fe-oxyhydroxides,
57 organic matter, and assimilation by phytoplankton (e.g. Szilagyi, 1967; Head and Burton,
58 1970; Berrang and Grill, 1974; Nissenbaum and Swaine, 1975; Yamazaki and Gohda, 1990;
59 Cole, 1993; Tuit and Ravizza, 2003). Substantial temporary Mo depletion in coastal and
60 offshore waters was first observed by Dellwig et al. (2007) who suggested Mo fixation in
61 oxygen-depleted microzones of aggregated suspended matter and/or adsorption to freshly
62 formed organic matter.

63 In sulphidic environments MoO_4^{2-} is transformed to particle-reactive thiomolybdates
64 (Erickson and Helz, 2000) until final burial as MoS_2 . Furthermore, Mo can be incorporated
65 into Fe sulphides or bound to organic matter (e.g. Huerta-Diaz and Morse, 1992; Helz et al.,
66 2004; Vorlicek et al., 2004; Helz et al., 2011). In addition, substantial adsorption of Mo on the
67 surfaces of Mn and Fe oxi(hydroxi)des has been found (e.g., Berrang & Grill, 1974) which

68 may lead to a cycling between the oxic and suboxic zones of aquatic and sedimentary systems
69 when these species are oxidized or reduced.

70 In permeable sediments influenced by advective pore water transport, Mo attached to
71 metal oxides can be transported into anoxic sediment layers (Boudreau and Jørgensen, 2001;
72 Rusch and Huettel, 2000) and may be released when the metal oxides are reduced by H₂S
73 (Adelson et al., 2001). Complexation by dissolved organic compounds has been suggested to
74 cause stabilisation of dissolved Mo (Brumsack and Gieskes, 1983) which may retard the
75 fixation in anoxic sediments thereby allowing again the release into the overlying water
76 column (Dellwig et al., 2007; Beck et al., 2008; Kowalski et al., 2009).

77 Mo isotope fractionation is known to occur when Mo is removed from the aqueous
78 solution during fixation by different solid interfaces under anoxic and oxic conditions (e.g.,
79 Barling and Anbar, 2004; Arnold et al., 2004; Nägler et al., 2005; Goldberg et al., 2009,
80 2012). Thus, Mo isotopes are a useful tool to identify the processes involved in Mo
81 partitioning between water column and sediment. While the scavenging of Mo by Mn oxides
82 is suggested to result in light isotope signatures (Barling et al., 2001; Siebert et al., 2003;
83 Poulson et al., 2006; Wasylenki et al., 2008; Goldberg et al., 2012), more effective removal of
84 Mo from solution under euxinic conditions leads to smaller to negligible isotope fractionation
85 depending on the sulphide level (e.g. McManus et al., 2002; Arnold et al., 2004; Neubert et
86 al., 2008; Nägler et al., 2011).

87 Reoxidation of sedimentary sulphidic compounds may take place during e.g. extensive
88 sediment displacement (Aller et al., 1986) or bioturbation (Boudreau and Jørgensen, 2001;
89 Volkenborn et al., 2007) and may result in a significant release of trace metals like Mo. A
90 partial reoxidation can be also caused by advective circulation of oxygenated waters through
91 the top sediments which enhances O₂ penetration into permeable sediments (de Beer et al.,
92 2005).

93 Large scale sediment erosion and resuspension of tidal flat sediments is caused by tide-
94 and wind-driven wave activity (e.g. de Jonge and van Beusekom, 1995; You, 2005; Stanev et
95 al., 2006; Christiansen et al., 2006; Bartholomä et al., 2009; Fettweis et al., 2007, 2010).
96 Pronounced sediment transport may in particular take place during storm events. Such
97 resuspension processes also cause remobilisation and transfer of trace metals into the water
98 column (e.g., Cantwell et al., 2002; Saulnier and Mucci, 2000; Audry et al., 2006, 2007;
99 Kalnejais et al., 2007, 2010) finally altering the geochemical signature of the open water
100 column. The extent of the impact will depend on the reservoir sizes and the residence time of
101 sedimentary compounds under oxic conditions (Morse, 1994; Saulnier and Mucci, 2000).

102 With the help of modelling approaches, the residence times and fluxes of suspended
103 particulate matter in the water column during storm conditions can be estimated (e.g. Warner
104 et al., 2008; Lettmann et al., 2009; Gräwe and Wolff, 2010; Dobrynin et al., 2010).

105 In this contribution, we investigate the seasonal dynamics of Mo in two tidal systems of
106 the German Wadden Sea with different sedimentological and hydrodynamic properties.
107 Possible mechanisms for non-conservative behaviour of Mo as expressed by temporary
108 negative and positive concentration anomalies in the water column are discussed. In this
109 context, the oxidative release of Mo from the sediments during resuspension is examined by
110 experimental and modelling approaches estimating the potential consequences for the Mo
111 inventory in the water column. Furthermore, we present first Mo isotope data from the coastal
112 area of the North Sea, which provide complementary information about the geochemical
113 behaviour of Mo.

114

115 **2. Study areas**

116 The Wadden Sea is about 450 km long stretching from Den Helder in the Netherlands to
117 Blåvandshuk in Denmark along the southern North Sea coastline (Streif, 1990). Sampling was
118 carried out in the backbarrier tidal flats of the Islands of Spiekeroog in the southern part of the
119 German Wadden Sea and in the backbarrier tidal flats of the Islands Sylt and Rømø in the
120 northern part (Fig. 1).

121 The backbarrier tidal area of Spiekeroog Island (Fig. 1A) covers an area of about 74 km²
122 (Walther, 1972) and water exchange with the open North Sea occurs via the tidal inlet
123 (Otzumer Balje, OB) between the Islands of Langeoog and Spiekeroog. Tides are semi-
124 diurnal with a mean range of 2.6 m (Flemming and Davis, 1994). The backbarrier area is
125 dominated by sand and mixed flat sediments with grain sizes decreasing towards the mainland
126 due to lower current velocities (e.g. Postma, 1961; Reineck et al., 1986; Flemming and
127 Nyandwi, 1994).

128 The Sylt-Rømø tidal basin (Fig. 1B) is a semi-enclosed bight encompassing an area of
129 about 407 km² and is characterised by semi-diurnal tides with a mean range of about 2 m.
130 Tidal water transport occurs via a single tidal inlet branching into three main tidal channels
131 (Gätje and Reise, 1998). Most of the sediment consists of mixed sand and sandy sediments
132 whilst fine sediments prevail along the fringes (Bayerl et al., 1998).

133

134

135

136 **3. Material and Methods**

137 **3.1. Sampling**

138 Water and suspended particulate matter (SPM) samples were taken aboard R/V
139 “Navicula” close to a time series station in the tidal inlet of site Spiekeroog (site OB, Fig. 1A,
140 53°45.0'N, 7°40.3'E; water depth ca. 13 metres, Grunwald et al., 2007). At Sylt Site, sampling
141 was carried out in the tidal channel called Lister Ley (LL, Fig. 1B, 55°01.30' N, 8°27.10' E,
142 water depth ca. 10 metres) using R/V “Mya”.

143 For SPM, 0.5 to 1 L seawater was filtered through pre-weighted polycarbonate filters
144 (Millipore Isopore membrane filters, 0.4 µm pore size, low-pressure max -20 kPa).
145 Afterwards the filters were rinsed with 100 mL purified water and dried for 48 h at 60° C. For
146 algae cells counts, water samples were fixed with Lugols solution and stored in amber glass
147 bottles at 4°C.

148 Seawater samples were filtered through 0.45 µm SFCA (surfactant-free cellulose
149 acetate) syringe filters and acidified to 1% (v/v) with concentrated HNO₃ (supra pure,
150 Merck).

151 Surface sediment samples were taken with cut plastic 60 ccm syringes, placed into 60
152 ccm plastic centrifuge tubes, and, after return to the laboratory, kept frozen until freeze-drying
153 and further analysis as described by Neubert et al. (2008).

154

155 **3.2. Analytical methods**

156 At site Spiekeroog, temperature was determined as a mean of ten minutes intervals at
157 the time series station (OB). Salinity was calculated from temperature, conductivity and
158 hydrostatic pressure (UNESCO, 1985). In the Sylt area, temperature was measured with an
159 electronic reversing thermometer (SiS, Sensoren Instrumente Systeme GmbH) which was
160 mounted on a niskin bottle. Salinity was measured with a salinometer (Guildline Instruments,
161 Autosal 8400).

162 For analysis of Mo in suspended particulate matter (SPM) the polycarbonate filters were
163 digested with a mixture of HNO₃, HClO₄, and HF using a pressure digestion system PDS-6
164 (Loftfields Analytical Solutions; Heinrichs et al., 1986) at 180°C for 6h and were measured
165 by ICP-OES (Thermo, iCAP 6300 Duo). A detailed description of the digestion method,
166 which was also used for sediment samples, is given by Dellwig et al. (2007). Accuracy and
167 precision of the analyses were determined by simultaneous measurements of the certified
168 reference standard SGR-1 (green river shale, United States Geological Survey) and were
169 better than 7.3% and 5.6%, respectively.

170 Dissolved Mo and Mn in seawater samples were measured by ICP-OES (Thermo, iCAP
171 6300 Duo) and HR-ICP-MS (Element II, Thermo Fisher Scientific) using 2-fold and 10-fold
172 diluted aliquots, respectively. Accuracy and precision were determined with the certified
173 seawater standard CASS-4 (National Research Council of Canada) and were better than 7.5%
174 and 6.5%, respectively.

175 Taxa determination and cell counting was performed using an inverted microscope
176 following the Utermöhl method (Utermöhl 1931, Lund et al. 1958). Phytoplankton cell
177 dimensions were measured for up to 25 cells of every taxon that occurred at the respective
178 sampling date. Cell volumes were calculated according to the geometric shapes proposed by
179 Hillebrand et al. (1999).

180 For $\delta^{98/95}\text{Mo}$ measurements 100 ml water were spiked with a ^{97}Mo and ^{100}Mo double-
181 spike. After evaporation, the samples were redissolved in 4 M HCL with trace H_2O_2 . Mo
182 purification applying anion and cation exchange columns followed Neubert et al. (2011). The
183 isotopic composition of Mo was measured with a Nu instruments MC-ICP-MS. A detailed
184 description of the analytical technique is given by Siebert et al. (2001) and Wille et al. (2007).
185 A minimum of 20 ng Mo was used per analyses. Analytical blanks (<2 ng) were small
186 compared to the typical total amount of sample Mo processed (<1.5%). For isotope data
187 presentation the $^{98}\text{Mo}/^{95}\text{Mo}$ ratio was used. The standard reproducibility was better than
188 0.06‰ (2 σ). Isotope composition was presented as ‰ deviation from Johnson Matthey ICP
189 standard solution (lot 602332B, Siebert et al., 2001):

190

$$191 \quad \delta^{98/95}\text{Mo} = [({}^{98}\text{Mo}/{}^{95}\text{Mo})_{\text{sample}}/({}^{98}\text{Mo}/{}^{95}\text{Mo})_{\text{standard}} - 1] * 10^3 \quad [1].$$

192

193 The $\delta^{98/95}\text{Mo}$ of NIST SRM 3134 is 0.25‰ relative to this standard, and ocean water (Mean
194 Ocean Molybdenum, MOMo) is $2.34 \pm 0.07\text{‰}$ (Greber et al 2012).

196 3.3. Oxidation experiment

197 A laboratory experiment with natural anoxic tidal flat sediments was conducted to
198 investigate the liberation of Mo during mixing with oxygenated seawater. After removal of
199 the thin oxic surface layer (1-5 mm), the first 10 cm of anoxic sediment material were
200 collected in March 2008 from a sand flat (Fig. 1A, Janssand JS, 53°44.18' N, 7°41.90' E, mud
201 fraction <5%) and a mixed flat site (Fig. 1A, NN, Neuharlingersieler Nacken, 53°42.15' N,
202 7°42.57' E, mud fraction about 15%) to consider the dominant sediment types of the study
203 area (e.g., Flemming and Ziegler, 1995; Al-Raei et al., 2009). In the laboratory, the sediments

204 were sub-sampled in a glove bag under N₂ atmosphere (Sigma-Aldrich, Milwaukee, USA) to
205 avoid O₂ contamination. For metal analysis of the original material, samples were taken from
206 both sediment types and stored frozen in plastic petri dishes until analyses. For the experiment
207 about 1 kg of the sediment material was filled into plexiglass tubes (length 45 cm, diameter 5
208 cm) closed with rubber plugs. The experiment started with the addition of 0.5 L oxygenated
209 artificial sea water containing no Mo. The tubes were agitated continuously during the entire
210 experiment duration of 6 h using a shaking bed (Gerhardt Analytical systems, Königswinter,
211 Germany) to ensure homogenous resuspension of the sediment material. Aliquots of 2 mL
212 were taken from the water column every 15 min with a 5 mL syringe for the analysis of
213 dissolved Mo released during oxidation. Based on pore water Mo concentrations and the
214 water content of the used sediment, a possible interference of pore water Mo can be excluded.
215 Immediately after sampling the aliquots were filtered through 0.45 µm SFCA syringe filters
216 and acidified to 1% (v/v) with concentrated HNO₃. The solutions were analysed by ICP-OES
217 as described above.

218

219 **3.4. Estimating SPM residence times with a Lagrangian particle tracking model**

220 A Lagrangian particle tracking model (Gräwe and Wolff, 2010) was used to simulate
221 short-term SPM dynamics and particle residence time in the water column of the backbarrier
222 area of Spiekeroog Island using the conditions during the storm event “Britta” (31 October - 2
223 November 2006). On that account, the Lagrangian SPM module was adapted to a
224 hydrodynamic core model (GETM, General Estuarine Transport Model, Burchard and
225 Bolding, 2002) which was coupled to a wave model (SWAN, Simulating Waves Nearshore,
226 Booij et al., 1999). A detailed description and validation of the hydrodynamic model and the
227 Lagrangian particle tracking model can be found in Lettmann et al. (2009) and Gräwe and
228 Wolff (2010).

229 The model simulated the time period from 20 October to 4 November 2006. To estimate
230 the residence time of particles in the water column the following procedure was used: 1500
231 particles with a diameter of 50 µm were placed randomly distributed in each 200 x 200 m grid
232 cell (20 million particles in total). The diameter was chosen as a fair estimate for the present
233 grain size spectrum ranging from clayey to sandy material. As soon as the bottom stress of
234 0.12 N/m² was reached, particles could be resuspended and released into the water column.
235 For bottom stress values below 0.12N/m² only sedimentation was possible. For a detailed
236 description and validation of the erosion and sedimentation modules the reader is referred to
237 Gräwe and Wolff (2010).

238 For each particle, the residence time in the water column, i.e., the time from
239 resuspension until deposition, was calculated. Afterwards, a mean value was calculated for all
240 particles in a grid box. This procedure was done over one tidal cycle computing a temporal
241 average over these 12.4 hours (this limits the maximum residence time to 12.4 hours).
242 Thereafter, the particle positions were reset and the simulation was started again with a time
243 shift of 2 hours until the final simulation time was reached.

244

245 **4. Results and discussion**

246 **4.1. Negative concentration anomalies of dissolved Mo**

247 Distinct deviations of dissolved molybdenum (Mo_{diss}) from salinity-based theoretical
248 values appeared repeatedly in the water column of Site Spiekeroog (OB) during certain time
249 periods between 2007 and 2010 (Fig. 2a). In comparison to previous studies (Dellwig et al.,
250 2007; Kowalski et al., 2009), the time-series presented in this contribution revealed
251 significant fluctuations of Mo_{diss} throughout the years due to a higher sampling resolution over
252 an extended time period. During early summer Mo_{diss} decreased temporarily down to a
253 minimum value of 50 nM representing less than 50% of the salinity-based Mo concentration.
254 Unfortunately, this behaviour could not be shown in 2009 due to lacking samples for the time
255 period between mid-June until the end of August. The negative Mo_{diss} concentration anomaly
256 was also observed at the Sylt Site in 2008, less pronounced in 2010, and again in 2011 (Fig.
257 3a). This observation allows the conclusion, that Mo depletions are common phenomena in
258 the investigated tidal basins of the North Sea, thus likely appearing within the entire Wadden
259 Sea. The decrease in Mo_{diss} concentrations at the Sylt Site was observed in the years 2008-
260 2010 about four weeks later than at the Spiekeroog Site. This is in line with previous
261 observations (Dellwig et al., 2007) which indicated a development of the Mo_{diss} concentration
262 anomaly from the western to the eastern parts of the East Frisian Wadden Sea.

263 Several authors reported coupled transport behaviour between Mo and Mn via
264 scavenging of Mo by Mn oxides (e. g., Berrang and Grill, 1974). The time-series of site
265 Spiekeroog in 2007 and 2008 revealed a parallel decrease of Mo_{diss} and Mn_{diss} concentrations
266 which may be a result of elevated photochemical and/or bacterial Mn oxidation (Emerson et
267 al., 1982; Anbar and Holland, 1992; Nico et al., 2002) and subsequent scavenging of Mo.
268 However, observations by Dellwig et al. (2007) and Kowalski et al. (2012) showed that the
269 decreasing Mn_{diss} concentrations in summer were not caused by Mn oxidation but were due to
270 decreasing availability of reactive Mn in the surface sediments.

271 A comparison with the phytoplankton dynamics (Figures 2b and 3b) implied a
272 connection between the Mo_{diss} depletion and phytoplankton blooms (expressed as cell carbon)
273 in early summer. Although the diatom blooms in spring seemed to have a limited influence on
274 the Mo_{diss} concentrations, pronounced depletions occurred after the *Phaeocystis* blooms. This
275 early summer depletion persisted for the longest period at the Spiekeroog Site in 2008. A
276 significant loss of Mo_{diss} is seen in June followed by a second smaller decline in August
277 which may be attributed to the influence of the *Phaeocystis* bloom in April/May and the less
278 pronounced summer diatom bloom in June/July. At the Sylt Site, the diatom bloom occurred
279 about one month later at the end of March 2008 (Figs. 3b). Similar to the diatoms,
280 *Phaeocystis* sp. also bloomed later in Sylt, which was followed by a significant negative
281 concentration anomaly of Mo_{diss} . These differences in timing of the blooms were probably
282 related to local factors including temperature (e.g. van Beusekom et al., 2009) and light
283 conditions during the previous winter months (e.g. Cadée, 1986). The shorter duration of the
284 Mo depletion near Sylt might be due to the less pronounced *Phaeocystis* bloom ($390 \mu\text{g}$
285 carbon L^{-1}). The importance of the *Phaeocystis* bloom in early summer became especially
286 clear in the time series data of Sylt Site in 2010. Although the diatom bloom in spring lead to
287 exceptionally high cell carbon concentrations, the Mo_{diss} depletion was only weakly expressed
288 as *Phaeocystis* sp. also showed only low abundance. However, the lacking Mo depletion at
289 Sylt Site in 2009, albeit a pronounced *Phaeocystis* bloom was present, remains enigmatic.

290 The crucial difference between diatom and *Phaeocystis* blooms is the enormous release
291 of organic mucus during breakdown of the latter species (e.g. Schoemann et al., 2005).
292 Although the mucilaginous matrix is not included in the determined cell carbon (Figs. 2b and
293 3b) a considerable release of excess organic matter to the water column can be assumed
294 which probably traps Mo_{diss} . This assumption is supported by measurements of suspended
295 particulate matter during a Mo depletion period in July 2005 when organic matter contents
296 (max. 29%) corresponded with elevated Mo values (max. 40 mg kg^{-1}) (Dellwig et al., 2007).
297 Furthermore, the proposed relationship between Mo and organic matter is in accordance with
298 a number of studies (Szilagyi, 1967; Head and Burton, 1970; Nissenbaum and Swaine, 1975;
299 Yamazaki and Gohda, 1990; Coveney et al., 1991; Helz et al., 1996; Lyons et al., 2003; Algeo
300 et al., 2007).

301 The transfer of Mo_{diss} onto SPM was also indicated by $\delta^{98/95}\text{Mo}$ values showing an
302 enrichment of the lighter isotope on SPM whereas the residual Mo_{diss} fraction revealed a
303 heavier isotopic composition finally pointing towards isotopic fractionation and preferential
304 removal of the lighter Mo isotope from the aqueous phase (Table 1, Fig. 4). The net non-

305 conservative behaviour of dissolved Mo suggests that in a first-order approach the water
306 column can be regarded as a closed system with respect to Mo_{diss} . Therefore, based on the
307 development of the aqueous solution, an enrichment factor was calculated considering a
308 Rayleigh approach:

309

$$310 \quad \varepsilon = (\delta^{98/95}\text{Mo} - \delta^{98/95}\text{Mo}_{\text{MOMo}}) / \ln f \quad [2]$$

311

$$312 \quad \delta^{98/95}\text{Mo} = \delta^{98/95}\text{Mo}_{\text{MOMo}} + \varepsilon \cdot \ln f \quad [3]$$

313

314 with f representing the residual fraction of Mo_{diss} in the water column. Evaluation of the field
315 data yields an enrichment factor ε of -0.3‰ (Fig. 5). Isotope enrichment factors describing the
316 behaviour of Mo isotopes during the interaction between Mo_{diss} and Mn oxides or Fe-
317 oxyhydroxides as well as during the assimilation by microorganisms (soil bacteria,
318 cyanobacteria) have already been established experimentally (Wasylenki et al., 2008;
319 Goldberg et al., 2009; Zerkle et al., 2011). The application of equation (3) using the
320 experimentally derived enrichment factors indicates, that the observed field data cannot be
321 reproduced assuming sorption onto metal (oxyhydr)oxide surfaces as responsible process
322 (Fig. 5). Moreover, the calculated enrichment factor was close to results determined
323 experimentally during active Mo uptake by cyanobacteria (Zerkle et al., 2011). Although
324 cyanobacteria may be important in the sediments of the study area (Evrard et al., 2008), they
325 are not expected to influence the Mo reservoir in the open water column due to negligible
326 abundances and dissolved sulphate at seawater level competing with molybdate for active
327 assimilative uptake (Howarth and Cole, 1985; Cole et al., 1993; Marino et al., 2003).
328 Furthermore, Mo depletion occurred during periods of decreasing phytoplankton abundance
329 and not during the growth period (Fig. 2). Thus, active uptake of Mo by phytoplankton can be
330 ruled out to cause significant Mo_{diss} depletion in early summer. Therefore, it is hypothesised
331 that extracellular Mo-binding to algae-derived organic matter may have caused the observed
332 Mo isotope fractionation, although the actual isotope enrichment factor for Mo adsorption
333 onto organic matter is not known so-far. A more detailed analysis of the processes leading to
334 the observed Mo isotope fractionation effects requires further field and in particular further
335 experimental and modelling studies.

336 Several studies document adsorption of metal cations onto algal and bacterial cell walls
337 (e.g. Gonçalves et al., 1987; Xue et al., 1988; Fein et al., 1997; Daughney et al., 1998; Seders
338 and Fein, 2011). For instance, Mn is known to be adsorbed to *Phaeocystis* mucus (Davidson

339 and Marchant, 1987; Schoemann et al., 2005). Phytoplankton releases surface-active
340 exopolymeric substances, supporting the aggregation of organic and inorganic particles (e.g.
341 Passow, 2002a). The increased release of organic matter during and after the breakdown of
342 *Phaeocystis* blooms together with higher water temperatures leads to enhanced microbial
343 activity in early summer (Lemke et al., 2010). The additional release of exudates by bacteria
344 as well as the bacterial modification of phytoplankton-derived substances to transparent
345 exopolymer particles (TEP) by bacteria (Passow, 2002b; Bhaskar et al., 2005) leads to the
346 formation of large aggregates and thus an enhanced flux of organic-rich particles to the
347 sediment surface in the summer months (Riebesell, 1991a, b; Kiørboe et al., 1994; Logan et
348 al., 1995; Simon et al., 2002; Chang et al., 2006; Lunau et al., 2006). Harvey and Leckie
349 (1985) studied the importance of extracellular polysaccharides (EPS) for metal adsorption and
350 found that EPS released by bacteria competes with bacteria cell walls for available metals.
351 Acharya et al. (2009) found anionic uranyl (UO_2^{2+}) being bound to EPS of a marine
352 cyanobacterium. Although less is known about the adsorption of anions (e.g., Fein et al.,
353 2001), Mo_{diss} adsorption to surface-active TEP directly released by *Phaeocystis* sp. as well as
354 organic compounds produced after their blooms is postulated to play a key function in
355 removing Mo_{diss} from the water column in the study area. Such sequence of organic matter
356 production by algae followed by bacterial modification may also explain the time gap
357 between *Phaeocystis* breakdown and Mo depletion (Figs. 2 and 3). In contrast, the less
358 pronounced response of Mo_{diss} dynamics during spring diatom blooms is probably explained
359 by a lower release of organic matter by these species as well as a reduced microbial activity
360 due to lower temperatures (Lemke et al., 2010).

361 Subsequent aggregation of suspended particles by released organic matter may lead to
362 deposition of organically bound Mo in the sediment (Dellwig et al., 2007). The relatively
363 short time necessary to produce Mo concentration anomalies may be explained by a rapid,
364 event-like sinking and deposition of the large aggregates as it has been reported by e.g.
365 Riebesell (1991a), Alldredge and Gotschalk (1989), and Chang et al. (2006). The transfer of
366 Mo to the surface sediments as well as its release after the decomposition of deposited
367 organic-rich particles is indicated by enrichments of Mo_{diss} in the shallow pore waters of site
368 Spiekeroog partly exceeding the usual seawater value by a factor of four (Dellwig et al., 2007;
369 Beck et al., 2008; Kowalski et al., 2009).

370 Additionally, the analysis of the periostraca (protective organic coatings) of bivalves
371 found in the sediments of the study area supported the assumption of a tight relation between
372 Mo and organic matter under natural conditions in this environment. While Mo_{part} contents of

373 the periostracum of *Mytilus edulis* living in colonies above the sediment surface showed
374 values of up to 8 mg kg⁻¹, the burrowing *Ensis americanus* reached contents of up to 256 mg
375 kg⁻¹. The isotopic composition of the latter periostracum resembled those of SPM with a
376 $\delta^{98/95}\text{Mo}$ value of +1.3 ‰ (Table 1) thereby indicating a Mo isotope fractionation between
377 dissolved and organically bound Mo and an enrichment of the lighter isotope in the organic
378 matrix compared to the aqueous solution.

379

380 **4.2. Positive concentration anomalies of dissolved Mo**

381 Apart from depletion periods, the time series of pelagic Mo_{diss} at both sites also revealed
382 positive Mo concentration anomalies. While the time-series of Mo_{diss} generally showed a
383 slightly enhanced level at Spiekeroog Site in 2009 and at Sylt Site in 2011 most prominent
384 anomalies occurred especially in late summer 2007, 2010 and spring 2008 at Spiekeroog Site
385 and early summer 2009 as well as spring 2011 at Sylt Site. The enrichments were about 20
386 nM above the theoretical salinity-based Mo_{diss} values (Mo_{sal} ; Figs 2a and 3a) and thus
387 significantly above the analytical error (compare Chapter 3.2). Enhanced Mo_{diss}
388 concentrations in spring may be caused by the release of Mo_{diss} during the reduction of Mn
389 oxides in the surface sediments when anoxic conditions reach the uppermost sediment layer
390 (Burdige and Nealson, 1985). However, the water column data from both sites did not clearly
391 support a direct relation between Mo_{diss} and Mn_{diss} dynamics within the study area (Figs. 2a
392 and 3a). Although a certain relation might be inferred from slightly increasing Mo_{diss} values in
393 spring at Spiekeroog Site, distinctly lower Mn_{diss} enrichments at Sylt Site argue against a
394 significant release of Mo due to the reduction of Mn oxides in the surface sediments. This is
395 also true for reduction of Fe-oxihydroxides as seen in pore water profiles from Spiekeroog
396 Site showing no relation between Fe and Mo dynamics (Kowalski et al., 2009). Assuming a
397 comparable Mo content of the sedimentary Mn oxides at both sites, the about four-times
398 higher Mn maxima at Spiekeroog, e.g. in spring 2008 and 2009, should lead to much more
399 pronounced positive concentration anomalies.

400 High concentrations after depletion periods at the Spiekeroog Site may be due to Mo_{diss}
401 release from the sediments into the overlying water column after the occurrence of high Mo_{diss}
402 enrichments in the pore waters (Dellwig et al. 2007; Kowalski et al., 2009). Furthermore,
403 sediment resuspension due to wind-induced wave action and tidal currents during tidal
404 drainage and inundation (Roman and Tenore, 1978; Lavelle et al., 1984; de Jonge and van
405 Beusekom, 1995; Christiansen et al., 2004, 2006; Sterckx et al., 2007; Bartholomä et al.,
406 2009) may contribute to Mo inventories. Intense sediment displacement and transport

407 influencing biogeochemical element budgets have been reported especially during storm
408 events (e.g. You, 2005; Grunwald et al., 2009; Bartholomä et al., 2009; Kolditz et al., 2012).
409 Busch et al. (1998) observed a clear seasonality of strong wind and storm events occurring
410 mainly in autumn and winter months. As shown in Figure 6a, even wind speeds of about 12 m
411 s^{-1} (6 bft) were able to increase SPM concentrations significantly. As the permanently
412 oxidised sediment layer is only a couple of millimetres thick during the summer months
413 (Jansen et al., 2009) and local areas with reduced sediment surfaces, so called “black spots”,
414 may occur (Böttcher et al., 1998; Böttcher 2003), resuspension may transfer reduced sediment
415 components as iron-monosulphides (FeS) and associated trace elements like Mo into the oxic
416 water column (Fig. 6b).

417 An oxidation experiment with natural anoxic sand and mixed flat sediments was carried
418 out to estimate the amount and rate of Mo potentially released during sediment resuspension.
419 The results showed a rapid Mo_{diss} release from the sediments within the first hour reaching
420 maximum values of 0.75 μM for the sand and 4 μM for the mixed flat sediment (Fig. 7a).
421 Further differences between the sediment types were visible in the rates of Mo_{diss} release (Fig.
422 7b). In the initial phase of the experiment (>15 min) around 0.1 $g\ m^{-3}\ h^{-1}$ more Mo was
423 released from the sand than from the mixed flat sediment. The decrease in oxidation rate and
424 the different steady-state levels were due to differences in the Mo pool sizes and the initial
425 reactive particle surfaces. The isotopic composition of the released Mo_{diss} (Fig. 7c) matched
426 the sedimentary isotope data (Table 1). Although Mo isotope data for Mo_{diss} in the water
427 column during positive Mo concentration anomalies are not available, these results suggest an
428 intense release of isotopically light Mo from the sediments to the water column possibly also
429 causing a shift to a lighter isotopic composition of the water column. Table 1 compares the
430 Mo contents and isotopic composition of sandy surface sediments (from site JS) with typical
431 oxidised surfaces with those which were reduced and coloured black by iron sulphides. The
432 latter should be in particular sensitive to modifications upon storm- or current-induced re-
433 suspension. Compared to the oxidised surfaces they are slightly higher enriched in the
434 contents of total Mo and the heavy stable Mo isotope, likely due to a slightly higher fixation
435 of Mo from pore waters under sulphidic conditions.

436 Figure 8 shows results of a model simulation estimating residence times of mud
437 particles (diameter 50 μm) in the water column over a tidal cycle during calm conditions (Fig.
438 8a) and the storm event “Britta” from 31 October to 2 November 2006 (Fig. 8b) as well as the
439 difference between both situations (Fig. 8c). During calm conditions, highest residence times
440 due to elevated current velocities were generally seen in the main tidal channel reaching more

441 than 10 hours (Fig. 8a). At the tidal flat margins particles were still suspended around 5-7
442 hours while on the tidal flats suspension was shortest (<2 hrs) due to a lower water level
443 (<2m) and less tidal activity.

444 During the storm event, high erosion and particle resuspension occurred at the northern
445 coasts of the barrier islands due to elevated wave energy (Fig. 8b). On the sand flats within
446 the backbarrier area resuspension was also enhanced (2-4 hrs, Fig. 8c) as the winds from
447 north-westerly direction (Bartholomä et al., 2009) pushed the water masses into the
448 backbarrier area against the ebb current thereby extending duration of water coverage on the
449 tidal flats.

450 Essential sediment erosion down to 16 cm sediment depth was observed during a storm
451 event in the backbarrier area of Spiekeroog Island by Tilch (2003). This area is even subjected
452 to pronounced sediment displacement under normal conditions as indicated by own
453 observations revealing maximum erosion of about 8 cm in April 2008 and still about 5 cm in
454 summer during wind speeds reaching only up to 16 m s^{-1} (data not shown).

455 Based on the experimental Mo release rates and the particle tracking model a rough
456 calculation was made to elucidate the potential impact of resuspension on the Mo budget in
457 the open water column. To assure conformity with sediment-water ratio in the study area,
458 which was approximated to 0.08 (74 km² area, Walther, 1972; $145 \times 10^6 \text{ m}^3$ water volume,
459 Lübben et al., 2009; assumed sediment depth of 1 cm = $1.1 \times 10^9 \text{ kg}$ sediment and $145 \times 10^9 \text{ L}$
460 seawater) the experimental results (Fig. 8a; sediment-water ratio = 2) were adjusted with a
461 factor 0.04 (sediment-water ratio study area / sediment-water ratio experimental setup). When
462 considering a homogenous sediment erosion of 5 cm depth (1 cm oxic zone + 4 cm anoxic
463 sediment) and a sediment distribution of 62% sand flat and 38% mixed/mud flat in the back
464 barrier area of Spiekeroog Island (Al-Raei et al., 2009), $2.8 \times 10^9 \text{ kg}$ anoxic sand and $1.4 \times$
465 10^9 kg anoxic mixed/mud flat sediments may be suspended in the water column. Assuming a
466 mean residence time of the sediment particles within the oxic water column of two hours, the
467 Mo_{diss} level may be increased by about 25 nM. Thus, in addition to Mo release from deposited
468 organic-rich particles, resuspension is able to considerably affect the pelagic Mo budget and
469 most likely represents an important mechanism contributing Mo to the open water column.

470

471 **5. Conclusions and outlook**

472 Temporary Mo depletions of 50% of the usual level were found repeatedly in the water
473 column of the German Wadden Sea in early summer between 2007 and 2011, thus
474 representing a typical feature of this ecosystem. The major processes influencing the Mo

475 cycle in the investigated coastal system are summarized in Fig. 9. As Mo depletions often
476 appeared during/after breakdown of algae blooms, a coupling to algae-derived organic matter
477 is feasible. Especially during the summer months, *Phaeocystis*-derived organic mucus is
478 probably able to trap significant amounts of dissolved Mo which is subsequently transferred
479 to the surface sediment after aggregation of particles and organic matter. Associated Mo
480 isotope fractionation of dissolved Mo during a negative Mo concentration anomaly is
481 assumed to be caused by bonding of Mo to algae-derived organic matter. During the
482 decomposition of deposited organic matter, Mo may be released again leading to significant
483 Mo enrichments in the shallow pore waters.

484 Besides Mo removal from the water column, Mo concentrations exceeding the salinity-
485 based theoretical values were observed. Laboratory experiments and modelling approaches
486 suggest a significant contribution of resuspended anoxic surface sediments during tidal wave
487 action and storm events on water column Mo budgets due to oxidative release of sulphide-
488 bound Mo. The transfer of isotopically light molybdate, released from degraded organic
489 material or from reoxidised sulphidic sediments, into the water column probably closes the
490 isotope balance between burial of isotopically light Mo adsorbed to aggregates and recycling
491 of light Mo into the water column. The present study shows for the first time the importance
492 of benthic-pelagic coupling for the Mo mass balance in a tidal system based on stable Mo
493 isotope fractionation.

494 Future work may also focus on the relevance of Mo removal from oxic surface waters
495 and associated Mo isotope fractionation during periods of high productivity in ancient near-
496 coastal systems e.g. during Proterozoic and Mesozoic oceanic anoxic events (OAE) as
497 isotopic pre-fractionation of Mo in oxic surface waters may influence the sedimentary
498 signatures (e. g. Helz et al., 1996; Arnold et al., 2004; Wille et al., 2007). Additionally to the
499 impact of sulphide concentrations (Neubert et al., 2008) as well as metal oxide cycles on the
500 Mo isotopic composition (Reitz et al., 2007), a transfer of isotopically light Mo to the
501 underlying anoxic/sulphidic water body or sediment of a stratified coastal system via sinking
502 aggregates may be assumed.

503

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519

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Table 1: Mo concentrations/contents and isotopic composition in the water column, SPM, and sediments at Spiekeroog Site and of biota collected from different sites. Uncertainties of $\delta^{98/95}\text{Mo}$ represent run precisions. External reproducibility is +/- 0.06 (2s).

Sample	$\delta^{98/95}\text{Mo}$	2σ	Mo [nM]
Water column			
29 Apr 2008	2.23	0.05	110
16 June 2008	2.52	0.04	60
24 June 2008	2.45	0.05	50
11 Aug 2008	2.37	0.05	90
23 Sept 2008	2.25	0.06	100
28 June 2007	-	-	70
19 July 2007	-	-	130
4 Sept 2007	-	-	90
SPM			
28 June 2007	0.28	0.03	0.60
19 July 2007	0.93	0.06	0.31
4 Sept 2007	1.09	0.05	1.07
Sediment			mg kg⁻¹
<i>Janssand July 2006:</i>			
Oxic surface: 0.8-1.0 cmbsf	0.34		0.10
8.0-10.5 cmbsf	0.56		0.12
Anoxic surface: 0-1.0 cmbsf	0.79		0.16
9.0-10.5 cmbsf	0.89		0.12
<i>27 Mar 2008: (used for experiments)</i>			
Anoxic sandy sediment (JS)	0.46	0.06	0.44
Anoxic mixed sediment (NN)	1.45	0.03	1.31
Periostraca			mg kg⁻¹
<i>Mytilus edulis</i>	-	-	8

<i>Ensis americanus</i>			
Sylt June 2009	-	-	118
<i>Ensis americanus</i>			
Sylt Nov 2009	-	-	256
<i>Ensis americanus</i>			
Norderney Jan 2010	1.29		160

Figure captions

Fig. 1: Map of the study areas in the German Wadden Sea;

A) Backbarrier area of Spiekeroog Island with sampling sites for seawater (OB, time series station) and sediments (Janssand, JS, Neuharlingersieler Nacken, NN).

B) Sylt-Rømø tidal basin (Sylt Island) with sampling site LL.

Fig. 2: Time series of a) dissolved molybdenum (open circles: measured values; black circles: calculated from salinity, black arrows indicate the most prominent positive concentration anomalies) and manganese (grey circles), b) water temperature and cell carbon of diatoms (open squares) and *Phaeocystis sp.* (black squares) in the water column of the backbarrier area of Spiekeroog Island. The grey line marks the usual seawater value of Mo.

Fig. 3: Time series of a) dissolved molybdenum (open circles: measured values; black circles: calculated from salinity, black arrows mark the most prominent positive concentration anomalies) and manganese (grey circles), b) water temperature and cell carbon of diatoms (open squares) and *Phaeocystis sp.* (black squares) in the water column of the Sylt-Rømø tidal basin. The black arrow indicates a further increase of cell carbon in March 2010 up to $1202 \mu\text{g L}^{-1}$. The grey line marks the usual seawater value of Mo.

Fig. 4: a) Mo_{diss} concentrations (black circles) in the water column of Site Spiekeroog (OB) during the depletion period in 2008 with corresponding $\delta^{98/95}\text{Mo}$ values (open circles). The grey line marks the mean ocean molybdenum value (MOMo). Error bars indicate measurement uncertainties. b) Scatterplot of Mo_{diss} and $\delta^{98/95}\text{Mo}$ showing a distinct negative correlation of $r = -0.94$. The grey circle denotes the MOMo.

Fig. 5: Estimation of Mo isotope fractionation with a calculated enrichment factor using a Rayleigh-based equation and comparison with factors determined during Mo scavenging by Mn oxides (*Wasylenki et al., 2008) and FeOOH (**Goldberg et al., 2009) and by biological Mo uptake (***)Zerkle et al., 2011).

Fig. 6: a) Wind speed (*open circles*) and SPM concentrations (*black circles*) in the backbarrier area of Spiekeroog Island in August 2003.

b) Anoxic surface sediments are suspended in the main tidal channel at the eastern margin of the Jansand flat after a change from an eastern to a north-western wind regime (spring 2006; photo: M.E. Böttcher). The black colour (*arrows*) is caused by resuspension of iron monosulphide-rich sediment material.

Fig. 7: Oxidation experiment with natural anoxic sand flat (*grey open circles*) and mixed flat (*black circles*) sediments suspended in oxygenated artificial seawater; a) concentration of dissolved Mo versus the time of the experiment; b) calculated rates of Mo release from the sediments during oxidation; c) Isotopic composition of the released Mo_{diss} .

Fig. 8: Model-derived residence times of suspended particles (grain size diameter 50 μm) in the water column of the backbarrier area of Spiekeroog Island a) during calm weather conditions, and b) during the storm event “Britta” (November 2006). Figure c) presents a difference map (b minus a).

Fig. 9: Generalised illustration of the benthic-pelagic interactions influencing the Mo cycle in a tidal system.

Figure 1
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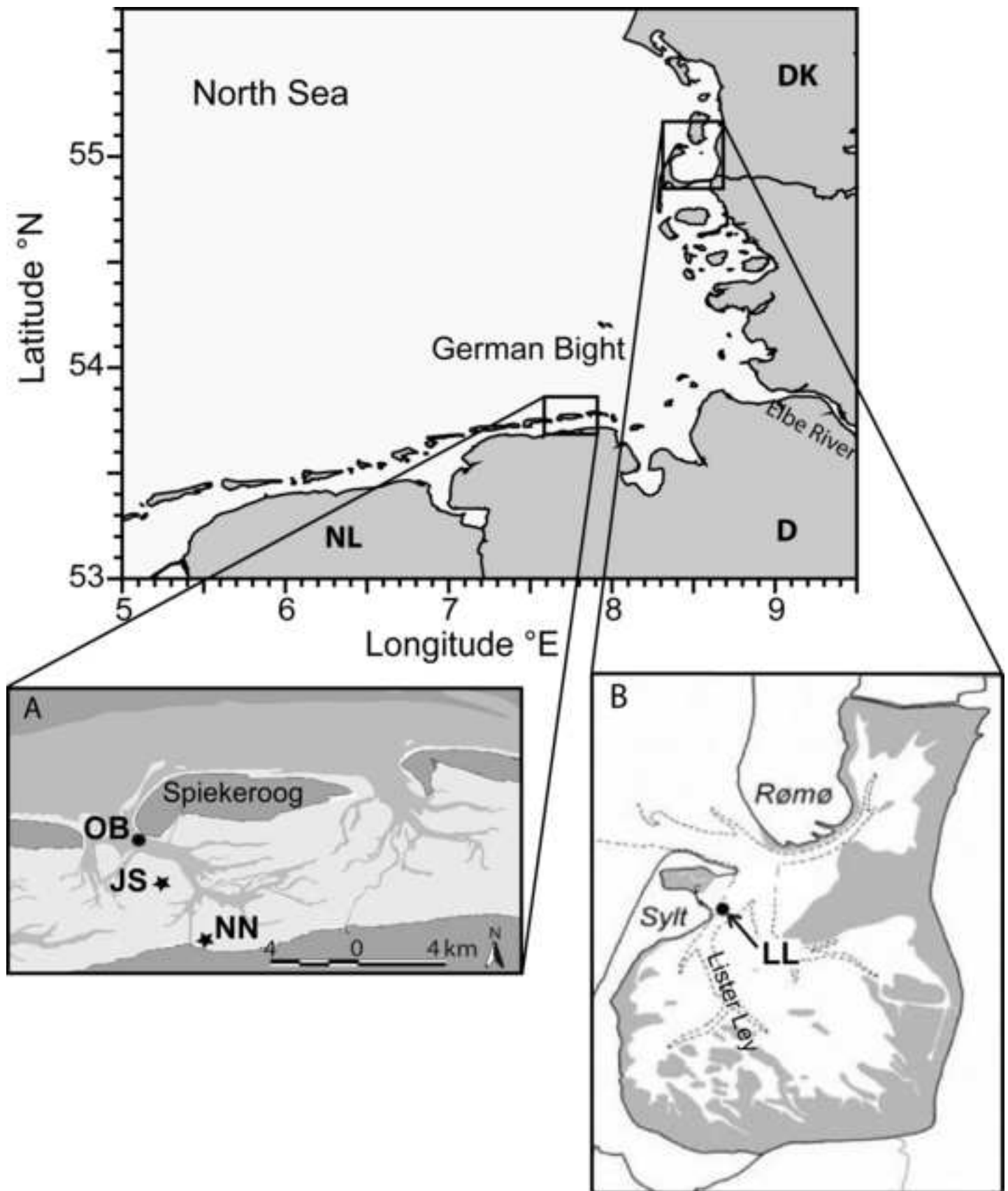


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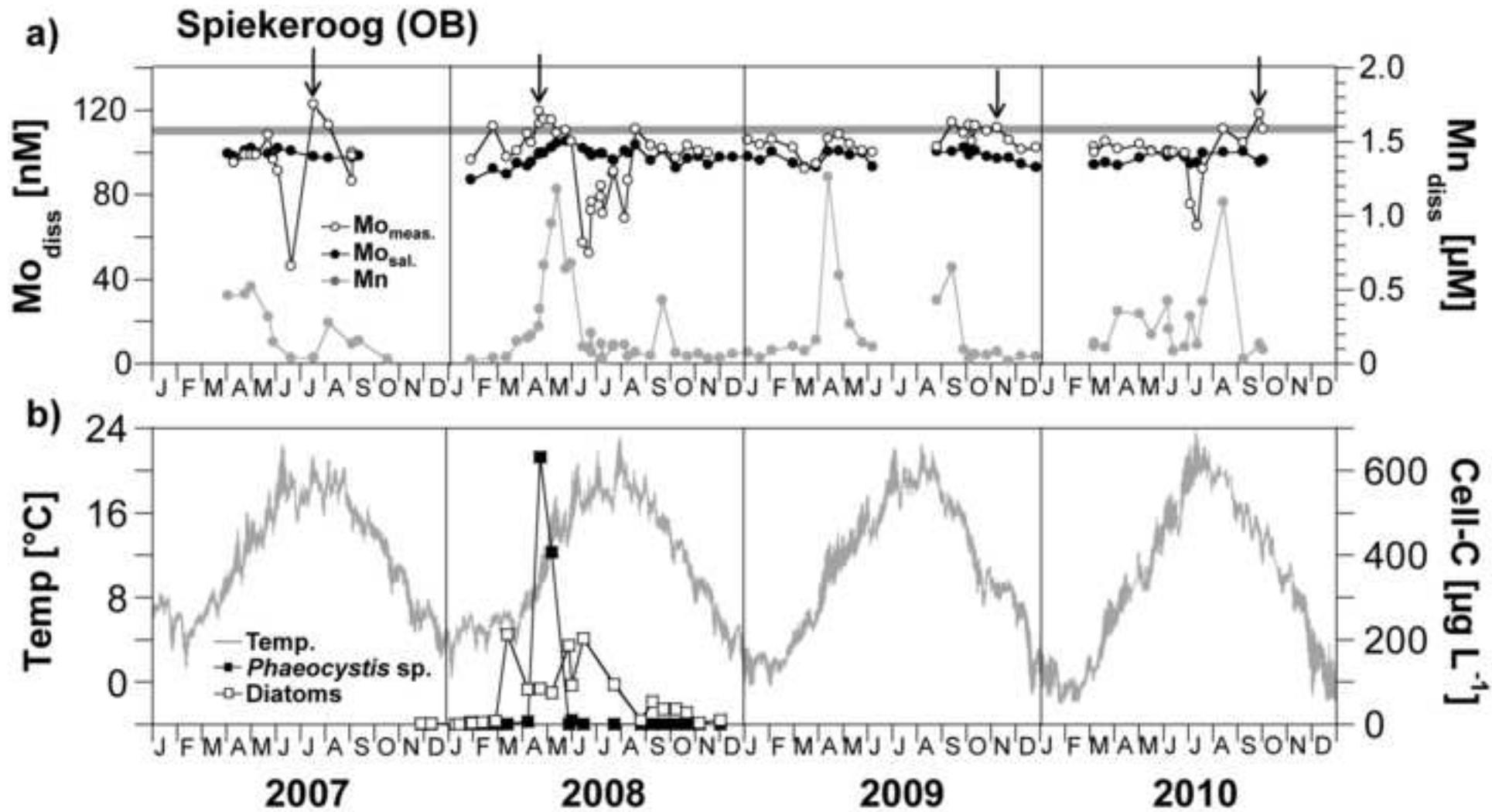


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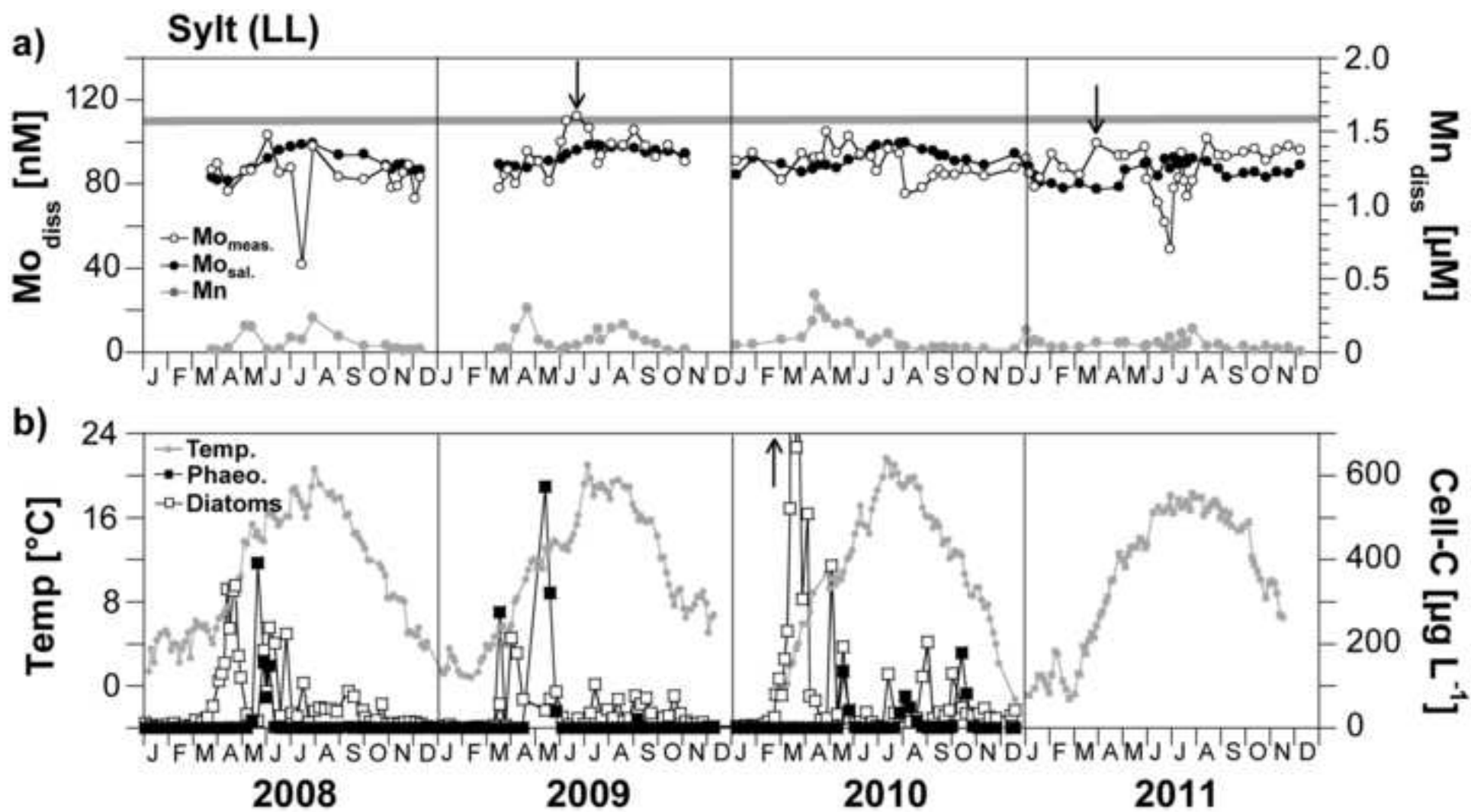


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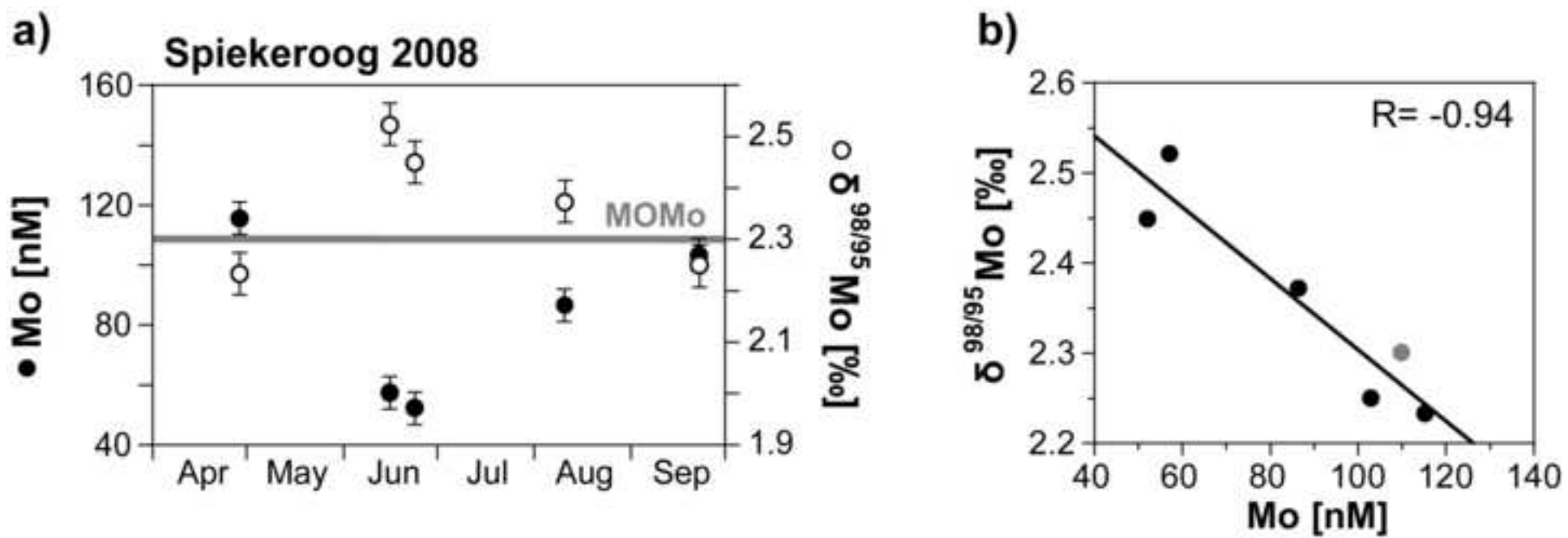


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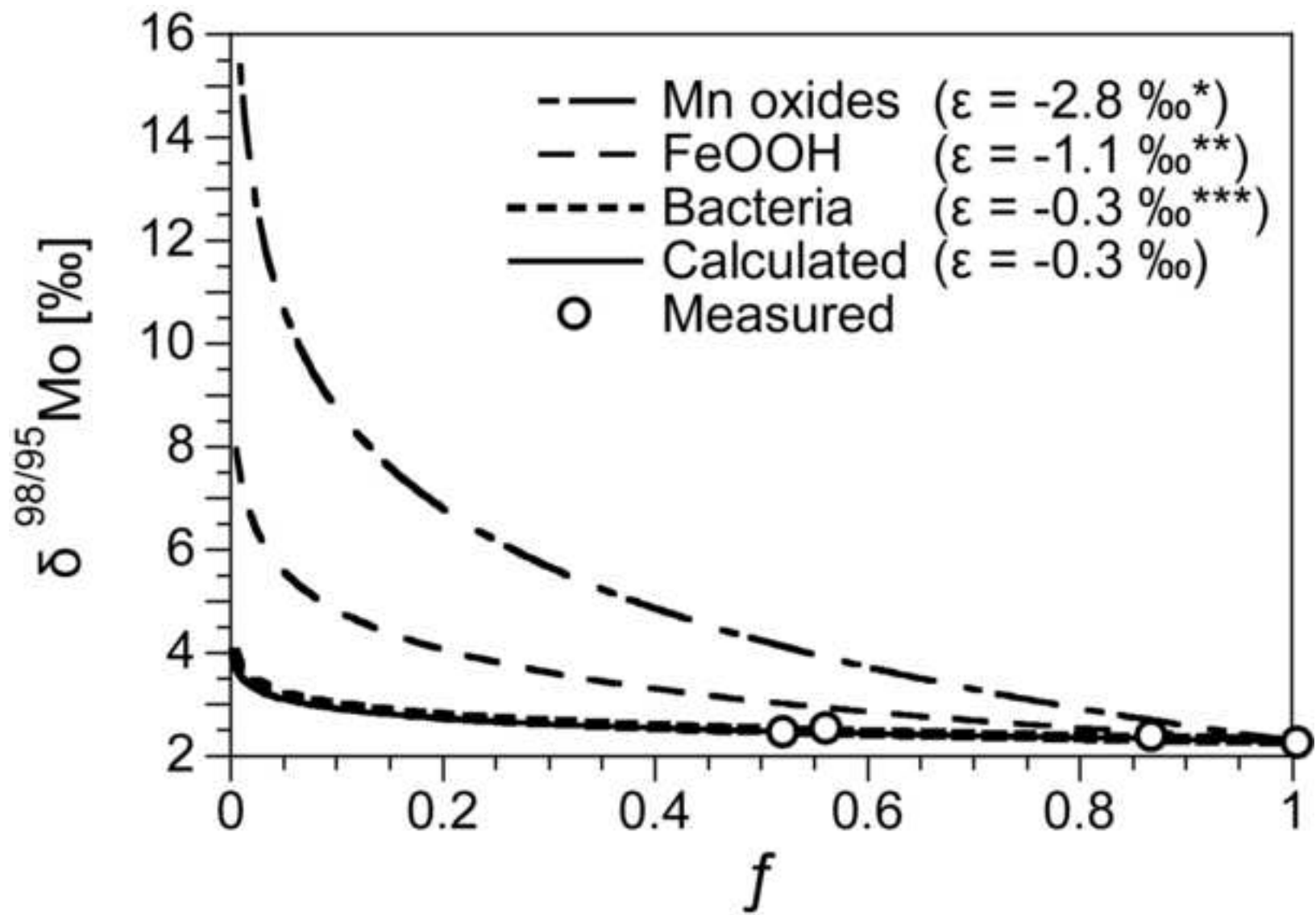


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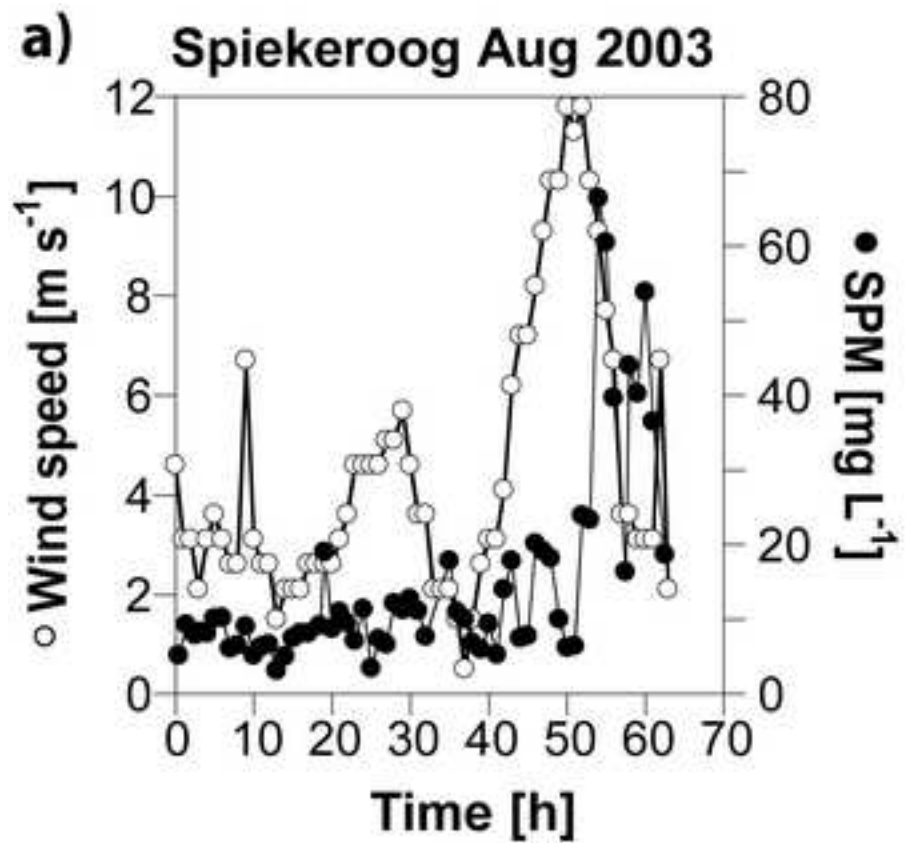


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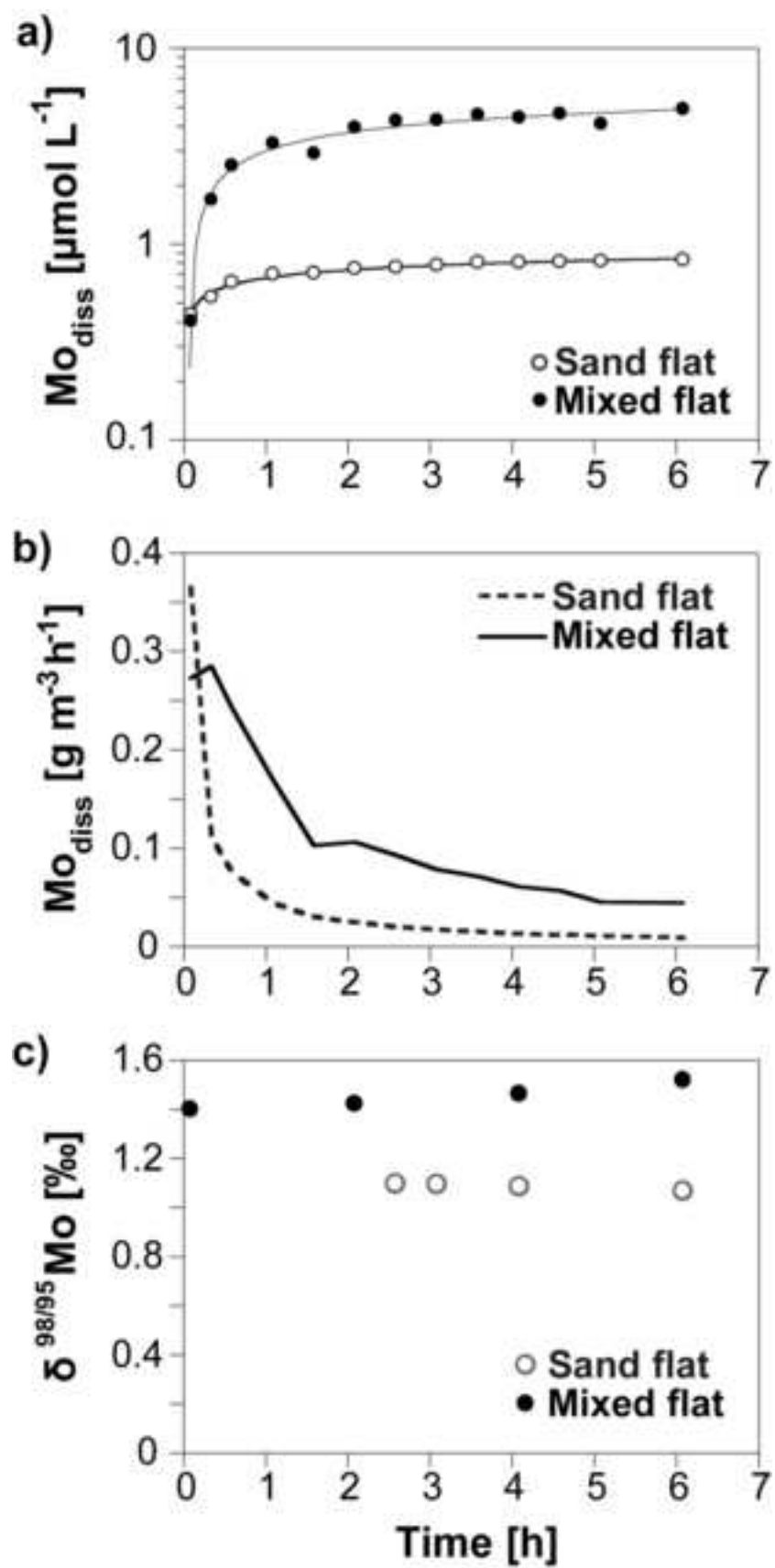


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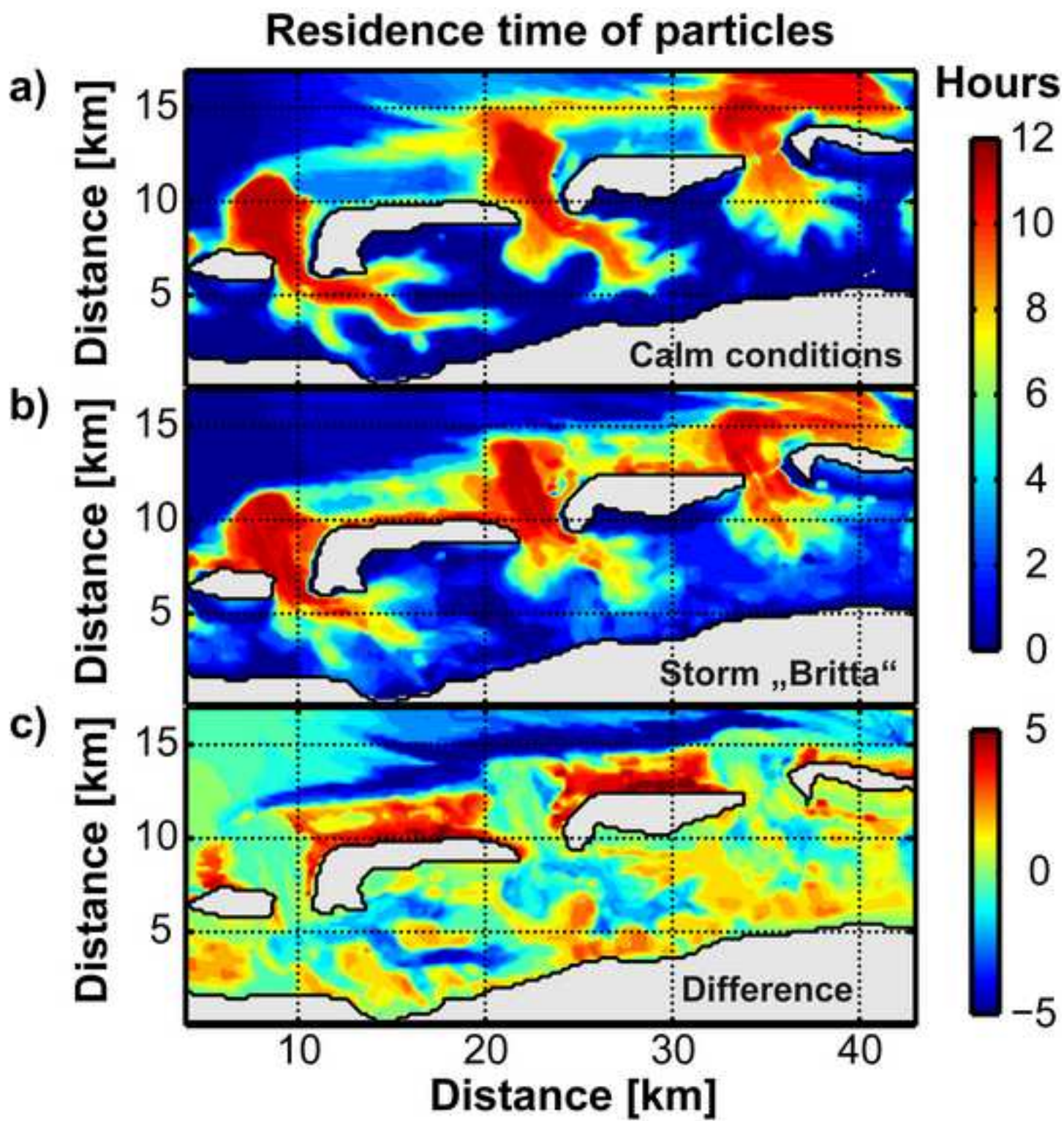


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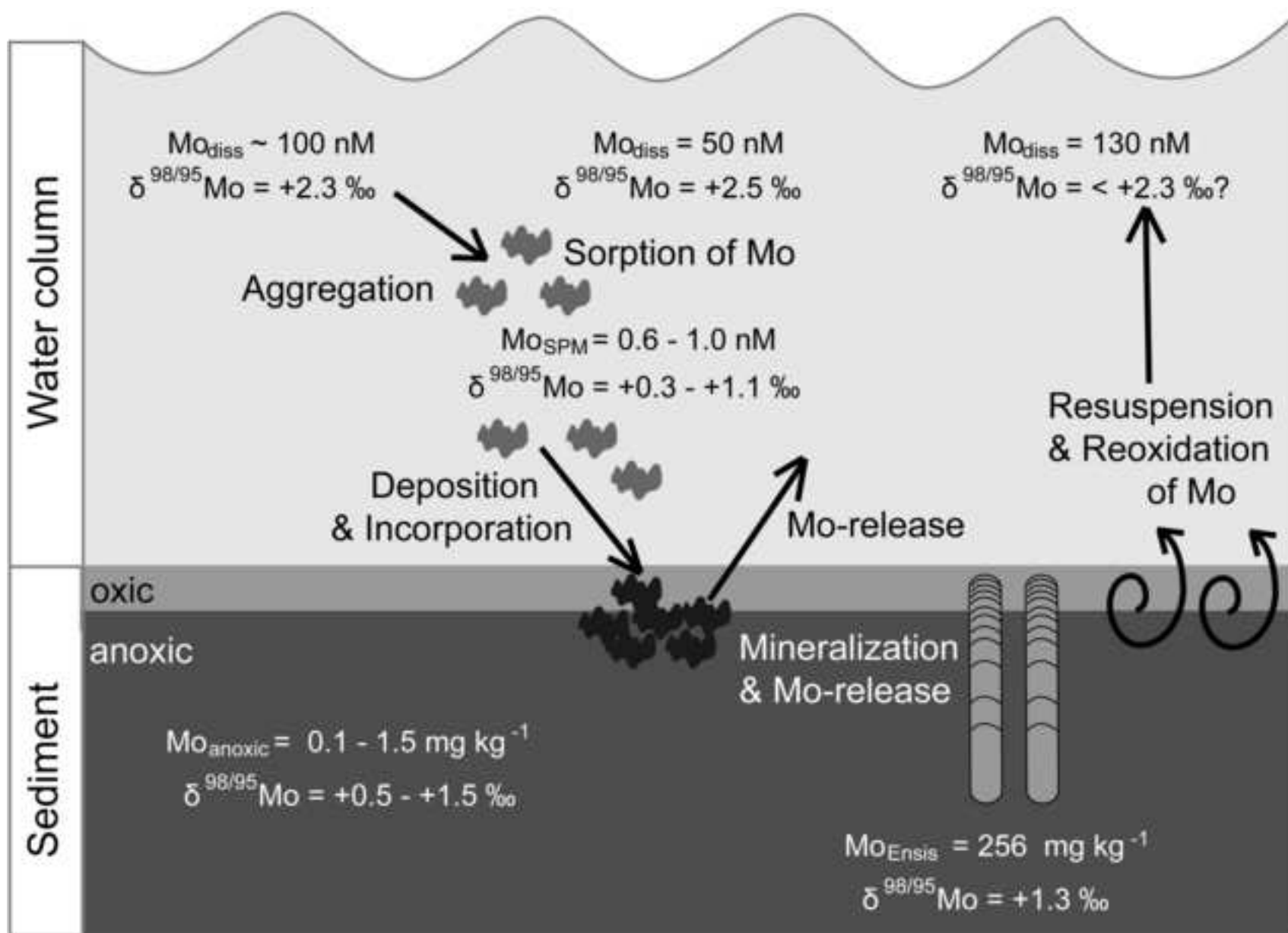


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