## Organic Matter Composition of Biomineral Flocs and its Influence on Suspended Particulate Matter Dynamics along a Nearshore to Offshore Transect

Michael Fettweis<sup>1</sup>, Markus Schartau<sup>2</sup>, Xavier Desmit<sup>1</sup>, Byung Joon Lee<sup>3</sup>, Nathan Terseleer<sup>1</sup>, Dimitry Van der Zande<sup>1</sup>, and Rolf Riethmüller<sup>4</sup>

<sup>1</sup>Royal Belgian Institute of Natural Sciences
<sup>2</sup>GEOMAR Helmholtz Center for Ocean Research
<sup>3</sup>Kyungpook National University
<sup>4</sup>Institute of Coastal Research, Helmholtz-Zentrum Geesthacht

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#### Abstract

The seasonal variation in concentration of transparent exopolymer particles (TEP), particulate organic carbon (POC) and nitrogen (PON) were investigated together with floc size and the concentration of suspended particulate matter (SPM) along the cross-shore gradient, from the high turbid nearshore towards the low-turbid offshore waters in the southern Bight of the North Sea. The analyses of TEP, POC and PON result in a set of parameters that incorporate labile and refractory organic matter (OM) fractions. Our data demonstrate that biophysical flocculation cannot be explained by these heterogeneous parameters, but requires a distinction between a more reactive labile ("fresh") and a less reactive refractory ("mineral-associated") fraction. Based on all data we separated the labile and mineral-associated POC, PON and TEP using a semi-empirical model approach. The model's estimates of fresh and mineral-associated OM show that great parts of the POC, PON and TEP are associated with suspended minerals, which are present in the water column throughout the year, whereas the occurrence of fresh TEP, POC and PON is restricted to spring and summer months. In spite of a constantly high abundance of total TEP throughout the entire year, it is its fresh fraction that promotes the formation of larger and faster sinking biomineral flocs, thereby contributing to reduce the SPM concentration in the water column over spring and summer. Our results show that the different components of the SPM, such as minerals, extracellular OM and living organisms, form an integrated dynamic system with direct interactions and feedback controls.

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## 5 Terseleer<sup>1</sup>, Dimitry Van der Zande<sup>1</sup>, Rolf Riethmüller<sup>4</sup>

- <sup>6</sup> <sup>1</sup> OD Natural Environment, Royal Belgian Institute of Natural Sciences, rue Vautier 29, 1000
- 7 Brussels, Belgium
- <sup>8</sup> <sup>2</sup> GEOMAR Helmholtz Center for Ocean Research, Wischhofstr. 1-3, 24148 Kiel, Germany
- <sup>9</sup> <sup>3</sup> Department of Advanced Science and Technology Convergence, Kyungpook National
- 10 University, 2559 Gyeongsang-daero, Sangju, Gyeongbuk 742-711, Korea
- <sup>4</sup> Institute of Coastal Ocean Dynamics, Helmholtz Center Geesthacht, Max-Planck-Str. 1, 21502
- 12 Geesthacht, Germany
- 13

14 Corresponding author: Michael Fettweis (<u>mfettweis@naturalsciences.be)</u>

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### 16 Key Points:

- Floc sizes vary as a function of tides and seasons in the high turbid nearshore. In the low
   turbid offshore floc sizes have mainly a seasonal signal.
- The median floc size increases in the presence of fresh TEP, which is mostly present in spring and summer. Mineral-associated TEP has no detectable influence on the floc size.
- Separation of POC, PON and TEP in fresh and mineral-associated components using a
   semi-empirical model approach.
- 23

#### 24 Graphical Abstract



- Phytoplankton
- Mixing

#### 27 Abstract

28 The seasonal variation in concentration of transparent exopolymer particles (TEP), particulate

- 29 organic carbon (POC) and nitrogen (PON) were investigated together with floc size and the
- 30 concentration of suspended particulate matter (SPM) along the cross-shore gradient, from the
- 31 high turbid nearshore towards the low-turbid offshore waters in the southern Bight of the North
- 32 Sea. The analyses of TEP, POC and PON result in a set of parameters that incorporate labile and
- refractory organic matter (OM) fractions. Our data demonstrate that biophysical flocculation
- cannot be explained by these heterogeneous parameters, but requires a distinction between a
- 35 more reactive labile ("fresh") and a less reactive refractory ("mineral-associated") fraction.
- Based on the data at all sample stations, we separated the labile and mineral-associated POC,
- PON and TEP using a semi-empirical model approach. The model's estimates of fresh and
   mineral-associated OM show that great parts of the POC, PON and TEP are associated with
- suspended minerals, which are present in the water column throughout the year, whereas the
- 40 occurrence of fresh TEP, POC and PON is restricted to spring and summer months. In spite of a
- 41 constantly high abundance of total TEP throughout the entire year, it is its fresh fraction that
- 42 promotes the formation of larger and faster sinking biomineral flocs, thereby contributing to
- reduce the SPM concentration in the water column over spring and summer. Our results show
- that the different components of the SPM, such as minerals, extracellular OM and living
- 45 organisms, form an integrated dynamic system with direct interactions and feedback controls.

#### 46 Plain Language Summary

- 47 Particles, suspended in coastal waters, occur as loose aggregates of tiny mineral and organic
- 48 particles, also known as flocs. Their mass concentration is higher in winter than in summer, but
- 49 their sizes are smaller in winter. The seasonal cycle of phytoplankton activity drives this
- 50 phenomenon. In spring, phytoplankton blooms and starts to produce fresh and sticky organic
- 51 matter. This glue binds particles together after collisions and promotes increasingly larger and
- 52 yet stable flocs. Analytical lab methods cannot distinguish between the freshly produced sticky
- and the older inactive, mineral bound organic material that is stored in the sediments and
- 54 entrained into the water by erosion and resuspension. Therefore, previous studies were not able
- 55 to detect the relation between the occurrence of the sticky material and the floc-sizes in coastal
- 56 waters. However, our new innovative model approach allows a separation into both fractions.
- 57 We observe a clear increase in floc sizes during spring and summer when fresh sticky material is
- 58available. As larger particles sink faster, they are removed from the waters which allows more
- 59 light to penetrate. In this way, phytoplankton changes its growth conditions, a nice example how
- an integrated dynamic system with direct interactions and feedback loops forms.

#### 61 **1 Introduction**

Interactions and feedback loops between organic and mineral particles have an impact on 62 sediment dynamics as well as on primary production in nearshore marine ecosystems (Droppo, 63 2001; Muylaert et al., 2006; Jago et al., 2007; Fettweis et al., 2014; Maerz et al., 2016; Liénart et 64 al., 2017; Neumann et al., 2019; Schartau et al., 2019, Skinnebach et al., 2020; Fall et al., 2021). 65 The suspended particulate matter (SPM) concentration can be highly variable in these areas due 66 to hydrodynamic (tidal currents) and atmospheric (waves and solar radiation) energy 67 entrainment, weather and climate, biological activity and terrestrial export (Schlünz & Schneider, 68 2000; Pietrzak et al., 2011; Fettweis et al., 2012; Wang et al., 2013), as well as human activities 69 such as trawling, dredging and dumping operations, and major engineering works (e.g. Milliman 70 et al., 1987; Manning et al., 2011; Baeye & Fettweis, 2015). SPM controls marine ecosystems 71 through, for example, its influence on water clarity, filter-feeding animals, mineral and organic 72 seabed composition or as carriers of pollutants (van Hoey et al., 2005; Regnier et al., 2013; 73 Capuzzo et al., 2015; Zhang et al., 2017; Hendriks et al., 2020). The interactions between 74 physical forcing, biological and chemical processes, and human activities result in highly 75 variable spatial and temporal scales of SPM concentration and composition (Eisma & Kalf, 76 1979; Ittekkot & Laane, 1991; Mayer, 1994; Fettweis et al., 2006; Van Beusekom et al., 2012; 77 Adriaens et al., 2018; Blattmann et al., 2019). SPM is composed of particulate inorganic (PIM) 78 79 and particulate organic matter (POM). Flocculation processes combine these particles into biomineral flocs (Shen et al., 2018; Lee et al., 2019), which overcompensates the resulting 80 decrease in overall density and therefore yields higher settling velocities compared to most of 81 their individual constituents (e.g. Engel & Schartau, 1999; Mietta et al., 2009). In tidally 82 dominated, mostly shallow environments, floc break-up dominates during periods of high 83 currents and waves with strong shear. In contrast, the formation of larger flocs prevails during 84 slack water periods (e.g. Winterwerp, 1998). The size of the flocs is theoretically determined by 85 the smallest turbulent eddies (Braithwaite et al., 2012). But floc size can exceed those of the 86 turbulent eddies in the presence of biogenic particles whose surfaces can become exceedingly 87 88 sticky (Cross et al., 2013).

SPM concentration in the North Sea is higher in winter and lower in summer (Howarth et 89 90 al., 1993). This seasonality appears to be caused mainly by biological cycles and only to a minor 91 part by the higher storm frequencies in winter (Fettweis et al., 2014; Lai et al., 2018). Biological processes influence flocculation, seabed erodibility and transport of the suspended particles, 92 93 because of the emergence of polysaccharides such as exopolymeric substances (EPS; e.g. Verdugo et al., 2004), including gel-like particles like transparent exopolymer particles (TEP; 94 e.g. Alldredge et al., 1993; Logan et al., 1995) and Coomassie stainable particles (e.g. Long & 95 Azam, 1996). Dissolved EPS are the precursors of these particles and refer to any extracellular 96 dissolved organic matter released from phytoplankton and bacteria, either actively by exudation 97 or passively via viral lysis, sloppy feeding or through bacterial degradation (Passow, 2000; Engel 98 99 & Passow, 2001; Engel et al., 2020). TEP are known to be a common component of the organic matter (OM) in marine environments, having specific characteristics such as adhesiveness, 100 transparency, flexibility and may form biofilms (Zhou et al., 1998; Passow, 2002; Mari & 101 Robert, 2008). 102

103 The interactions between TEP and SPM have mainly been studied in open ocean 104 environments where mineral concentrations are low and the hydrodynamics is weaker than in 105 coastal regions. Typically, under open ocean conditions TEP concentrations are correlated with 106 the rise and decline of phytoplankton blooms (Fukao et al. 2010; Mari et al., 2017). But for

- 107 nearshore and estuarine environments TEP data in combination with SPM measurements are
- scarce. Here, hydrodynamical forces are strong, the SPM dynamics is complex and the mineral
- 109 fraction of the SPM is dominant. Published data show that in winter, when SPM concentration 110 frequently reaches high values, also concentrations of OM, including TEP, become high,
- frequently reaches high values, also concentrations of OM, including TEP, become high,
  displaying maxima within high turbid areas (Malpezzi et al. 2013; Morelle et al., 2018). Thus, a
- correlation between total TEP concentration and floc size is inextricable. Extensive mixing
- events in spring and summer can generate SPM concentrations similar to those found in winter,
- but with floc sizes that are significantly larger. This apparent contradiction indicates that TEP
- 115 concentration alone cannot sufficiently explain biophysical flocculation.

The aim of our study is to gain deeper insight into the connection of TEP as a driver of 116 flocculation with the temporal and spatial variation in SPM and floc size dynamics. This is based 117 118 on numerous water samples collected between 2004 and 2020 in the Belgian part of the North Sea. We investigate the seasonal variations of the interrelation between concentration and OM 119 composition of SPM. Further, we provide insight to unraveling apparent discrepancies in 120 observations with respect to SPM concentration, floc size and the qualitative composition of the 121 particulate organic matter (POM), notably the fresh and labile vs mineral-associated and more 122 recalcitrant fraction. This paper is structured as follows: First, the fresh and mineral-associated 123 124 POM concentration in the particulate organic carbon (POC), nitrogen (PON) and TEP fractions is differentiated, refining the POM-SPM modelling approach of Schartau et al. (2019). Then, the 125 seasonality of the size and density of biomineral flocs along the coastal to offshore gradient, 126 127 using in situ data, is related to fresh and mineral-associated POM. Finally, the model is applied to estimate fresh and mineral-associated POM from in situ and satellite SPM measurements to 128 discuss the temporal and geographical variability of SPM concentration and composition across 129

130 the onshore-offshore gradient.

#### 131 **2 Methods**

- 132 2.1 Measuring Strategy
- 133 2.1.1 Water and Seabed Samples

Water samples were taken in the Belgium part of the North Sea from March 2018 until 134 July 2020 at three locations along a cross-shore section (MOW1, W05 and W08; Figure 1). It 135 ranges from the nearshore coastal turbidity maximum (MOW1) to the offshore under complete 136 137 Channel water influence (W08). W05 is located in between at the outer margin of the coastal turbidity maximum. Lacroix et al. (2004) deduce from model tracer experiments backed-up by 138 long-term salinity observations that at W05 and MOW1 Channel waters still dominate and that at 139 MOW1 fresh waters from the Rhine-Meuse and the Scheldt contribute with about 6%. The 140 present-day SPM in the Belgian-Dutch nearshore area originates mainly from the erosion and 141 resuspension of the existing mud deposits situated in the Belgian nearshore and the present-day 142 143 Scheldt estuary can be excluded as source of fine-grained sediments (Adriaens et al., 2018).



144

145 **Figure 1**: Map of sampling stations MOW1, W05 and W08 (BE: Belgium, NL: The

146 Netherlands). The background displays the averaged near surface SPM concentrations in the

147 Belgian coastal zone (southern North Sea) computed from satellite images taken by Sentinel-

3/OLCI from April 2019 to September 2019 (above) and from November 2019 to March 2020(below).

Sampling was carried out every 1 or 1.5 hours during a tidal cycle (12.5 hours) at 2 m 150 below the surface and about 2 m above the seabed using 51 Niskin bottles attached to a rosette 151 CTD system. During this period about 6 Van Veen grab samples have been taken in each station 152 for the analysis of POC and PON content in the <63 µm fraction. In total 17 tidal cycles have 153 been sampled at the nearshore station MOW1, 10 at the intermediate station W05, and 9 at the 154 offshore station W08. The water samples were filtered on board and analyzed in the laboratory to 155 obtain the concentration of SPM, POC, PON, pigments (Chlorophyll-a: Chl-a; Pheophytin-a: 156 Pheo-a) and, from December 2018 onward, TEP. The Particulate Organic Matter (POM) content 157 was determined by loss-on ignition until November 2019. The sample turbidity (in FNU) was 158

measured with a Hach TL2360 LED Turbidimeter and salinity was analyzed from the water

160 samples. Samples for dissolved inorganic nutrients and Dissolved Organic Carbon (DOC) were

taken from the filtrate. From 2004 until 2011, 25 tidal cycle measurements of SPM, POC, PON,

and from 2012 until March 2018, 25 additional cycles including pigment concentration have
 been sampled at station MOW1. During the period March 2004 to March 2018, 7 tidal cycles

have been sampled at two offshore stations, in the intermediate zone and 18 in the high turbidity

164 nave been sampled at two onshore stations, in the intermediate zone and 16 in the high tarbitry 165 zone for SPM, POC, PON and pigment (the latter from 2012 onward) concentration. The

166 sampling strategy was different before March 2018 as samples have only been taken at about 2 m

above the bed and not at the surface. The total amount of samples collected with at least SPM

and POC concentration amounts to 1841; the other parameters have respectively 1663 (PON),

169 1810 (Chl-a), 1716 (Pheo-a), 1414 (Salinity), 935 (Hach turbidity) and 659 (TEP) good data.

#### 170 2.1.2 Sensor Measurements

171 A LISST 100X was attached to the rosette to measure volume concentrations in 32 logarithmically spaced size groups over the range of 2.5–500 µm using laser diffraction 172 (Agrawal & Pottsmith, 2000). Long-term measurements with a LISST 100X and an OBS are 173 available at the station MOW1 from tripod deployments over the period 2005-2019. In the 174 beginning, the tripod was moored for 3 to 6 weeks and then recovered. From December 2009 an 175 advanced tripod system allowed continuous time series. The LISST 100X was mounted at 2 m 176 above bed (mab) and the OBS at 0.2 and 2 mab. In total about 1716 days of "good" LISST data 177 have been collected and about the double of "good" OBS data. "Good" LISST data are defined 178 179 by a smooth (i.e., no sudden decrease) optical transmission within a range between 0.15 and 0.98, a smooth floc size distribution (FSD) and no biofouling. The latter two disturbances have 180 regularly been observed in the long-term data series. Disturbed FSDs occur when the laser beam 181 is misaligned. Biofouling occurs mainly in spring and summer and is identified by a gradual 182 decrease in transmission or optical backscatter and increase in SPM volume concentration. OBS 183 184 data have been discarded when the sensor output changed over time unrelated to changes in inherent particle properties or SPM concentration. This was caused by variations in voltage 185 supply, changes in the transmittance of the window that is the interface between the sensor and 186 187 the water and the signal was attenuated by biofouling (Fettweis et al., 2019). The OBS output has first been calibrated against a laboratory standard (AMCO clear) in order to convert the sensor 188 output to a backscatter turbidity unit, before being calibrated in situ with SPM concentration 189 derived from water samples in order to obtain a mass concentration. 190

#### 191 2.1.3 Remote Sensing Measurements

Surface SPM and Chl concentration have been derived from the Ocean and Land Color 192 Instrument (OLCI). OLCI is a multispectral radiometer carried on board Sentinel-3A (launched 193 in 2016) and B (launched in 2018) with 21 bands on the 400-1200 nm spectral range and a 194 spatial resolution of 300 m. The two satellites provide a daily revisit time over the southern 195 196 North Sea. Sentinel-3/OLCI baseline water products (L2-WFR) were retrieved from the Copernicus Online Data Access (CODA) service hosted by EUMETSAT (coda.eumetsat.int). 197 The baseline products were processed with IPF-OL-2 version 06.13 (EUMETSAT, 2019) with 198 standard masking applied, i.e. excluding INVALID, LAND, CLOUD, CLOUD AMBIGUOUS, 199 CLOUD MARGIN pixels. Additionally, a custom quality control was applied to remove outlier 200 pixels with a spectrally flat signal. The SPM product was generated by an artificial neural 201 202 network as a multiple non-linear regression technique to deal with the optically complex waters

203 in the study area. The artificial neural network, originally developed by Doerffer and Schiller

204 (2007), was updated to become the Case 2 Regional (C2RCC) processor suitable for Sentinel-3

(EUMETSAT, 2019). Generating reliable satellite estimates of Chl-a in optically complex
 coastal waters is still challenging. Many algorithms exist and give quite different performance

for different optical conditions. For this reason, we applied the approach of Lavigne et al. (2021)

who clearly defined the limits of applicability of three popular and complementary algorithms: 1.

the OC4 blue-green band ratio algorithm which was designed for open ocean waters; 2. the OC5

algorithm which is based on look-up tables and corrects OC4 overestimation in moderately

turbid waters; and 3. a near infrared-red (NIR-red) band ratio algorithm designed for high turbid

212 waters. This approach allows automatic pixel-based switching between the most appropriate 213 algorithms for a certain water type. For the measuring stations these are depending on the season,

OC4 and OC5 for W08, OC5 and NIR-red for W05 and NIR-red for MOW1.

215 2.2 Sample and Data Analysis

#### 216 2.2.1 Water Samples

At every sampling occasion, three subsamples for SPM concentration were taken and 217 filtered on board using annealed (24 hours in a muffle furnace at 400°C) and pre-weighted 47mm 218 GF/C filters. The filters were then rinsed with MilliQ water and immediately stored at -20°C, 219 before being dried during 24 hours at 50°C and weighted to obtain the concentration. The 220 absolute detection limit is 0.4 mg and the uncertainty (expressed as the RMSE of the triplicates 221 divided by the mean value) decreases with increasing concentration from 8.5% (SPM 222 concentration < 5 mg/l) to 6.7% (<10 mg/), 3.5% (10-50 mg/l) and 2.1% (>100 mg/l) and 223 represent the random error related to the lack of precision during filtrations. Especially in clearer 224 225 water, systematic errors due to the offset by salt or other errors become much larger than the random errors (Neukermans et al., 2012; Fettweis et al., 2019). These are not included, and have 226 been estimated based on Stavn et al. (2009) and Röttgers et al. (2014) as 1 mg/l. One of the SPM 227 filters was used to determine the POM content, through Loss-on-Ignition (LoI) in a muffle 228 furnace at 500°C during a few hours and reweighting. The samples for POC and PON were 229 filtered on board using 25mm glass fiber filters, stored immediately at -20°C and analyzed in the 230 laboratory through catalytic oxidation and gas chromatography using a FLASH EA 1112 -231 Element analyzer. The analytical uncertainty for POC and PON are 12% and 18% and the 232 detection limits 0.018 mg/l and 0.009 mg/l respectively. The sample for pigment concentration 233 was filtered on 47mm GF/C glass fiber filters, stored in liquid Nitrogen and determined in the lab 234 using ultra high-performance liquid chromatography. The analytical uncertainty for Chl-a and 235 Pheo-a is 23% and 31% and the detection limits are 0.023  $\mu$ g/l and 0.015  $\mu$ g/l. We added to these 236 analytical uncertainties the random errors due to filtration, which we assumed to be equal to the 237 238 ones of SPM concentration. The method for TEP analysis follows the one described in Nosaka et al. (2017). This method is, as many other semi-quantitative methods, based on Aldredge et al. 239 (1993) and Passow and Aldredge (1995). Three subsamples for TEP concentration have been 240 taken and filtered using 25mm 0.4 µm polycarbonate filters with low under-pressure. The filters 241 have been colored immediately after filtration with 1 ml of Alcian blue, rinsed with 1 ml of 242 MilliQ water and stored at -20°C. The stained particles are related to a weight equivalent for the 243 244 anion density of TEP and standardized using xanthan gum (Passow and Alldredge, 1995; Passow 2002). The units for TEP are expressed as mg xanthan gum equivalents per liter (mg XG eq./l). 245 The filtrates were collected in sample tubes for DOC, inorganic nutrients and analyzed using 246

standard spectrophotometric methods with a Skalar autoanalyzer. The detection limit for DOC is 247 0.09 mg C/l. 248

2.2.2 Sediment Samples 249

The POC and PON content of the bed surface samples was determined for the fraction < 250 63 µm using the same method as described above. 251

#### 2.2.3 Floc Size Distribution and Effective Floc Density 252

The volume concentration of each size class is used to build the floc size distributions 253 (FSD), and thus the median floc size (D50) and total SPM volume concentration are computed 254 from the FSDs. The uncertainties and limitations of the LISST 100X detectors are related to the 255 shape, size and inherent optical properties of the particles occurring in nature, and to the 256 measuring principle (Mikkelsen et al., 2006; Andrews et al., 2010; Davies et al., 2012; Schwarz 257 et al., 2017) and will influence the FSD. In case of a too low turbidity (transmission >90%) the 258 data becomes less accurate. The diameter of a particle is an exact proxy of its size if the particle 259 is a sphere. Natural particles, such as flocs, have irregular shapes and generally follow Junge or 260

multimodal log-normal distributions (e.g. Liley, 1992; Buonassissi & Dierssen, 2010). 261

Measurements by laser diffraction result thus intrinsically in a particle size distribution that is 262

generally lognormally distributed. The effective floc density ( $\rho_{eff}$ ) is the ratio of floc mass (M<sub>f</sub>) 263

over floc volume ( $V_f$ ) minus the water density ( $\rho_w$ ). The floc mass,  $M_f$ , can be calculated as: 264

265 
$$M_f = M_p + M_w = M_p + \rho_w (V_f - V_p) = M_p + \rho_w (V_f - M_p / \rho_p)$$
 (1)

where  $\rho_p$  is the primary particle density,  $M_w$  is the mass of water and  $M_p$  the mass of primary 266

particles in the flocs. The latter can be obtained from the SPM filtrations, the water density was 267

fixed at 1025 kg/m<sup>3</sup>, the primary particle density was estimated as 2500 kg/m<sup>3</sup> (Fettweis, 2008) 268

and the floc volume is the volume concentration measured by the LISST. 269

270

#### 2.2.4 Long-Term Measurements of the FSD and SPM Concentration

The structure of the long-term FSD time series at MOW1 has been investigated using the 271 entropy analysis (e.g. Mikkelsen et al., 2007). Applied to FSDs, entropy analysis allows 272 grouping the size spectra without assumptions about the shape of the spectra. It is therefore 273 274 suited to analyze unimodal as well as multimodal distributions. Firstly, the 60 minutes averaged FSD time series were normalized by dividing each of the 32 size classes by the total volume 275 concentration of the FSD and then pl64 low-pass filter (Beardsley et al., 1985) removed the tidal 276 signal. Next, a climatological FSD over the period 2006-2019 was generated by averaging the 277 data of each time stamp related to the start of the respective year. Finally, a climatological 278 entropy classification was carried out using the FORTRAN routine of Johnston and Semple 279 (1983). In accordance with Fettweis et al. (2014) four entropy groups have been chosen for the 280 classification. The pl64 low-pass filter was also applied to the long-term SPM concentration time 281 series before a climatological SPM concentration was calculated over the period 2005-2016 282 283 similar as the climatological FSD time series.

284
 2.3. Model Based Differentiation of OM between Fresh and Mineral-Associated
 285
 Fractions

The inorganic and organic components of the SPM have different origins. The mineral 286 particles may have a detrital or biogenic origin. The detrital PIM typically incorporates clays, 287 quartz and other minerals, while biogenic PIM consists of minerals such as carbonates and 288 amorphous silicates. In the further considerations, we will only consider PIM as a whole. The 289 POM is a mixture of compounds derived from marine photosynthesis or terrestrial sources. It is a 290 combination of diverse detrital organic substances as well as of living organisms such as 291 bacteria, phyto- and zooplankton. The POM can be refractory, mineral-associated, or fresh. The 292 first two have a low susceptibility and the last one a high susceptibility towards microbial 293 degradation (Arndt et al., 2013). We will use the adjectives 'mineral-associated' ( $POM_m$ ) for the 294 more recalcitrant and 'fresh' ( $POM_f$ ) for the labile and semi-labile fraction. The  $POM_m$  is 295 296 incorporated in the mineral fraction where it is particularly bound with clay minerals (Mayer, 1994). 297

#### 298 2.3.1 Model Assumptions

For the differentiation between the  $POM_f$  and  $POM_m$  we follow the approach of Schartau et al. (2019), who considered Loss-on-Ignition (LoI) measurements for describing the POM:SPM ratio as a function of SPM concentration using a semi-empirical model. The conceptual basis of the POM-SPM model is that the POM concentration can be written as the sum of the POM<sub>f</sub> and POM<sub>m</sub> concentrations and that POM<sub>m</sub> is assumed to be linearly correlated with the PIM concentration by a constant proportionality factor m<sub>POM</sub>:

$$305 \quad POM = POM_f + POM_m = POM_f + m_{POM} PIM$$
(2)

The assumption is that the seasonal built up of fresh POM ( $POM_f$ ) can be described as a saturation function of the SPM concentration:

$$308 \quad POM_f = \frac{K_{POM}}{\frac{K_{POM}}{SPM} + 1} \tag{3}$$

with the parameter  $K_{POM}$  (in the same units as SPM concentration) being the second parameter of 309 the POM-SPM model. The function reaches a saturation at high SPM concentrations where 310  $POM_f$  equals  $K_{POM}$ , while at low SPM concentration  $POM_f$  concentration tends to zero. This 311 approach assumes that the production of POM<sub>f</sub> is eventually limited by nutrients, temperature 312 and light availability. Optimized values of  $K_{POM}$  were shown to be subject to seasonal variations, 313 whereas values estimated for mPOM turned out to be fairly constant and independent of seasonal 314 315 conditions (Schartau et al., 2019). According to the POM-SPM model, the POM content of SPM can be approximated by: 316

$$317 \quad \frac{POM}{SPM} = \frac{POM_f}{SPM} \frac{1}{m_{POM} + 1} + \frac{POM_m}{SPM} \tag{4}$$

- 318 A non-linear dependency between POM content and SPM concentration is obtained by including
- eq. (3) in eq. (4). The combined equation has some meaningful and desired convergence
- 320 characteristics. For SPM concentration approaching zero, POM content converges to 1 (and
- 321 POM<sub>f</sub> fraction dominates POM) and for high SPM it approaches  $\frac{m_{POM}}{m_{POM}+1}$  (and POM<sub>m</sub> fraction
- dominates POM). Instead of using LoI data for POM content, we considered three different types
- 323 of organic matter data, namely the concentrations of POC, PON, and TEP. The POM-SPM

model was refined by introducing two parameters ( $f_1$  and  $f_2$ ) for every observational type  $X_i$ 324

(POC, PON, and TEP) to the POM-SPM model (Eq. 5): 325

326 
$$\frac{Xi}{SPM} = f_{1,X_i} \frac{POM_f}{SPM} \frac{1}{m_{POM}+1} + f_{2,X_i} \frac{POM_m}{SPM}; X_i [POC, PON, TEP];$$
 (5)

These additional parameters  $f_{1,Xi}$  and  $f_{2,Xi}$  represent relative proportions of X<sub>i</sub> to POM, e.g.  $f_{1,X2}$ 327

and  $f_{2,X2}$  express the ratios of fresh- and of mineral-associated PON to POM (or  $f_{1,X1}$  and  $f_{2,X1}$  for 328

respective ratios of POC to POM) in units of molecular weight (g  $g^{-1}$ ) or TEP to POM in units of 329

(g XG eq.)/(g POM), respectively. In this manner, consistent and meaningful estimates of  $f_{1,Xi}$ 330

and  $f_{2,Xi}$  could be derived. Values assigned to or estimated for  $K_{POM}$  and  $m_{POM}$  should be largely 331

independent of the observational type, no matter whether POC, PON, or TEP concentrations are 332 333 considered. Overall, the refined model requires values to be assigned to four parameters ( $m_{POM}$ ,

 $K_{\text{POM}}$ ,  $f_1$  and  $f_2$ ). Consequently, and somewhat different from the POM:SPM model, the 334

respective fraction of  $X_i$  converges to  $f_{I,Xi}$  at SPM concentration approaching zero. For high SPM 335

concentrations the portion X<sub>i</sub> of SPM approaches  $f_{2,X_i} \frac{m_{POM}}{m_{POM+1}}$ . 336

#### 2.3.2 Parameter Optimization 337

338 The mineral-associated  $POM_m$  of the SPM is entirely determined by the value assigned to the parameter  $m_{POM}$  (eqs. 2 and 4). The parameters  $m_{POM}$  and  $f_2$  are collinear and therefore they 339 cannot be estimated independently. For maintaining consistency between the previous parameter 340 estimates of  $m_{POM}$ , and the added parameters of  $f_2$  ( $f_{2,POC}$ ,  $f_{2,PON}$ , and  $f_{2,TEP}$ ) we used the 341 optimized value ( $m_{POM} = 0.13$ ) of Schartau et al. (2019). This estimate was obtained by using 342 data of all seasons within the German Bight and German part of the Wadden Sea in the south-343 344 eastern region of the North Sea. The uncertainty of this estimate for  $m_{POM}$  is small (<3%) and the seasonal variations between estimates turned out to be small as well (0.12 - 0.14). With a fixed 345 value assigned to  $m_{POM}$  we only require values of three parameters to be optimized. The values of 346  $f_1, f_2$ , and  $K_{\text{POM}}$  were estimated by minimizing the negative logarithm of a likelihood and a prior 347 (cost function) that was used as a metric for assessing the deviation between observational data 348 and the model counterparts. In general, for the likelihood (description of the data, given the 349 model) and prior (deviation between estimated and some prescribed characteristic parameter 350 value) we assumed respective probability densities to be normal, represented as Gaussian 351 functions of the data-model residuals and of the deviation of parameter estimates from a prior 352 value assigned to  $K_{\text{POM}}$ . Reasons for why we had to account for prior information will be 353 explained in the following paragraph. We explicitly accounted for uncertainties in the 354 observations and in the prior value of K<sub>POM</sub>. Optimal combinations of parameter values were 355 determined for seasonally sorted data sets of POC, PON, and TEP. The observational data reveal 356 pronounced variability at low SPM concentrations, which becomes much reduced at high SPM 357 concentrations. At high SPM concentrations (>100 mg/l), uncertainties in measurements were 358 much lower than the variations due to spatio-temporal variability. Like in the approach of 359 Schartau et al. (2019), we added the variance of the observed POC:SPM, PON:SPM, and 360 TEP:SPM to the measurement uncertainties for SPM concentrations >100 mg/l, otherwise 361 individual data points at such high SPM concentrations can introduce severe biases in the 362 estimates of the parameters  $f_l$  and  $K_{POM}$ . For all data points we calculated variances for 363 POC:SPM, PON:SPM, and TEP:SPM, following the law of error propagation, based on 364 individual measurement errors of SPM, POC, PON concentrations. Errors for TEP were assumed 365

to be 15% of the measured concentrations, which was approximately the highest relative error found for the POC concentration measurements.

The cost functions' minima yield the best model representations of the POC:SPM, PON:SPM, 368 and TEP:SPM data. Respective minima (best parameter values) were identified by exploring the 369 parameter space including combinations of the three parameters of interest,  $f_1$ ,  $f_2$ , and  $K_{\text{POM}}$ . 370 Intervals and resolution differed between the observational types for  $f_1$  and  $f_2$ . For POC and TEP 371 we chose  $f_1$  and  $f_2 \in [0.01,1]$  with a resolution of  $\Delta = 0.01$  (with 100 elements respectively). For 372 PON we had to increase the variational range and resolution for  $f_I \in [10^{-3}, 1]$  (resolution  $\Delta = 10^{-3}$ ) 373 as well as for  $f_2 \in [5x10^{-4}, 1]$  ( $\Delta = 10^{-4}$ ). Possible values of KPOM span two orders of magnitude 374 and we therefore assigned a constant resolution on logarithmic scale ( $\Delta \log = 5 \times 10^{-3}$ ) within the 375 interval  $\log_{10}(KPOM) \in [\log_{10}(0.1), \log_{10}(10)]$ , which approximates a precision of 1%. The 376 parameter screening is fast enough for deriving confidence intervals of respective parameter 377 estimates via subsampling. A range of best parameter estimates was confined from 100 378 individual optimizations, based on random data subsamples that each included 30% of respective 379 total data points. Doing so we learned that estimates of  $f_l$  can become poorly constrained (mainly 380 when using autumn data) for some subsamples that yield estimates of  $K_{POM} < 0.5 \text{ mg/l}$ . By 381 382 introducing an additional term as a prior to the likelihood-based cost function, the optimization problem became well-posed for all subsample cases and we could obtain robust parameter 383 estimates. For the prior we imposed a  $K_{POM}$  value of 2.0 mg/l, with a 100% uncertainty (=2.0 384 mg/l) for all seasons apart from autumn, for which we had to prescribe a 25% uncertainty (=0.5 385 mg/l) for the prior. Based on the 100 individual optimizations, each with a different set of 386 subsampled data, we determined statistical properties of the estimates, including lower and upper 387 388 limits of 95% confidence intervals respectively. Instead of the arithmetic mean, the median of the parameter estimates turned out to be a better representation of the overall model fit to the data. 389 390 This is because curved collinearities appeared in few cases and respective mean values did not 391 coincide with the curved (banana-shaped) spread of optimal parameter values. In all other cases the median was similar to the mean of the estimates. 392

393 For model descriptions of POC:SPM and PON:SPM we considered seasonal variations and distinguished between in parameter estimates accordingly, combining data from three months: 394 winter (December, January, and February), spring (March, April, and May), summer (June, July, 395 and August), and autumn (September, October, and November). Monthly parameter estimates 396 were elaborated for model fits to TEP:SPM data. Instead of using data from a single month, we 397 included data from the two adjacent months. For example, optimal parameter values for January 398 399 were constrained with data from December, January, and February. Likewise, in June the parameter estimates were determined with data from May, June, and July. We recommend such a 400 procedure, because it facilitates the identification of gradual temporal changes in parameter 401 402 estimates, similar to the low-pass filtering of a moving average.

#### 403 **3 Results**

404 3.1 Temporal and Spatial Variabilities

Some of the measured data together with some physical parameters are shown in Figure
The tidal amplitude (Figure 2a) is for Zeebrugge and has been calculated from harmonic
analysis, the significant wave height is from a wave buoy near MOW1 (Figure 2b) and has been
downloaded from the Measurement Network Flemish Banks (https://meetnetvlaamsebanken.be)

and the daily solar radiation at Zeebrugge (Figure 2c) has been obtained from the Royal 409 Meteorological Institute (https://www.meteo.be). The dissolved and particulate matter data have 410 been averaged over the measuring period (usually 12 hours) and over the vertical. The data 411 averaged over four seasons for all available parameters (2004-2020) are given in the tables in 412 Appendix A. For completeness these tables comprise also parameters that are not further 413 discussed in this study. Variations in parameters occur at tidal, lunar and seasonal scales. Winter 414 (December - February) is the period with low solar radiation, high nutrient concentration and low 415 primary production. In spring (March - May) increasing solar radiation and temperature initiate 416 phytoplankton blooms under nutrient replete conditions. Summer (June-August) has the highest 417 solar radiations (Figure 2c) and nutrients are largely consumed. In late summer - early autumn, a 418 419 second phytoplankton bloom shows up, but from autumn (September-November) on phytoplankton activity ceases with the decreasing solar radiation and nutrients pile up again. It is 420 interesting to note that for the majority of parameters the more offshore stations W05 (red) and 421 W08 (blue) displayed the same overall course as in MOW1 (black) but with lower values and a 422 lower seasonal variability. Exceptions are median floc size and salinity. Observed variability 423 during a tidal cycle is also less pronounced in the offshore stations. The water column was well 424 mixed in all stations, the variations in salinity between them are, in accordance with Lacroix et 425 al. (2004), caused to a large part by different freshwater contributions from the Rhine-Meuse and 426 the Scheldt rivers. Temperature varied during 2019 sampling between 6.0°C at MOW1 in 427 428 January (6.3°C at W05, 8.7°C at W08) and 19.9°C in June (19.5°C at W05, 18.2°C at W08). At each station, the highest SPM concentrations occurred in winter and the lowest in summer 429 (Figures 1 and 2d). The volume SPM concentration has a nearly 75% more pronounced 430 seasonality than the mass SPM concentration (Figure 2d, 2e and Table A.1-3). The lower spring-431 summer volume SPM concentrations correspond to larger floc sizes (Figure 2f) and also to lower 432 effective floc densities (Figure 2g). Median floc size increased towards offshore by about 2. POC 433 and PON concentrations (Figure 2h and 2i) are correlated with SPM concentrations, although 434 higher POC:SPM and PON:SPM ratios occurred during the spring phytoplankton bloom (see 435 Tables in Appendix A). The yearly mean value of the POC/PON ratio is 6.61 molC molN<sup>-1</sup>, 436 practically equal with the Redfield ratio (6.62 molN molC<sup>-1</sup>). Lower values occur in spring (6.37) 437 and summer (6.06) and higher ones in winter (7.01) and autumn (6.75). According to Frigstad et 438 al. (2011), this seasonal variation reflects variations in the water mass characteristics, nutrient 439 concentrations, biomass and OM composition. TEP concentration (Figure 2j) at MOW1 varied 440 441 between 0.31 and 17.2 mg XG eq./l in winter, 0.62 and 17.57 mg XG eq./l in spring and 1.53 and 6.97 mg XG eq./l in summer. At W05 these values were between 0.11 and 3.31 mg XG eq./l 442 (winter), 0.76 and 4.13 mg XG eq./l (spring) and 0.61 and 1.74 mg XG eq./l (summer); and at 443 W08 between 0.10 and 0.59 mg XG eq./l (winter), 0.52 and 1.09 mg XG eq./l (spring) and 0.28-444 1.60 mg XG eq./l (summer). The seasonal variation in TEP concentration was similar to POC, 445 PON and SPM concentration and all were somewhat opposite to the DOC concentration (Figure 446 447 2k). Although patchy, DOC concentration had generally higher values in summer than in winter, which is explained by the production of DOC by phytoplankton in spring and summer and the 448 subsequent slow degradation (Van Engeland et al., 2010). Chl-a concentration (Figure 21) was 449 highest during the spring phytoplankton bloom. Except for the spring plankton bloom, the Chl-a 450 concentration at MOW1 was higher than in the offshore stations. This is probably due to the 451 higher availability of nutrients, in spite of the lower water clarity. The winter Chl-a 452 453 concentrations reached values of a few  $\mu g/l$  in winter, and were thus of the same order of magnitude or even higher than the offshore concentrations in spring and summer. Pheophytin is 454

- 455 one of the breakdown products of chlorophyll and is thus an index of decomposable organic
- 456 matter (Fuchs et al., 2012). The Pheo-a concentration had an opposite, although weaker, seasonal
- 457 pattern than the Chl-a concentration. Inorganic nutrient concentrations (for example total
- 458 dissolved nitrogen, total dissolved phosphate and silicates, see Tables in Appendix A) showed
- 459 the typical pattern of the North Sea with relatively high concentrations in winter and low
- concentrations in summer due to nutrient utilization by phytoplankton (Lancelot et al., 2005).



Figure 2: Physical (harmonic tidal amplitude, significant wave height, solar radiation)
parameters and dissolved and particulate matter parameters from 2019 (TEP is from 2019 until
August 2020) versus time (see § 2.1.1). For the latter, geometric means over the tidal sampling
period are shown with their standard errors of the mean in the three sampling stations (MOW1:
black, W05: red, W08: blue).

467 3.2 Floc Size

461

The hourly floc size distributions measured during a tidal cycle are shown in Figure 3 for the three stations for a winter, summer and autumn month. Common to all, are the tidal changes in volume concentration as a result of deposition, resuspension/erosion and advection. The FSDs at MOW1 were more variable during a tide than at W05 and W08, meaning that break-up and aggregation are dominating the FSD. At W05 and W08, the particles in suspension were not changing significantly in size. This points to strong aggregates and particles of biological origin

- that are not subject to turbulence-driven flocculation processes. In spring and, to some extent, in 474 autumn, the FSD at MOW1 became bimodal, with a main peak around 60 µm and a second one 475 around 300 µm. The latter is an indication of the occurrence of large biomineral flocs (Shen et 476 al., 2018). The FSDs at W05 and W08 were unimodal in spring with a peak at 300  $\mu$ m. In early 477 autumn (September) and in winter they became bimodal, with a secondary peak at around 70 µm 478 (winter) or 100 µm (early autumn). The winter FSD at W05 was more variable as it is located at 479 the edge of the turbidity maximum zone. When the turbidity is higher, then the FSD resembles 480 that of MOW1, in the opposite case it is similar to the offshore station W08 (the latter is shown 481 in the figure). The low-pass filtered median floc sizes from the long-term LISST measurements 482 (2016-2019) at MOW1 are shown in Figure 4. The median floc size is about 50 µm in winter and 483 484 increases up to 150 µm in summer. The four-class entropy analysis and the associated mean FSD show a mirrored evolution over the year as a function of seasonal changes. The FSD of class 1 485  $(D50 = 47 \text{ }\mu\text{m})$  are most prominent between about 15 October and 15 March, those of class 2 486  $(D50 = 60 \ \mu m)$  in the transitional periods characterized by an increase (15 March to 15 April) or 487 decrease (15 September to 15 October) of biological activity. Class 3 (D50 =  $81 \mu m$ ) and 4 (D50 488 = 116  $\mu$ m) prevail over spring and summer. The large biomineral flocs (>200  $\mu$ m) are more 489 frequent from late spring till early autumn during the decaying phytoplankton blooms, as 490
- 491 indicated by the course in Chl-a.



493 Figure 3: Hourly particle size distribution at about 2 m above the seabed during a tidal cycle at

494 stations MOW1 (January, May, September), W05 (December, May, September) and W08

495 (December, May, September). The volume concentration is normalized by dividing all values

with the largest one measured during the tidal cycle. FSD at MOW1 are highlighted around

497 maximum flood currents (light blue), HW slack (light red), maximum ebb currents (blue) and

498 LW slack (red).





502 the corresponding floc size distributions are shown in the right panel.

#### 5033.3 Particulate Organic Matter Content of the SPM

499

The POC and PON fractions of SPM as a function of SPM concentration are shown in 504 Figure 5. The graphs indicate an increase of the OM content with decreasing SPM concentration, 505 which has been documented as a characteristic feature (e.g. Eisma & Kalf, 1987; Jago et al., 506 1994; Fettweis et al., 2006; Schartau et al., 2019). The POM content (measured as Loss-on-507 Ignition, LoI) of the SPM (not shown) varies between about 10% to more than 90%. The fraction 508 of POC incorporated in SPM varies between ~2.5% and 30% (POC), while the PON fraction is 509 clearly lower, ranging between ~0.35% and 4%. Thus, the POC and PON content of SPM are 510 511 about 4 and 28 times smaller than the POM content respectively. From about a 100 mg/l SPM concentration onward the POC and PON content reach an asymptotic value of about 2.5% and 512 0.35% respectively. The 10 to 15 time increase of the POC and PON content occurs over two 513 orders of magnitude in SPM concentration and shows that SPM in the nearshore contains 514 proportionally significantly less OM than in the offshore (see Tables A.1 - A.3 in Appendix A 515 for exact values). The best estimates of K<sub>POM</sub>, f<sub>1</sub> and f<sub>2</sub> for annual (all year) representations of 516 POC:SPM, PON:SPM and TEP:SPM are listed in Table 1. In all cases m<sub>POM</sub> was taken as the 517 best estimate for the POM model (eq. 4) for the LoI data set from the German Bight and amounts 518 to 0.13 (see Schartau et al., 2019). 519

520 TEPs incorporate mainly organic carbon. Thus, measured TEP concentrations are not independent of the POC measurements, which is reflected in the significant (p<0.05) correlation 521 522 between POC and TEP in the data with an  $R^2=0.59$ . Accordingly, the dependency between TEP and SPM concentration (Figure 5c) is similar to those found for POC and PON (Figures 5a and 523 5b). Instead of a percentage fraction of SPM, the TEP:SPM ratio is given here in mass units (g 524 XG eq.)/g (Figure 5c), because the concentration of the Alcian blue stained microgels cannot be 525 easily related to a mass concentration e.g. of organic carbon, in the presence of resuspended 526 mineral particles. A derivation of a dependency between Alcian blue stained particles and their 527 carbon content at different SPM concentrations is a relevant side aspect of our study (see 528 Appendix D). The TEP:SPM ratio is approximately 0.05 (g XG eq.)/g at SPM concentrations529

greater than 100 mg/l. With decreasing SPM concentrations, the ratio increases by one order of magnitude, to  $\sim 0.3$  (g XG eq.)/g at SPM concentrations below 6 mg/l.



**Figure 5**: Model fit and 95% confidence intervals through all data for the POC content (left), PON content (middle) and the TEP content (right) as a function of the SPM concentration. The error bars represent the uncertainties of the measurements (see § 2.2.1). The shaded area is the 95% confidence interval of an ensemble of individual model fits, based on 100 optimizations

537 with different, randomly sampled, data subsets.

#### 538 3.4 Model Estimates of the Seasonally Sorted Data of POC, PON and TEP

The annual composite data of POC:SPM, PON:SPM and TEP:SPM, as depicted in Figure 539 5, exhibit extensive variability. For the most part, this variability can be attributed to seasonal 540 changes. The fits of the models to annual composite data resolve and explain only differences 541 between the different observational types. Seasonal variations have been further resolved by 542 fitting the models to seasonally sorted data. Table 1 includes estimates of  $K_{POM}$ ,  $f_1$  and  $f_2$  all four 543 544 seasons separately. A higher resolution of temporal changes of parameter values was derived for model fits to TEP:SPM data, with monthly parameter estimates (see Table B.1 in Appendix B). 545 In general, the non-linear dependency of the POC and PON content of SPM (Figure 6) varies in a 546 similar way as the TEP:SPM ratio (Figure 7), with clearly altered seasonal signals. 547

At high SPM concentrations, greater than 100 mg/l, the variability remains small and 548 temporal differences between the model solutions are indistinguishable for POC:SPM and 549 PON:SPM. A large spread in the seasonally resolved model solutions were obtained for 550 TEP:SPM ratio at SPM > 100 mg/l (Figure 7). The only noticeable difference is the lower 551 552 estimate of f<sub>2</sub> obtained for modelling the TEP:SPM ratio at high SPM concentrations in winter. Whether this estimate is actually associated with a clear difference in the mineral-associated 553 fraction of TEP in winter is unclear. Apart from this, the overall spread does not follow any 554 seasonal pattern and must be attributed to larger uncertainties in the model fits of the TEP:SPM 555 ratio. Overall, seasonal variations in the mineral-associated fractions of POC, PON, and TEP in 556 SPM could not be identified and appear to be negligible. The small changes may rather be 557 associated with variations in sediment types that contain variable constituents and fractions of 558 559 minerals.

- 561 **Table 1**: Model parameters for POC, PON and TEP for all data (year) and for the four seasons.
- 562 The units for  $K_{POM}$  are mg/l (same unit as SPM concentration) and for  $f_1$  and  $f_2$  [g/(g POM)] for
- 563 POC and PON and in [g XG eq./(g POM)] for TEP.

m <sub>РОМ</sub> =0.13	K <sub>POM</sub>	$\mathbf{f}_2$							
	CI 95% [lower, upper]	CI 95% [lower, upper]	CI 95% [lower, upper]						
Year									
POC	3.25 [0.24, 5.53]	0.122 [0.065, 0.981]	0.268 [0.248, 0.291]						
PON	2.73 [0.13, 5.75]	0.021 [0.006, 0.203]	0.033 [0.031, 0.036]						
TEP	1.61 [0.20, 4.36]	0.367 [0.100, 1.200]	0.422 [0.285, 0.583]						
Winter									
POC	3.02 [1.34, 4.49]	0.058 [0.038, 0.112]	0.260 [0.248, 0.273]						
PON	3.20 [2.16, 4.22]	0.008 [0.007, 0.011]	0.032 [0.030, 0.033]						
TEP	4.25 [2.68, 6.00]	0.097 [0.058, 0.152]	0.251 [0.185, 0.318]						
Spring									
POC	4.92 [3.11, 6.70]	0.197 [0.158, 0.261]	0.239 [0.216, 0.258]						
PON	4.31 [2.95, 5.61]	0.032 [0.027, 0.038]	0.031 [0.028, 0.034]						
TEP	3.67 [2.12, 4.83]	0.489 [0.386, 0.641]	0.457 [0.265, 0.677]						
		Summer							
POC	2.79 [0.28, 5.40]	0.173 [0.105, 0.993]	0.267 [0.237, 0.306]						
PON	2.82 [1.34, 4.05]	0.028 [0.022, 0.043]	0.034 [0.031, 0.039]						
TEP	3.27 [1.63, 4.62]	0.379 [0.281, 0.567]	0.456 [0.296, 0.601]						
Autumn									
POC	2.18 [0.63, 3.62]	0.141 [0.085, 0.350]	0.282 [0255, 0.304]						
PON	0.90 [0.08, 8.00]	0.033 [0.009, 0.106]	0.031 [0028, 0.033]						
TEP	1.46 [0.10, 10.00]	0.267 [0.020, 1.200]	0.514 [0.392, 0.647]						

For SPM concentrations below ~100 mg/l, we identified clear and distinctive seasonal 565 patterns. Our results show a correlation with season (and thus with primary production), which is 566 most pronounced in the low-turbid data. In all cases, the seasonal changes could be well resolved 567 (Figures 6 and 7). During the winter season the variations of the SPM's content of POC, PON, 568 and TEP remain small for a large range of SPM concentrations, with only a small increase of 569 respective fractions at low SPM concentrations. The general picture changes drastically for the 570 spring period when phytoplankton blooms induce a substantial increase in the POC and PON 571 content of the SPM, and also the TEP:SPM ratios follow this signal. At SPM concentrations of 1 572 mg/l, the lower end of the sample values, the POC and PON fractions of SPM are  $\sim 17\%$  and 573  $\sim 2.5\%$ , and for TEP  $\sim 0.4$  (g XG eq.)/g. During spring the measured POC and PON contents of 574 the SPM feature some high values at SPM concentration between 10 to 50 mg/l, which are not 575 captured by the model solution and are likely caused by the high spatio-temporal variability of 576 patches with elevated phytoplankton biomass concentrations. Still, the model's optimized 577 solutions for spring yield highest in the production of fresh POC, PON, and TEP in this range of 578 SPM concentrations. According to the optimized model solutions, the elevated spring values 579 gradually decrease during summer and autumn, a trend that can hardly be recognized on the basis 580 of the highly scattered sample data alone. The differences between the summer and autumn 581 signals are somewhat less distinctive than their differences to spring conditions. This is because 582 transitional months like September may include a prolonged bloom signal from summer or 583

involve secondary bloom events due to the recurrence of elevated nutrient concentrations. Thetransitions from autumn to winter conditions are again well pronounced.

The ratio  $(f_{1,POC}):(f_{1,PON}) = (POC_f:POM_f)/(PON_f:POM_f)$  is indicative for the C:N ratio of 586 the estimated fresh POM (POC<sub>f</sub>:PON<sub>f</sub>), while the same ratio for the  $f_2$  parameter represents the 587 C:N ratio of the estimated mineral-associated POM (POC<sub>m</sub>:PON<sub>m</sub>), see Table 2 and Figure C.1 588 in Appendix C. Both ratios have a seasonal variability, the POCf. PONf ratio compares well with 589 the POC:PON ratio from the observations, which confirms the credibility of our parameter 590 estimates. The winter and autumn values of the fresh POC<sub>f</sub>:PON<sub>f</sub> and of the POC<sub>obs</sub>:PON<sub>obs</sub> are 591 above the Redfield ratio (6.62 molN molC<sup>-1</sup>) and the summer-spring values below it, but all 592 values agree within the levels of uncertainty. The mineral-associated ratio POC<sub>m</sub>:PON<sub>m</sub> is always 593 above the Redfield ratio well beyond the lower 95% confidence limits (except summer), 594

<sup>595</sup> implying that the mineral-associated POM is more enriched in C than the fresh POM.





individual model fits, based on 100 optimizations with different, randomly sampled, data subsets.



**Figure 7**: TEP content (left) and TEP concentration (right) as a function of SPM concentration. The lines are the result of the TEP-SPM model for the different seasons. The error bars represent the uncertainties of the TEP measurements, see § 2.2.1. Bottom panels show the 95% confidence interval of an ensemble of individual model fits, based on 100 optimizations with different,

607 randomly sampled, data subsets.

608

609 **Table 2**: C/N ratios of the model parameters  $f_1(POC)$ : $f_1(PON)$  and  $f_2(POC)$ : $f_2(PON)$  and of the 610 ratio POC<sub>obs</sub>:PON<sub>obs</sub> from in situ measurements.

	f <sub>1,POC</sub> :f <sub>1,PON</sub> CI 95% [lower, upper]	f <sub>2,POC</sub> :f <sub>2,PON</sub> CI 95% [lower, upper]	POC <sub>obs</sub> :PON <sub>obs</sub> CI 95% [lower, upper]
Winter	7.99 [4.35, 16.15]	8.39 [7.78, 8.98]	7.67 [5.27, 11.99]
Spring	6.85 [5.12, 9.14]	7.81 [6.80, 8.83]	7.13 [5.14, 10.19]
Summer	7.37 [1.41, >20]	8.06 [6.43, 9.95]	6.76 [4.99, 10.33]
Autumn	5.42 [2.66, >20]	9.12 [8.31, 9.96]	7.64 [5.11, 12.76]

#### 612 4 Discussion

The main objective of the study is to investigate to what extent a model-based separation 613 of the organic particulate matter into fresh and mineral-associated, i.e. fresh and labile versus 614 more recalcitrant fractions, may unravel a signal that relates to the seasonal buildup and 615 breakdown of flocs in coastal oceans. In principle, flocculation is depending on a number of 616 local environmental conditions, e.g. turbulence, cation concentration, SPM concentration as a 617 proxy particle number density, mineral composition, POM concentration and composition (e.g. 618 TEP) and microorganism (Dyer, 1989; Mietta et al., 2009; Keyvani & Strom, 2014; Lai et al., 619 2018; Zhang et al., 2021). The bulk mineralogical composition of the SPM in the study area is 620 relatively constant and consists of 32-39% clays, 25-33% carbonates, 12-18% quartz, 11-15% 621 amorphous silicates and 5-8% feldspars and accessory minerals (Adriaens et al., 2019). The 622 cation concentrations are high and well above the threshold for salinity induced flocculation so 623 624 that flocculation in the study area is above all controlled by the POM composition of the SPM, the SPM concentration and the hydrodynamic conditions. The effect of turbulence and SPM 625 concentration on flocculation in the study area has been described in previous studies (Fettweis 626 et al., 2006; Fettweis et al., 2014; Fettweis & Baeye, 2015). They reported that maximum floc 627 size was mainly controlled by turbulence intensity (tides and waves), which is higher in the 628 nearshore area than offshore, but does not exhibit a pronounced seasonal signal. Our LISST data 629 (Figure 3) confirm that the size of the largest flocs is similar during all seasons, but their 630 abundance is higher in spring and summer, because they seem to be more tightly bound and 631 resist better shear-induced breakup. 632

The seasonal dependence of SPM concentration with lowest values in summer (Figure 633 634 2d) contrasts with the inverse dependence of the median floc sizes which are highest in summer (Figure 4, left panel). Thus, SPM concentration in itself can be ruled out to explain flocculation 635 and the qualitative properties of SPM may provide a much better clue. Given the large variability 636 in SPM concentration within the nearshore areas and along their transition to the offshore waters, 637 638 their variation may unravel predominant variations of the processes involved. In the following discussion we will show how the modified application of the POM-SPM model of Schartau et al. 639 (2019) to the POC, PON and TEP sample data turned out to be beneficial. With the aid of the 640 calibrated model solutions we could estimate how the relative fractions of freshly produced 641 labile and semi-labile OM (of POC, PON, and TEP) along with the rather recalcitrant mineral-642 associated OM content of the SPM change with SPM concentration. A starting point of this 643 approach is the obvious concurrence of seasonal rises and declines in median floc size (Figures 3 644 and 4) with the model parameter  $K_{POM}$ , which numerates the seasonal built up of fresh organic 645 material and its components (Figures 5-7 and Table 1). Our synthesis between model application 646 and in situ measurements delivers important insight into the complex process of flocculation in a 647 region of great variability. Based on results of our analyses we can expand the scope of 648 discussion on how the fresh and the mineral-associated OM fractions of the SPM affect the 649 process of biophysical flocculation. 650

4.1 Spatio-Temporal Variations of Floc Characteristics

652 Flocs in the nearshore high turbid station MOW1 were subject to extensive temporal

variations in volume concentration, density and size during a tidal cycle (Figures 2 and 3). The
 FSDs were skewed towards smaller sizes around peak flow (blue in Figure 3) and developed a

peak in the larger size classes around slack water (red in Figure 3). Lee et al. (2012) have shown

that the flocs at MOW1 are characterized by a multimodal size distribution that consists of small 656 particles, flocculi, microflocs, and macroflocs. The smallest particles likely consist of clay-sized 657 particles of various mineral composition, the flocculi are breakage-resistant aggregates of clay 658 minerals, microflocs can be attributed to the medium size aggregates, whereas macroflocs can be 659 identified as the large aggregates with diameters up to a few hundred micrometers. Tran and 660 Strom (2017) have shown in a laboratory experiment that silt and clay combine into flocs. In 661 some contrast to this, we observe (Figure 3 and 4) that the FSDs at MOW1 all had well 662 pronounced modes within the smallest size classes in winter. This mode diminished towards 663 summer. This indicates that in winter abundant fine-grained mineral particles do not aggregate 664 into flocs. They settle slowly and remain in suspension longer, resulting in a background 665 turbidity that is higher than in summer. In general, lower turbulence intensities before slack 666 water promote the aggregation of the more mineral (i.e. with a POC content of about 3%) 667 flocculi and microflocs into larger macroflocs. In winter these macroflocs have similar 668 characteristics than the microflocs, i.e. they are mineral enriched (Tang & Maggi, 2016). In 669 summer, according to Fettweis and Baeye (2015), the small particles, flocculi and microflocs 670 also coagulate with freshly produced OM to form quite stable aggregates that are enriched with 671 biogenic substances, including phytoplankton cells and detrital substances. These spring and 672 summer flocs have lower densities than the winter and autumn flocs (see Figure 2g and Tables in 673 Appendix A) but reach floc sizes that involve settling velocities that exceed those of the smaller 674 675 winter flocs leading to their accumulation near the bed and the decrease of the average SPM concentrations in the water column. 676

677 In contrast, in the offshore stations W05 and W08, the seasonal variabilities in the concentration of SPM and the OM parameters were less pronounced and the FSD distribution 678 rather constant over the tides (Figure 3), showing that here aggregation dominates disaggregation 679 kinetics (Fettweis and Lee, 2017). The principal variations in these parameters occurred between 680 seasons and not within tides. In winter and autumn, the FSDs were multimodal, with a first mode 681 around 10 µm, a second one around 50-100 µm and a third one around 300 µm (Figure 3). The 682 683 first mode could consist of flocculi, while the second mode could be formed by minerals from biogenic origin (carbonates, amorphous quartz). In spring, the 300 µm peak dominated the FSDs. 684 In summer, the increase of the median floc size in these offshore stations (see Figure 2) indicates 685 that the observed decrease of the lower modes is caused by the incorporation of these particles 686 into the larger aggregates. These larger biological aggregates can be lighter and even settle 687 slower than smaller bio-mineral aggregates found at MOW1 (Maggi & Tang, 2015). 688

689 4.2. TEP Concentration and its Relation to Floc Size

#### 690 4.2.1 Seasonal Variation in TEP Concentration

A correlation of TEP concentrations with the rise and decline of phytoplankton blooms is 691 reported from lab cultures (Fukao et al., 2010), estuarine and nearshore areas (Ramaiah et al., 692 2001; Bhaskar and Bhosle, 2006; Chowdhury et al., 2016), and from the open ocean (Mari et al. 693 2017). Others report temporary disconnection of TEP from Chl-a concentrations (Ortega-694 Retuarta et al., 2017, Lee et al., 2020). Our data do not show a close relationship between Chl-a 695 and TEP concentration (See Figure 2j and 2l). In the shallow nearshore station MOW1 a 696 substantial fraction of TEP seems to be rather mineral-associated, entering the water column via 697 resuspension of sediment particles. The TEP concentration followed the SPM concentration 698 699 irrespective of the season and thus also during winter when primary production has largely

ceased (Figure 2d, 2j and Figure 7, right panel). This general dependency is modulated by a

seasonal signal, depending on the amount of POC and PON being built up via primary

702 production. Our seasonal pattern is in line with findings from the turbidity maximum of the Seine

estuary (Morelle et al., 2018). There, the highest TEP concentrations coincide with the lowest
 EPS and DOC concentration in winter and vice versa in summer. In contrast, the more offshore

stations, where SPM concentration remained most of the time below 10 mg/l, had TEP and POC

concentrations that were generally higher in spring and summer than in winter. The offshore

environments with low turbid conditions agree with the correlation found by Mari and Burd

(1998) between DOC and TEP concentrations suggesting that TEP are formed by coagulation of

the dissolved EPS (Mari & Burd, 1998). These results indicate the occurrence of two types of

TEP, presumably having different chemical characteristics with respect to their stickiness and

711 their potential to promote the formation of flocs of large size.

712 An immediate dependency between the total abundance of TEP and floc size cannot be inferred from our data. The interpretation of the results for the station MOW1 is complicated by 713 the fact that similar TEP concentrations resulted in different floc sizes in winter and summer (see 714 Figure 2f and 2j). Morelle et al. (2018) have explained the higher TEP concentration in winter by 715 deposition and resuspension processes. This would mean that due to the larger flocs in spring and 716 summer, a large part of the TEP is found in the benthic boundary layer or on the bed, while in 717 winter it is resuspended. However, this interpretation does not explain why floc sizes were 718 smaller in winter and is not supported by studies relating floc size to TEP concentration (e.g. 719 Passow, 2002; Verney et al., 2009; Deng et al., 2019) and by our data that show larger floc sizes 720 721 in spring and summer. Our analysis suggests that biophysical flocculation in highly turbid areas is strongly affected by the occurrence of fresh OM rather than the total amount of OM. TEP 722 production rapidly increased when the maximum capacity for the build-up of fresh POC and 723 PON was reached (Figure 8). This occurs when phytoplankton approaches nutrient limited 724 growth conditions (Engel et al., 2004; Schartau et al., 2007). Part of the fresh OM consists of 725 EPS and will partly be transformed into TEP. We could not explicitly resolve the process of TEP 726 727 formation from dissolved precursors, but found generally higher DOC concentration in spring and summer. Figure 2k shows that DOC concentration, which contains EPS, has a maximum in 728 late spring and summer, as in the Seine estuary (Morelle et al., 2018). 729

In order to assess the relationship between the time evolution of SPM and TEP in their 730 quantities and qualities, Figure 9 shows the low-pass filtered median floc size data at the high 731 turbid station MOW1 (as in Figure 4) together with the low-pass filtered long-term SPM 732 concentration time series (upper panel), as well as the seasonal evolution of fresh and total TEP 733 concentration (lower panel) derived from calibrated results of the TEP-SPM model based on 734 monthly model parameter estimates of  $K_{POM}$ ,  $f_1$  and  $f_2$  (Appendix B). When fresh TEP is 735 produced (from half February onward), the median floc size increases (in particular from March 736 on, when the proportion of fresh TEP to total TEP ratio increases) and SPM concentration 737 decreases. Although fresh TEP concentration is at its maximum in early spring, the increase in 738 median floc size, the changes in floc size distribution (Figure 4) and the decrease in SPM 739 concentration occur more gradually. The progressive raise in floc size follows the increase and 740 the decrease of the fresh TEP fraction (TEP<sub>fresh</sub>:TEP<sub>total</sub>). This ratio is low during winter (about 741 2%) and starts to increase from the beginning of February to about 15% in March and then more 742 quickly to reach a maximum around 60% in May-June. The peaks in floc sizes as well as the 743 lowest SPM concentrations were observed during this period. 744



Figure 8: The observed total TEP concentration versus the model derived fresh (upper panel)
and mineral-associated (lower panel) POC and PON concentration. The lines are the estimated
total TEP concentration as a function of POC and PON concentration derived from the POM-

<sup>749</sup> SPM model.



#### 751

Figure 9: (a) Long-term and low-pass SPM concentration (2005-2016) and median floc size
(2007-2019) at 2 m above bed. The shaded area is the standard deviation if more than 2 data
points are available. (b) The model estimates of total (black) and fresh (blue) TEP concentration
calculated from the long-term SPM concentration time series. The red line is the fraction of fresh

TEP in the total TEP. All data are from the near shore station MOW1.

The decrease of the fresh TEP concentration after its quick accumulation in spring occurs gradually over a period of about 6 months (May-November) and can be due to hydrolyzation, consumption and/or deposition. This is in contrast with the early spring period, where most of the fresh TEP accumulation occurs within about one month (February-March), before reaching a maximum in early May. The production of fresh TEP correlates with the first increase in Chl a concentration in February in 2019 and the first decrease of SPM concentration from beginning of March onward (Figure 10). These findings support the hypothesis that in early spring in the

turbid nearshore, when light conditions are still depleted, light adapted phytoplankton species

- <sup>765</sup> initiate the spring bloom and also induce the formation of fresh TEP. In contrast to the mineral-
- associated TEP, it is this initial occurrence of fresh TEP that eventually promotes aggregation
- and the formation of larger flocs with higher settling rates. This in turn lowers SPM
- concentration and reduces light attenuation, which paves the way for species with higher light
- requirements in the phytoplankton seasonal succession. Altogether, the results underline that the
- different components of the SPM (i.e., mineral, organic matter and living particles) form an
- 771 integrated dynamic system with direct interactions and feedback controls.



Figure 10: Time series of surface SPM and Chl-a concentration in 2019 derived from remote
sensing (Sentinel-3/OLCI) and in situ observations at station MOW1 (nearshore). The in-situ
data are mean values over a tidal cycle, the error bars are the standard error of the mean.

#### *4.2.2. TEP in Autumn and Winter*

What are the quantitative and qualitative characteristics of TEP outside the growth 777 season? The presence of high concentrations of TEP in autumn and winter above all in the turbid 778 nearshore (Figure 2k) raises questions on the characteristics of this organic matter. Mari et al. 779 (2007) mention that the efficiency of the transformation of EPS into TEP and the TEP reactivity 780 decrease with time. This would mean that the TEP stickiness varies as a function of the 781 degradation stage and age. Winter TEP would then be smaller in size and less sticky, while in 782 spring and summer it would consist of larger and more sticky particles that become actively 783 involved in flocculation dynamics (Engel et al., 2020). The biomineral flocs resist better to 784 shear-induced break-up in spring and summer due to availability of more reactive TEP and of the 785 inclusion of free-floating bacteria and other microorganisms into the flocs that produces 786 themselves exopolymers (Fettweis et al., 2014; Jachlewski et al., 2015; Shen et al., 2019). The 787 bacteria associated with TEP contribute to the hydrolysis of the OM and thus foster the gradual 788 decay and disaggregation of the biomineral flocs in autumn (Smith et al., 1992; Alldredge et al., 789 1993; Passow & Alldredge, 1994), which is reflected in the observed decrease in floc size in our 790

791 data. As the transition from summer to winter is gradual, one would expect that TEP

- concentration decreases through microbial respiration until a minimum is reached just before the
- onset of the algae bloom in early spring. The latter is observed in the low turbid offshore stations
- W05 and W08, but not in the turbid MOW1 station, see Figure 2j. Other studies highlight the relationship between OM content and mineral surface area (Keil et al., 1994; Mayer, 1994). This
- relationship between OM content and mineral surface area (Keil et al., 1994; Mayer, 1994).
   means that with increasing SPM concentration, the OM concentration and thus also TEP
- <sup>790</sup> inclusion increases, while the POM content of the SPM decreases until reaching an
- asymptotic value at high SPM concentrations (>100 mg/l) of about 3% POC, 0.4% PON, and
- 799 0.04 (mg XG eq.)/mg TEP (Figures 5-7). At high SPM concentrations the fresh OM represents
- only a small part of the total OM and is hardly detectable due to the high variability of the
   measurements. Both the fresh and recalcitrant OM can be associated to the mineral surfaces,
- measurements. Both the fresh and recalcitrant OM can be associated to the mineral surfaces,
  being protected from microbial respiration (Keil et al., 1994; Kalbitz et al., 2005; Hemingway et
- al., 2019; Chen et al., 2021). The protected mineral-associated OM explains the high TEP
- sold concentrations in winter in high turbid areas such as the Belgian nearshore, Chesapeake Bay
- 805 (Malpezzi et al., 2013) or the Seine estuary (Morelle et al., 2018).

The mineral-associated POC over TEP ratio is about 1 in winter and between 0.52 and 806 0.59 (mean 0.56) during the other seasons (see Appendix D). The higher ratio in winter is the 807 result of the optimal estimation of the POC and TEP content in the SPM based on our data. The 808 809 model estimates a lower value of the TEP content in the SPM in winter at high SPM concentrations than for the other seasons (Figure 6). Such distinction could be explained by a 810 lower amount of mineral-associated TEP in winter and by the occurrence of two different 811 mineral-associated TEP fractions. One is more recalcitrant and remains, while the other one is 812 still subject to gradual but slow degradation and eventually disappears in winter. The first one 813 could consist of the TEP that occurs in between the layers of the clay crystal structures (Mayer, 814 1994; Blattmann et al., 2019). The second one could consist of a semi-labile biofilm on the 815 surface of the mineral particles (Decho & Gutierrez, 2017). Anyway, the mineral-associated 816 POC over TEP ratios indicates that the recalcitrant mineral-associated TEP makes up a great 817 portion of the mineral-associated POC. 818

To conclude, while also present during autumn and winter, fresh TEP occurs at much 819 lower concentration then. It could originate from winter biological activity, from bacteria or 820 phytoplankton (Chl-a concentration in winter is on average between 1.1  $\mu$ g/l at W08 and 3.5  $\mu$ g/l 821 at MOW1, see appendix A). The flocs in autumn and winter can thus be considered as 822 823 biophysical in nature as few fresh TEP is available to aggregate cohesive particles (such as clay minerals) with non-cohesive ones (such as carbonates) into larger floc. The rising tails in the 824 winter FSD at MOW1 (Figures 3 and 4) point to the occurrence of particles smaller than the 825 measuring range of the LISST (i.e. 2.72 µm) and indicate that the efficiency of biophysical 826 aggregation in winter is, however, much lower than in spring and summer in the high turbid 827 nearshore. 828

4.3 Spatial Variation in SPM Composition

#### 4.3.1 Asymptotic Decrease of OM Content with Increasing SPM Concentration

The surface sediments at W05 and W08 consist of medium sand with small amounts of

fines (a few %) and POC contents in the fraction <63  $\mu$ m of about 1.8% and 1.1% respectively. These values are lower by a factor of 4 and 8, respectively, than the mean POC content of the

SPM in these stations (see Tables A.2 and A.3 in appendix A). In these stations the SPM 834 concentration was generally below 10 mg/l. This is a clear indication that the suspended material 835 can only to a minor part originate from the sea bed. This illustrates nicely the increasing 836 decoupling of near bed and water column processes with water depth and distance from the 837 coastline. In the nearshore station MOW1, the amount of the fraction <63 µm in the sediments is 838 about 50% (Fettweis and Van den Eynde, 2003), the POC content of the surface sediments 839 (fraction  $<63 \mu m$ ) is only lower by a factor of 1.5 than of the SPM at high concentrations (2%) 840 versus 3%) and indicates that the surface layer of the seabed is actively involved in the tidally 841 induced resuspension and deposition of the particulate material (Table A.1 in appendix A). The 842 asymptotic value of 3% POC at high SPM concentration shows that the minerals are saturated 843 844 and that no long-term accumulation of OM occurs in the nearshore station MOW1. The fresh OM that is not associated with the mineral surfaces will thus quickly be consumed in the food 845 web. Similar values of the POC contents of the SPM have been found in the turbidity maxima of 846 the Seine and Loire estuary (Etcheber et al., 2007), lower ones in the Gironde estuary (Etcheber 847 et al., 2007) and higher ones in the Yangtze (Milliman et al., 1984) and Congo river (Bouillon et 848 al., 2012). It is remarkable that these variations in POC content between different areas are 849 relatively small (2%-5%), which points to a similar composition of the SPM in many turbid 850 aquatic ecosystems over the world. The small differences are probably caused by methodological 851 differences, measuring uncertainties and by different mineral-associations of the SPM, as the 852 853 preservation of OM is controlled mainly by its clay mineralogy (Blattmann et al., 2019).

#### 4.3.2 Nearshore to Offshore Gradient in Fresh and Mineral-Associated OM

We used the Sentinel-3/OLCI satellite images of SPM concentration to extract the cross-855 shore variation of mineral-associated and fresh components of POM, POC, PON and TEP at the 856 water surface. Taking the model parameters for  $f_1$ ,  $f_2$ ,  $K_{POM}$  and  $m_{POM}$  (see Table 1), we applied 857 the model pixelwise to the remote sensing data. In this way we generated eight further secondary 858 satellite products purely based on SPM surface concentration. For the purpose of this study we 859 discuss these data for all seasons along a transect the connects the three measuring stations from 860 the coast (MOW1) with SPM concentration  $\cong$  80 mg/l via W05 to the offshore (W08) with  $\cong$  2 861 862 mg/l (see Figure 11).

The mineral-associated part (middle) follows to a large part the SPM concentration and 863 has the same strong decrease with increasing distance from the coast. The fresh POM (left) in 864 contrast, nearly keeps his level along the whole transect. The major seasonal formation of fresh 865 POM thus occurs not only within the shallow coastal regions but extends along the whole area. 866 These patterns are similar for all components of the POM and TEP and for all seasons. For the 867 mineral-associated parts, winter has the highest and summer the lowest values except for TEP 868 where the highest values are during the periods of spring and autumn blooms. The fresh parts are 869 870 always highest in spring and lowest in winter. The ratios of fresh to mineral-associated POC, PON and TEP (right) show that there is a zone somewhere around station W05, where both 871 fractions are about equal (ratio = 1). This may be identified as a transition zone where, seen from 872 the land, the near coast conditions with particle dominance from the sea bed turn into open sea 873 conditions with particles who are of pelagic origin. This transition zone is located in between 874 MOW1 and W05 in spring and summer at a water depth around 10 to 15 m and corresponds with 875 a surface SPM concentration of about 40 mg/l in spring and about 20 mg/l in summer. It is 876 located more offshore in autumn where it occurs around W05 (water depth around 20 m) with 877 about 8 mg/l SPM concentration and close to W08 in winter. 878





Figure 11: Model estimates of the nearshore (MOW1) to offshore (W08) fresh (left column) and 881 mineral-associated (middle column) POC (a-b), PON (d-e) and TEP (g-h) concentrations 882

calculated from the Sentinel-3/OLC derived surface SPM concentrations (j) using the model 883

parameters of Table 1. The right column shows the ratios of fresh to mineral POC (c), PON (f) 884

and TEP (i) concentration. Values above 1 have a fresh POC, PON or TEP concentration that 885

exceed the mineral-associated one. The lower panel (k) shows the bathymetry (m below mean 886 sea level) along the transect. The large changes in bathymetry between W05 and W08 are from

887 sandbanks. 888

#### 4.4 Consequences for the Modelling and Monitoring of Coastal Ecosystems

Changes in coastal ecosystems are often correlated with changes in water clarity or SPM 890 concentration and thus with the POM content of the SPM (e.g. May et al., 2003; Capuzzo et al., 891 2015). The composition of SPM is the result of multiple natural processes that reflect the 892 continuous mixing of marine and terrestrial particles of various ages and origins over geological 893 894 time scales (Adriaens et al., 2018). Also, human activities have impacted the SPM concentration and composition. While the strongest anthropogenic changes in the study area occurred during 895 the last decades, human occupation and landscape development date back to the last two 896 millennia. They inevitably have had an impact on SPM composition and concentration 897 (Baeteman et al., 2002). In the last decades, the North Sea has been subject to changes in SPM 898 concentration and biological activities amongst which are the decrease in phytoplankton 899 production and changes in community structures (Capuzzo et al., 2018; Nohe et al., 2020); the 900 shift in chlorophyll a phenology (Desmit et al., 2020); the imbalance in the biogeochemical 901 cycles of nutrients (Rousseau et al., 2006, Desmit et al., 2018); and the increase of the SPM 902 concentration due to major construction works (Van Maren et al., 2015). 903

The area where the concentration of fresh and mineral-associated POM is about equal is 904 of particular interest Schartau et al., 2019). For the German Bight, this transition zone is typically 905 found at water depths of approximately 15 to 20 m along cross-shore transects and is 906 characterized by a maximum of the settling velocities (Maerz et al., 2016). Human activities, e.g. 907 dredging and dumping operations in the turbid nearshore, wind farms in the low turbid offshore 908 909 areas or the effect of global warming (Fettweis et al., 2012; Jaiser et al., 2012; Baeye et al., 2015; Høyer & Karagali, 2016) might influence the localization of this transition zone and could make 910 it a key element in monitoring programs such as the EU Marine Strategy Framework Directive. 911 With our data-model syntheses we could consolidate a relationship that can be applied to SPM 912 concentrations derived from other sources, e.g. from in situ long-term observations using optical 913 and acoustic sensors or from remote sensing. A good example for such an application was 914 915 documented by Schartau et al. (2019) for resolving spatio-temporal variations in fresh and mineral-associated fractions of POM in the German Bight. Though still imperfect, the 916 application of the refined model to satellite SPM concentration products or high-resolution in-917 918 situ time series of calibrated optical or acoustical instruments will yield spatio-temporal 919 compositional changes of the SPM, with respect to POC, PON, and TEP, both on large scales and for anomalous events. This greatly facilitates the monitoring of water quality parameters 920 921 along the gradient from a domination of mineral-associated OM towards a domination of fresh OM, as documented in Figures 9 and 11, and enhances its information content without the 922 increase of resources. 923

Many oceanographic quantities are often inaccessible to direct observation, due to the high cost of in situ sampling, the limitation of the standard water quality parameters and the low spatial and time resolution. Proxies, based on automated, highly resolving instruments are valuable as they help to extend undersampled or unobserved parameters. In this regard, SPM concentration as a proxy for POM, POC, PON, and TEP concentrations seems to be a key ingredient for the assessment and calibration of numerical models of coastal waters, ranging from SPM transport and deposition to key ecosystem processes.

931 Specifically, we have shown that the floc size distribution depends on the SPM
932 concentration and on the availability of fresh TEP. In areas where the fresh over mineral933 associated TEP is about unity and the SPM concentration low, flocculation occurs on a seasonal

time scale rather than a tidal one (Figure 3). In high turbid environments flocculation occurs on

both a tidal and seasonal time scale (Figure 3, 4 and 9). Our model-based differentiation between

936 fresh and mineral-associated POC, PON, and TEP shows, that SPM concentration can be used as

937 a proxy of the flocculation kinetic model parameters (i.e., break-up and aggregation) adopted in

938 numerical SPM transport models.

#### 939 **5 Conclusions**

940 The relevant processes and the critical parameters that drive the mutual interactions between sediment and biological dynamics occur on a wide range of spatial and temporal scales. The OM 941 content of the SPM is highly variable due to physical processes, such as tides and waves, varies 942 with season due to biological activities and with the SPM concentration. There is a distinct 943 difference between the offshore, more open ocean, and the turbid nearshore conditions. In the 944 turbid nearshore areas where SPM concentration often exceeds 100 mg/l the OM fraction in 945 946 association with the mineral particles is dominant, masking the smaller signal of fresh OM produced by primary production. In contrast, in the offshore stations the fresh OM components 947 prevail and therefore explain most of the variability seen in the SPM concentration. POC and 948 PON measurements represent bulk properties of the OM in suspension, combining compounds of 949 various types from labile, semi-labile, to refractory OM as well as specific components such as 950 TEPs and pigments. Our data demonstrate that biophysical flocculation cannot be explained by 951 these bulk observables. However, a model-based separation between a more reactive labile and a 952 less reactive mineral-associated fraction of POC, PON and specifically TEP is a productive 953 954 approach to make the impact of OM on the flocculation process detectable under long-time field observations. From our data-model synthesis we learned that the median floc size increases only 955 when fresh TEP becomes a substantial fraction of the SPM. With our study we could resolve the 956 contradiction that similar TEP concentrations result in different floc sizes in winter and summer. 957 Our results document that fresh TEP is one of the important controls of particles settling in 958

- 959 coastal waters.
- POM is associated with the mineral fraction and primarily with phyllosilicates (clays). It is
- therefore no surprise that the POM concentration increases with SPM concentration in coastal
- waters where due to water depths below 20 m and changing turbulence levels from tidal currents
- and waves, significant exchanges between pelagic and sea bed material exist. The fresh POM,
- and more specifically the presence of fresh TEP in spring and summer is not associated with
- these minerals but rather with the phytoplankton activity. This fresh TEP is responsible for the
- 966 formation of larger biophysical flocs in spring and summer in the high turbid areas rather than
- 967 the total TEP concentration. The nearly absence of fresh TEP in winter as a glue after particle
- collisions limits the floc sizes. Our results underline that the different components of the SPM, which are mineral, organic matter and living particles, form an integrated dynamic system with
- 970 direct interactions and feedback controls.
- 971 Collecting data, such as SPM, POC, PON and TEP concentrations, from samples in the oceans or
- 972 coastal seas, is expensive and often biased towards moderate weather conditions. Especially,
- anomalous, short-term events can often not be captured as shipping schedules are planned long
- 974 in advance. SPM concentration, however, as a key proxy, can be measured either by remote
- 975 sensing or automated in-situ systems. Samples then are only needed for better calibrations of
- 976 these instruments. We have shown that these standard water quality measurements can be used to
- 977 provide mathematical descriptions of additional complementary information, such as fresh and

- 978 mineral-associated POM. The models can be applied to measurements from optical or acoustical
- sensors or satellites to generate further secondary data products. Our approach could change the
- scope of in situ observations from merely the collection of data towards the improvement and
- validation of models that describe fundamental aspects of SPM composition in coastal seas. The
- 982 availability of proxies could have important implications for future monitoring programs, as they
- may fill the lack of continuous long-term data of POM properties and as such could help to improve the efficiency of our monitoring systems by identifying more efficient locations for
- 985 water sampling or for the deployment of observational instruments.

#### 986 Authors contributions

- 987 The conceptual idea of the study had been developed by MF, XD, NT, MS and RR. MF,
- XD and NT conceived and designed the water sampling and analyzed the data together with RR.
- MF and BJL analyzed the LISST data from long-term and tidal cycle measurements. MF
- analyzed the long-term SPM sensor measurements. DvdZ analyzed the remote sensing data. MS
- 991 devised the model and implemented the framework for parameter estimation. MS performed all
- model calibrations and worked out the associated statistical analyses. MF is lead author, who
- 993 incorporated ideas, individual text contributions and revisions from all co-authors. All authors
- helped attaining overall coherence of this study.

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1005The data (water samples, sensor measurements and remote sensing) used in this study can1006be found at url.

### 1007 Appendix A: Tables with Mean Values

1008 **Table A.1**: MOW1 (2004-2020), geometric mean and multiplicative standard deviation for the

1009 particulate and dissolved parameters (TDN: total dissolved nitrogen, TDP: total dissolved

1010 phosphate, Si: silicate) and arithmetic mean and standard deviation for the seabed parameters.

	year		winter		spring		summer		autumn	
	mean	std	mean	std	mean	std	mean	std	mean	std
Particulate parameters										
Hach Turbidity (FNU)	57	2.39	80	2.28	59	2.20	30	2.42	60	2.17
SPM-mass conc. (mg/l)	70	2.32	91	2.25	77	2.41	41	2.14	69	2.09
SPM-vol conc. (µl/l)	249	3.32	353	2.45	227	3.25	90	2.33	395	3.48
Median floc size (µm)	64	1.89	53	1.73	61	2.00	78	1.82	69	1.89
Effective floc density (mg/l)	246	2.48	370	2.11	228	2.46	117	2.02	320	2.30
POC conc. (mg/l)	2.62	2.05	2.91	2.10	3.20	2.01	1.61	1.66	2.56	1.97
PON conc. (mg/l)	0.35	1.99	0.38	2.04	0.44	1.93	0.23	1.61	0.33	1.97
TEP conc. (mg XG eq. /l)	3.57	2.05	2.80	2.34	4.12	1.95	3.30	1.66	4.61	1.85
Chl-a conc. (µg/l)	5.75	2.50	3.47	1.94	12.94	1.93	8.81	1.66	3.78	2.46
Pheo-a conc. (µg/l)	0.41	2.36	0.41	2.58	0.58	1.96	0.28	1.86	0.34	2.47
POC:SPM (%)	3.81	1.39	3.25	1.28	4.07	1.44	4.60	1.40	3.72	1.31
PON:SPM (%)	0.50	1.46	0.40	1.28	0.55	1.49	0.66	1.49	0.45	1.31
TEP:SPM (g XG eq./g)	0.054	2.27	0.033	2.26	0.066	2.26	0.067	2.27	0.071	1.62
LoI (%)	22.9	1.37	17.0	1.38	25.5	1.36	25.4	1.26	21.1	1.27
			Dissolv	ved para	ameters				-	
Salinity	31.6	1.03	31.7	1.03	30.6	1.02	31.8	1.02	32.5	1.02
DOC conc.(mg/l)	1.42	1.32	1.45	1.46	1.54	1.25	1.50	1.20	1.28	1.22
TDN conc. (µmol/l)	29.3	1.54	45.2	1.29	31.9	1.51	19.3	1.25	23.8	1.26
TDP conc. (µmol/l)	0.78	1.42	1.00	1.27	0.58	1.42	0.74	1.15	0.78	1.41
Si conc. (µmol/l)	11.08	1.82	18.5	1.29	9.81	1.54	4.54	1.54	14.0	1.26
	Seabed parameters									
POC in sediment (%)	1.98	0.18	-	-	-	-	-	-	-	-
PON in sediment (%)	0.27	0.02	-	-	-	-	-	-	-	-

	ye	ear	wi	nter	sp	ring	sur	nmer	aut	umn
	mean	std	mean	std	mean	std	mean	std	mean	std
Particulate parameters										
Hach Turbidity (FNU)	3.88	2.87	9.34	1.79	1.56	3.15	2.36	1.81	4.42	2.51
SPM-mass conc. (mg/l)	8.5	1.82	13.6	1.67	7.7	1.64	5.6	1.55	9.3	1.75
SPM-vol conc. (µl/l)	41	1.82	61	1.98	40	1.77	24	1.08	35	1.47
Median floc size (µm)	136	1.51	101	1.40	146	1.20	284	1.03	134	1.43
Effective floc density	47	1.80	71	1.88	45	1.74	26	1.07	40	1.46
(mg/l)										
POC conc. (mg/l)	0.56	1.61	0.52	1.60	0.83	1.61	0.39	1.32	0.49	1.27
PON conc. (mg/l)	0.074	1.47	0.067	1.61	0.094	1.34	0.071	1.34	0.072	1.14
TEP conc. (mg XG eq./l)	0.94	1.84	0.83	2.14	1.65	1.55	1.02	1.41	0.75	1.61
Chl-a conc. (µg/l)	3.03	2.23	1.46	1.49	4.82	3.02	3.62	1.90	3.88	1.22
Pheo-a conc. (µg/l)	0.14	2.67	0.10	1.76	0.13	2.30	0.19	4.87	0.15	1.33
POC:SPM (%)	6.74	1.76	3.80	1.26	10.84	1.45	9.52	1.69	7.21	1.47
PON:SPM (%)	0.93	1.83	0.49	1.22	1.45	1.34	1.46	1.71	1.13	1.58
TEP:SPM (g XG eq./g)	0.124	2.08	0.077	2.07	0.253	1.49	0.153	1.52	0.111	2.01
LoI (%)	40.6	1.48	26.2	1.18	54.0	1.58	57.5	1.29	36.8	1.22
		Disso	olved parameters							
Salinity	33.8	1.02	33.7	1.03	32.9	1.03	33.8	1.03	34.3	1.01
DOC conc.(mg/l)	1.10	1.34	1.08	1.53	1.52	1.20	1.07	1.23	1.01	1.18
TDN conc. (µmol/l)	14.7	1.72	25.5	1.44	18.2	1.18	9.5	1.62	12.4	1.54
TDP conc. (µmol/l)	0.48	1.47	0.69	1.26	0.47	1.17	0.37	1.29	0.44	1.52
Si conc. (µmol/l)	4.48	1.90	7.72	2.07	4.10	1.22	2.30	1.56	4.68	1.50
	bed parameters									
POC in sediment (%)	1.80	0.28	-	-	-	-	-	-	-	-
PON in sediment (%)	0.26	0.03	-	-	-	_	-	-	-	-

**Table A.2**: idem Table A.1 but now for W05.

	year winter		spring		summer		autı	ımn		
	mean	std	mean	std	mean	std	mean	std	mean	std
	Particulate parameters									
Hach Turbidity (FNU)	1.74	1.93	2.44	1.94	0.98	1.64	1.16	1.94	2.03	1.46
SPM-mass conc. (mg/l)	3.72	1.46	4.74	1.36	3.48	1.30	2.74	1.47	3.96	1.28
SPM-vol conc. (µl/l)	23	1.84	39	1.57	15	1.32	11	1.13	21	1.55
Median floc size (µm)	148	1.44	119	1.21	175	1.08	187	1.04	162	1.70
Effective floc density	27	1.77	44	1.50	17	1.30	13	1.12	23	1.50
(mg/l)										
POC conc. (mg/l)	0.32	1.42	0.26	1.38	0.45	1.24	0.33	1.45	0.37	1.21
PON conc. (mg/l)	0.045	1.43	0.038	1.47	0.057	1.28	0.045	1.30	0.053	1.26
TEP conc. (mg XG eq./l)	0.62	1.66	0.32	1.54	0.79	1.21	0.58	1.59	0.81	1.46
Chl-a conc. (µg/l)	1.00	1.53	1.09	1.49	0.63	1.37	0.80	1.48	1.33	1.26
Pheo-a conc. ( $\mu g/l$ )	0.044	1.50	0.044	1.44	-	-	0.029	1.54	0.056	1.27
POC:SPM (%)	8.71	1.70	5.56	1.43	13.05	1.20	13.63	1.58	9.34	1.37
POC:SPM (%)	1.20	1.77	0.77	1.54	1.65	1.30	2.17	1.53	1.42	1.39
TEP:SPM (g XG eq./g)	0.169	1.85	0.075	1.52	0.226	1.29	0.173	1.82	0.21	1.64
LoI (%)	40.2	1.44	28.9	1.36	74.9	1.11	49.5	1.21	38.0	1.34
			Dissolv	ved para	meters					
Salinity	34.94	1.004	34.98	1.004	34.76	1.002	34.91	1.006	34.96	1.002
DOC conc.(mg/l)	0.96	1.35	1.09	1.53	1.02	1.09	0.98	1.26	0.82	1.13
TDN conc. (µmol/l)	8.3	1.67	15.3	1.28	6.13	1.18	5.4	1.54	7.3	1.25
TDP conc. (µmol/l)	0.33	1.59	0.59	1.31	0.24	1.15	0.23	1.15	0.27	1.38
Si conc. (µmol/l)	2.53	1.58	3.60	1.37	1.99	1.12	1.89	1.60	2.44	1.51
Seabed parameters										
POC in sediment (%)	1.09	0.38	-	-	-	-	-	-	-	-
PON in sediment (%)	0.19	0.08	-	-	-	-	-	-	-	-

#### **Table A.3**: idem Table A.1 but now for W08.

#### 1016 Appendix B: Monthly Model Parameters for TEP:SPM model

1017 **Table B.1**: Monthly model parameters for TEP. The units for K<sub>POM</sub> are mg/l (POC, PON) and mg XG

1018 eq./l (TEP) and for  $f_1$  and  $f_2$  [g/(g POM)] for POC and PON and in [g XG eq./(g POM)] for TEP. For the

1019 monthly fits three months are combined, centered around the month of interest.

m <sub>POM</sub> =0.13	Кром	$\mathbf{f}_1$	$f_2$			
	CI 95% [lower, upper]	CI 95% [lower, upper]	CI 95% [lower, upper]			
January	4.25 [2.68, 6.00]	0.098 [0.059, 0.153]	0.251 [0.186, 0.319]			
February	2.37 [1.66, 3.61]	0.078 [0.006, 0.198]	0.656 [0.465, 0.845]			
March	1.91 [1.82, 1.99]	0.971 [0.583, 1.200]	0.444 [0.173, 0.793]			
April	3.67 [2.12, 4.83]	0.489 [0.386, 0.641]	0.457 [0.265, 0.677]			
May	4.96 [2.24, 7.11]	0.476 [0.386, 0.722]	0.090 [0.022, 0.154]			
June	4.69 [2.58, 6.54]	0.412 [0.305, 0.576]	0.136 [0.065, 0.235]			
July	4.78 [3.11, 6.80]	0.312 [0.233, 0.426]	0.297 [0.150, 0.531]			
August	2.68 [1.03, 4.32]	0.371 [0.226, 0.714]	0.540 [0.392, 0.695]			
September	1.91 [1.73, 2.10]	0.387 [0.285, 0.400]	0.526 [0.414, 0.653]			
October	1.77 [1.56, 1.95]	0.291 [0.183, 0.435]	0.499 [0.406, 0.518]			
November	1.99 [1.90, 2.13]	0.138 [0.058, 0.235]	0.346 [0.263, 0.441]			
December	2.50 [1.46, 3.67]	0.081 [0.027, 0.147]	0.314 0.251, 0.383[]			







**Figure C.1**: Probability density distribution of the POC:PON ratio from in situ measurements

and of the Carbon to Nitrogen ratios of the model parameters  $f_1(POC)$ :  $f_1(PON)$  and

1025  $f_2(POC)$ :  $f_2(PON)$ . The horizontal bars are the 95% CI.

#### 1026 Appendix D: Carbon Content of the TEP

Engel and Passow (2001) have reported that the carbon concentration of the TEP (mg/l) 1027 is linearly correlated with the TEP concentration (in (mg XG eq.)/l). The conversion factor 1028 1029 between both depends on the chemical composition of the TEP and ranges from about 0.51 to 0.88 (mg/ (mg XG eq.)). The slope of this regression line can be estimated by the POC:TEP 1030 ratio. The ratio derived from the measured POC and TEP concentrations is about 1 for all data, 1031 lower values are found in summer (0.64) and autumn (0.80) and higher ones in spring (2.08) and 1032 1033 winter (1.28). Clearly, only the summer and autumn values are realistic and within the range reported by Engel and Passow (2001). The ratios derived from the POM:SPM model have a 1034 lower variability than those from the measurements. The fresh POC over fresh TEP ratio is 1035 approaching a constant value at SPM concentration above about 50 mg/l, whereas the ratio 1036 POC:TEP for the mineral-associated fraction (also derived from the POM:SPM model) is 1037 constant. The ratio for the fresh POC and fresh TEP is on average about 0.50 (spring), 0.38 1038 (summer), 0.87 (autumn) and 0.45 (winter), corresponding with an overall slope factor of 1039 0.55±0.22. Similarly, the mineral-associated POC over TEP ratio for spring is 0.52, for summer 1040 0.63, for autumn 0.54 and for winter 1.04 (on average  $0.68\pm0.24$ ). If all the POC is TEP, then 1041 these ratios provide an upper limit of the C content of fresh TEP. It is remarkable that the 1042 differences between fresh and mineral-associated ratios are small and that, notwithstanding the 1043 large uncertainties associated with the ratios (see Figures 5-7), the values of the slope factor 1044 derived from the model agree with the estimates from Engel and Passow (2001). The overall 1045 1046 conversion of TEP concentration into carbon TEP concentration based on the model estimates is: C-TEP  $(mg/l) = 0.57 \pm 0.21$  TEP (mg XG eq./l). 1047

#### 1048 References

- 1049 Adriaens, R., Zeelmaekers, E., Fettweis, M., Vanlierde, E., Vanlede, J., Stassen, P., et al. (2018).
- Quantitative clay mineralogy as provenance indicator for recent muds in the southern North Sea.
   *Marine Geology*, 398, 48-58. <u>https://doi.org/10.1016/j.margeo.2017.12.011</u>
- 1052 Agrawal, Y., & Pottsmith, H. (2000). Instruments for particle size and settling velocity
- 1053 observations in sediment transport. *Marine Geology*, 168, 89–114.
- 1054 <u>https://doi.org/10.1016/S0025-3227(00)00044-X</u>
- 1055 Alldredge, A.L., Passow, U., & Logan, B.E. (1993). The abundance and significance of a class of
- 1056 large, transparent organic particles in the ocean. *Deep-Sea Research*, 40,1131–1140.
- 1057 <u>https://doi.org/10.1016/0967-0637(93)90129-Q</u>
- 1058 Andrews, S., Nover, D., & Schladow, S. (2010). Using laser diffraction data to obtain accurate
- particle size distributions: The role of particle composition. *Limnology and Oceanography Methods*, 8, 507–526. <u>https://doi.org/10.4319/lom.2010.8.507</u>
- 1061 Arndt, S., Jørgensen, B.B., LaRowe, D.E., Middelburg, J.J., Pancost, R.D., & Regnier, P. (2013).
- 1062 Quantifying the degradation of organic matter in marine sediments: A review and synthesis.
- 1063 Earth-Science Reviews, 123, 53-86. <u>https://doi.org/10.1016/j.earscirev.2013.02.008</u>
- Baeteman, C., Scott, D.B., & Van Strydonck, M. (2002). Changes in coastal zone processes at a
  high sea-level stand: a late-Holocene example from Belgium. *Journal of Quaternary Science*, 17,
  547–559. https://doi.org/10.1002/jqs.707
- Baeye, M., & Fettweis, M. (2015). In situ observations of suspended particulate matter plumes at an offshore wind farm. *Geo-Marine Letters*, 35, 247-255. <u>https://doi.org/10.1007/s00367-015-</u>
- 1069 <u>0404-8</u>
- 1070 Beardsley, R.C., Limeburner, R., & Rosenfeld, L.K. (1985). Introduction to CODE-2 Moored
- 1071 Array and Large-Scale Data Report. Woods Hole Oceanogr. Inst. Techn. Rep. WHOI-85-35,
- 1072 CODE Technical Report No 38, 234 pp.
- 1073 Bhaskar, P.V., & Bhosle, N.B. (2006). Dynamics of transparent exopolymeric particles (TEP)
- and particle-associated carbohydrates in the Dona Paula bay, west coast of India. Journal of
- 1075 Earth System Science, 115, 403–413. <u>https://doi.org/10.1007/BF02702869</u>
- 1076 Blattmann, T.M., Liu, Z., Zhang, Y., Zhao, Y., Haghipour, N., Montluçon, D.B., et al. (2019).
- 1077 Mineralogical control on the fate of continentally derived organic matter in the ocean. *Science*, 266, 742, 745, https://doi.org/10.1126/science.com/5245
- 1078 366, 742–745. <u>https://doi.org/10.1126/science.aax5345</u>
- 1079 Bouillon, S., Yambélé, A., Spencer, R.G.M., Gillikin, D.P., Hernes, P.J., Six, J., et al. (2012).
- 1080 Organic matter sources, fluxes and greenhouse gas exchange in the Oubangui River (Congo
- 1081 River basin). *Biogeosciences*, 9, 2045–2062, <u>https://doi.org/10.5194/bg-9-2045-2012</u>
- 1082 Braithwaite, K., Bowers, D., Nimmo-Smith, W., & Graham, G. (2012). Controls on floc growth
- in an energetic tidal channel. Journal of Geophysical Research Oceans, 117, C02024.
- 1084 <u>https://doi.org/10.1029/2011JC007094</u>
- 1085 Buonassissi, C.J., & Dierssen, H.M. (2010). A regional comparison of particle size distributions
- and the power law approximation in oceanic and estuarine surface waters. *Journal of*
- 1087 Geophysical Research Oceans, 115, C10028. <u>https://doi.org/10.1029/2010JC006256</u>

- 1088 Capuzzo, E., Lynam, C.P., Barry, J., Stephens, D., Forster, R.M., Greenwood, N., et al. (2018).
- 1089 A decline in primary production in the North Sea over 25 years, associated with reductions in
- zooplankton abundance and fish stock recruitment. *Global Change Biology*, 24, e352–e364.
   https://doi.org/10.1111/gcb.13916
- 1092 Capuzzo, E., Stephens, D., Silva, T., Barry, J., & Forster, R.M. (2015). Decrease in water clarity
- 1093 of the southern and central North Sea during the 20th century. *Global Change Biology*, 21,
- 1094 2206–2214. <u>https://doi.org/10.1111/gcb.12854</u>
- 1095 Chen, Y., Wang, M., Zhou, X., Fu, H., Qu, X., & Zhu, D. (2021). Sorption fractionation of
- 1096 bacterial extracellular polymeric substances (EPS) on mineral surfaces and associated effects on
- 1097 phenanthrene sorption to EPS-mineral complexes. *Chemosphere*, 263, 128264.
- 1098 <u>https://doi.org/10.1016/j.chemosphere.2020.128264</u>
- 1099 Chowdhury, C., Majumder, N., & Jana, T.K. (2016). Seasonal distribution and correlates of
- 1100 transparent exopolymer particles (TEP) in the waters surrounding mangroves in the Sundarbans.
- 1101 Journal of Sea Research, 112, 65-74. <u>http://doi.org/10.1016/j.seares.2016.01.004</u>
- 1102 Cross, J., Nimmo-Smith, W.A.M., Torres, R., & Hosegood, P.J. (2013). Biological controls on
- resuspension and the relationship between particle size and the Kolmogorov length scale in a
- shallow coastal sea. Marine Geology, 343, 29-38. https://doi.org/10.1016/j.margeo.2013.06.014
- 1105 Davies, E.J., Nimmo-Smith, W.A.M., Agrawal, Y.C., & Souza, A.J. (2012). LISST-100 response
- 1106 to large particles. *Marine Geology*, 307-310, 117–122.
- 1107 <u>https://doi.org/10.1016/j.margeo.2012.03.006</u>
- 1108 Decho, A. W., & Gutierrez, T. (2017). Microbial extracellular polymeric substances (EPSs) in
- 1109 ocean systems. Frontiers in Microbiology, 8 (922). https://doi.org/10.3389/fmicb.2017.00922
- 1110 Deng, Z., He, Q., Safar, Z., & Chassagne, C. (2019). The role of algae in fine sediment
- flocculation: In-situ and laboratory measurements. *Marine Geology*, 413, 71–84.
  https://doi.org/10.1016/j.margeo.2019.02.003
- 1113 Desmit, X., Nohe, A., Borges, A.V., Prins, T., De Cauwer, K., Lagring, R., et al. (2020).
- 1114 Changes in chlorophyll concentration and phenology in the North Sea in relation to de-
- 1115 eutrophication and sea surface warming. *Limnology and Oceanography*, 65, 828–847.
- 1116 https://doi.org/10.1002/lno.11351
- 1117 Desmit, X., Thieu, V., Billen, G., Campuzano, F., Dulière, V., Garnier, J., et al. (2018).
- Reducing marine eutrophication may require a paradigmatic change. *Science of the Total Environment*, 635, 444–1466. <u>https://doi.org/10.1016/j.scitotenv.2018.04.181</u>
- Doerffer, R., & Schiller, H. (2007). The MERIS Case 2 water algorithm. *International Journal of Remote Sensing*, 28, 517-535. <u>https://doi.org/10.1080/01431160600821127</u>
- Droppo, I.G. (2001). Rethinking what constitutes suspended sediment. Hydrol. Process. 15,
  1551–1564. <u>https://doi.org/10.1002/hyp.228</u>
- 1124 Dyer, K.R. (1989). Sediment processes in estuaries: Future research requirements. Journal of
- 1125 Geophysical Research Oceans, 94, 14327-14339. <u>https://doi.org/10.1029/JC094iC10p14327</u>
- 1126 Eisma, D., & Kalf, J. (1979). Distribution and particle size of suspended matter in the Southern
- Bight of the North Sea and the eastern Channel. *Netherlands Journal of Sea Research*, 13, 298-
- 1128 304. <u>https://doi.org/10.1016/0077-7579(79)90008-5</u>

- 1129 Engel, A., Endres, S., Galgani, L., & Schartau, M. (2020). Marvelous marine microgels: On the
- distribution and impact of gel-like particles in the oceanic water-column. *Frontiers in Marine*
- 1131 Science, 7, 405. <u>https://doi.org/10.3389/fmars.2020.00405</u>
- 1132 Engel, A., & Passow, U. (2001). Carbon and nitrogen content of transparent exopolymer
- 1133 particles (TEP) in relation to their Alcian Blue adsorption. *Marine Ecology Progress Series*, 219,
- 1134 1-10. doi:10.3354/meps219001
- 1135 Engel, A., & Schartau, M. (1999). Influence of transparent exopolymer particles (TEP) on
- sinking velocity of Nitzschia closterum aggregates. *Marine Ecology Progress Series*, 182, 69-76.
  doi:10.3354/meps182069
- 1138 Etcheber, H., Taillez, A., Abril, G., Garnier, J., Servais, P., Moatar, F., & Commarieu, M.-V.
- 1139 (2007). Particulate organic carbon in the estuarine turbidity maxima of the Gironde, Loire and
- Seine estuaries: origin and lability. *Hydrobiology*, 588, 245-259. <u>https://doi.org/10.1007/s10750-</u>
   <u>007-0667-9</u>
- EUMETSAT (2019). Sentinel-3 Product Notice OLCI level-2 Ocean Colour, EUM/OPS SEN3/TEN/19/1068317
- 1144 Fall, K.A., Friedrichs, C.T., Massey, G.M., Bowers, D.G., & Smith, J.S. (2021). The importance
- of organic content to fractal floc properties in estuarine surface waters: Insights from video,
- LISST, and pump sampling. *Journal of Geophysical Research Oceans*, 126, e2020JC016787.
- 1147 <u>https://doi.org/10.1029/2020JC016787</u>
- 1148 Fettweis, M., & Baeye, M. (2015). Seasonal variation in concentration, size and settling velocity
- of muddy marine flocs in the benthic boundary layer. *Journal of Geophysical Research Oceans*,
   120, 5648-5667. https://doi.org/10.1002/2014JC010644
- 1151 Fettweis, M., Baeye, M., Van der Zande, D., Van den Eynde, D., & Lee, B.J. (2014). Seasonality
- of floc strength in the southern North Sea. Journal of Geophysical Research Oceans, 119, 1911–
- 1153 1926. <u>https://doi.org/10.1002/2013JC009750</u>
- 1154 Fettweis, M., Francken, F., Pison, V., & Van den Eynde, D. (2006). Suspended particulate matter
- dynamics and aggregate sizes in a high turbidity area. *Marine Geology*, 235, 63-74.
  https://doi.org/10.1016/j.margeo.2006.10.005
- 1157 Fettweis, M., & Lee, B.J. (2017). Spatial and seasonal variation of biomineral suspended
- 1158 particulate matter properties in high-turbid nearshore and low-turbid offshore zones. *Water*, 9,
- 1159 694. <u>https://doi.org/10.3390/w9090694</u>
- 1160 Fettweis, M., Monbaliu, J., Nechad, B., Baeye, M., & Van den Eynde D. (2012). Weather and
- 1161 climate related spatial variability of high turbidity areas in the North Sea and the English
- 1162 Channel. Methods in Oceanography, 3-4, 25-39. <u>https://doi.org/10.1016/j.mio.2012.11.001</u>
- 1163 Fettweis, M., Riethmüller, R., Verney, R., Becker, M., Backers, J., Baeye, M., et al. (2019).
- 1164 Uncertainties associated with in situ long-term observations of suspended particulate matter
- concentration using optical and acoustic sensors. *Progress in Oceanography*, 178, 102162.
  https://doi.org/10.1016/j.pocean.2019.102162
- 1167 Fettweis, M., & Van den Eynde, D. (2003). The mud deposits and the high turbidity in the
- Belgian–Dutch coastal zone, southern bight of the North Sea. Continental Shelf Research, 23,
- 1169 669–691. <u>https://doi.org/10.1016/S0278-4343(03)00027-X</u>

- 1170 Frigstad, H., Andersen, T., Hessen, D.O., Naustvoll, L.-J., Johnsen, T.M., & Bellerby, R.G.J.
- 1171 (2011). Seasonal variation in marine C:N:P stoichiometry: Can the composition of seston explain
- 1172 stable Redfield ratios? *Biogeosciences*, 8, 2917–2933. <u>https://doi.org/10.5194/bg-8-2917-2011</u>
- 1173 Fuchs, E., Zimmerman, R.C., & Jaffe, J.S. (2002). The effect of elevated levels of phaeophytin in
- 1174 natural water on variable fluorescence measured from phytoplankton. *Journal of Plankton*
- 1175 Research, 24, 1221-1229. <u>https://doi.org/10.1093/plankt/24.11.1221</u>
- 1176 Fukao, T., Kimoto, K., & Kotani, Y. (2010). Production of transparent exopolymer particles by
- 1177 four diatom species. Fisheries Science, 76, 755–760. <u>https://doi.org/10.1007/s12562-010-0265-z</u>
- 1178 Hemingway, G.D., Rothman, D.H., Grant, K.E., Rosengard, S.Z., Eglinton, T.I., Derry L.A., &
- 1179 Galy V.V. (2019). Mineral protection regulates long-term global preservation of natural organic 1180 carbon. *Nature*, 570, 228-238. https://doi.org/10.1038/s41586-019-1280-6
- 1181 Hendriks, H.C.M., van Prooijen, B.C., Aarninkhof, S.G.J., & Winterwerp, J.C. (2020). How
- 1182 human activities affect the fine sediment distribution in the Dutch Coastal Zone seabed.
- 1183 Geomorphology, 367, 107314. <u>https://doi.org/10.1016/j.geomorph.2020.107314</u>
- Høyer, J.L., & Karagali, I. (2016). Sea surface temperature climate data record for the North Sea
  and Baltic Sea. *Journal of Climate*, 29, 2529–2541. <u>https://doi.org/10.1175/JCLI-D-15-0663.1</u>
- 1186 Ittekkot, V., & Laane, R.W.P.M. (1991). Fate of riverine particulate organic matter. In:
- Biogeochemistry of Major World Rivers (Degens, E.T., Kempe, S., Richey, R., eds). SCOPE 42.
  Wiley and Sons, New York, 233–242.
- 1189 Jachlewski, S., Jachlewski, W.D., Linne, U., Brasen, C., Wingender, J., & Siebers, B. (2015).
- 1190 Isolation of extracellular polymeric substances from biofilms of the thermoacidophilic archaeon
- 1191 Sulfolobus acidocaldarius. Frontiers in Bioengineering and Biotechnology, 3, 123.
- 1192 https://doi.org/10.3389/fbioe.2015.00123
- 1193 Jago, C.F., Bale, A.J., Green, M.O., Howarth, M.J., Jones, S.E., McCave, I.N., et al. (1994).
- 1194 Resuspension processes and seston dynamics, southern North Sea. In: Understanding the North
- 1195 Sea System (Charnock, H., Dyer, K.R., Huthnance, J.M., Liss, P.S., Simpson, J.H., Tett, P.B.,
- 1196 eds.), Springer Verlag. <u>https://doi.org/10.1007/978-94-011-1236-9\_8</u>
- 1197 Jago, C.F., Kennaway, G.M., Novarino, G., & Jones, S.E. (2007). Size and settling velocity of
- suspended flocs during a phaeocystis bloom in the tidally stirred Irish Sea, NW European Shelf.
   *Marine Ecology Progress Series*, 345, 51–62, doi:10.3354/meps07006.
- 1200 Jaiser, R., Dethloff, K., Handorf, D., Rinke, H., & Cohen, J. (2012). Impact of sea ice cover
- changes on the Northern Hemisphere atmospheric winter circulation. *Tellus A*, 64, 11595.
- 1202 <u>https://doi.org/10.3402/tellusa.v64i0.11595</u>
- Johnston, R.J., & Semple, R.K. (1983). Classification using information statistics. In: Concepts
  and Techniques in Modern Geography, 37, GeoBooks, Norwich, UK, 43pp.
- 1205 Kalbitz, K., Schwesig, D., Rethemaeyer, J., & Matzner, E. (2005). Stabilization of dissolved
- 1206 organic matter by sorption to the mineral soil. Soil Biology and Biochemistry, 37, 1319-1331.
- 1207 https://doi.org/10.1016/j.soilbio.2004.11.028
- 1208 Keil, R.G., Montluçon, D.B., Prahl, F.G., & Hedges, J.I. (1994). Sorptive preservation of labile
- 1209 organic matter in marine sediments. *Nature*, 370, 549-552. <u>https://doi.org/10.1038/370549a0</u>

- 1210 Keyvani, A., & Strom, K. (2014) Influence of cycles of high and low turbulent shear on the
- 1211 growth rate and equilibrium size of mud flocs. *Marine Geology*, 354, 1-14.
- 1212 <u>https://doi.org/10.1016/j.margeo.2014.04.010</u>
- 1213 Lacroix, G., Ruddick, K., Ozer, J., & Lancelot, C. (2004). Modelling the impact of the Scheldt
- and Rhine/Meuse plumes on the salinity distribution in Belgian waters (southern North Sea).
- 1215 Journal of Sea Research, 52, 149–163. <u>https://doi.org/10.1016/j.seares.2004.01.003</u>
- 1216 Lai, H., Fang, H., Huang, L., He, G., & Reible, D. (2014). A review on sediment bioflocculation:
- 1217 Dynamics, influencing factors and modeling. Science of the Total Environment, 642, 1184–1200.
- 1218 https://doi.org/10.1016/j.scitotenv.2018.06.101
- 1219 Lancelot, C., Spitz, Y., Gypens, N., Ruddick, K., Becquevort, S., Rousseau, V., et al. (2005).
- 1220 Modelling diatom and Phaeocystis blooms and nutrient cycles in the Southern Bight of the North
- 1221 Sea: The MIRO model. *Marine Ecology Progress Series*, 289: 63–78. doi:10.3354/meps289063
- 1222 Lavigne, H., Van der Zande, D., Ruddick, K., Dos Santos, J.C., Gohin, F., Brotas, V., & Kratzer,
- 1223 S., 2021. Quality-control tests for OC4, OC5 and NIR-red satellite chlorophyll-a algorithms
- applied to coastal waters. *Remote Sensing of Environment*, 112237.
- 1225 <u>https://doi.org/10.1016/j.rse.2020.112237</u>
- Lee, B.J., Fettweis, M., Toorman, E., & Molz, F.J. (2012). Multimodality of a particle size
- distribution of cohesive suspended particulate matters in a coastal zone. *Journal of Geophysical Research Oceans*, 117, C03014. <u>https://doi.org/10.1029/2011JC007552</u>
- 1229 Lee, B.J., Kim, J., Hur, J., Choi, I-H., Toorman, E., Fettweis, M., & Choi, J.W. (2019) Seasonal
- 1230 dynamics of organic matter composition and its effects on suspended sediment flocculation in
- 1231 river water. Water Resources Research, 55, 6968-6985. <u>https://doi.org/10.1029/2018WR024486</u>
- 1232 Lee, J.H., Lee, W.C., Kim, H.C., Jo, N., Jang, H.K., Kang, J.J., et al. (2020). Transparent
- Exopolymer Particle (TEPs) Dynamics and Contribution to Particulate Organic Carbon. *Water*, 12, 1057; https://doi.org/10.3390/w12041057
- 1235 Liénart, C., Savoye, N., Bozec, Y., Breton, E., Conan, P., David, V., et al. (2017). Dynamics of
- 1236 particulate organic matter composition in coastal systems: A spatio-temporal study at multi-
- 1237 systems scale. *Progress in Oceanography*, 156, 221–239.
- 1238 https://doi.org/10.1016/j.pocean.2017.03.001
- Liley, J.B. (1992). Fitting size distributions to optical particle counter data. *Aerosol Science and Technology*, 17, 84-92. <u>https://doi.org/10.1080/02786829208959562</u>
- 1241 Logan, B.E., Passow, U., Alldredge, A.L., & Grossarts, S.M. (1995). Rapid formation and
- sedimentation of large aggregates is predictable from coagulation rates (half-lives) of transparent
- 1243 exopolymer particles (TEP). *Deep-Sea Research II*, 42, 203-214. <u>https://doi.org/10.1016/0967-</u>
   1244 0645(95)00012-F
- Long, R.A., & Azam, F. (1996). Abundant protein-containing particles in the sea. *Aquatic Microbial Ecology*, 10, 213-221. doi:10.3354/ame010213
- 1247 Maerz, J., Hofmeister, R., van der Lee, E.M., Gräwe, U., Riethmüller, R., & Wirtz, K.W. (2016).
- 1248 Maximum sinking velocities of suspended particulate matter in a coastal transition zone.
- 1249 Biogeosciences, 13, 4863–4876. https://doi.org/10.5194/bg-13-4863-2016

- 1250 Maggi, F. (2009). Biological flocculation of suspended particles in nutrient-rich aqueous
- 1251 ecosystems. *Journal of Hydrology*, 376, 116–125. https://doi.org/10.1016/j.jhydrol.2009.07.040
- 1252 Maggi, F., & Tang, F.H.M. (2015). Analysis of the effect of organic matter content on the
- architecture and sinking of sediment aggregates. *Marine Geology*, 363, 102–111.
- 1254 https://doi.org/10.1016/j.margeo.2015.01.017
- 1255 Malpezzi, M.A., Sanford, L.P., & Crump, B.C. (2013). Abundance and distribution of
- transparent exopolymer particles in the estuarine turbidity maximum of Chesapeake Bay. *Marine*
- 1257 Ecology Progress Series, 486, 23–35. https://doi.org/10.3354/meps10362
- 1258 Manning, A.J., Van Kessel, T., Melotte, J., Sas, M., Winterwerp, H., & Pidduck, E.L. (2011). On
- the consequence of a new tidal dock on the sedimentation regime in the Antwerpen area of the Lower Sea Scheldt. *Continental Shelf Research*, 31, S150-S164.
- 1261 https://doi.org/10.1016/j.csr.2010.10.008
- 1262 Mari. X., & Burd, A. (1998). Seasonal size spectra of transparent exopolymeric particles (TEP)
- 1263 in a coastal sea and comparison with those predicted using coagulation theory. *Marine Ecology*
- 1264 Progress Series, 163, 63-76. doi:10.3354/meps171063
- 1265 Mari, X., Passow, U., Migon, C., Burd, A.B., & Legendre, L. (2017). Transparent exopolymer
- particles: Effects on carbon cycling in the ocean. *Progress in Oceanography*, 151,13-37.
   <u>https://doi.org/10.1016/j.pocean.2016.11.002</u>
- 1268 Mari, X., & Robert, M. (2008). Metal induced variations of TEP sticking properties in the
- 1269 southwestern lagoon of New Caledonia. *Marine Chemistry*, 110, 98-108.
- 1270 https://doi.org/10.1016/j.marchem.2008.02.012
- 1271 Mari, X., Rochelle-Newall, E., Torréton, J.-P., Pringault, O., Jouon, A., & Migon, C. (2007).
- 1272 Water residence time: A regulatory factor of the DOM to POM transfer efficiency. *Limnology*
- 1273 and Oceanography, 52, 808–819. https://doi.org/10.4319/lo.2007.52.2.0808
- 1274 May, C.L., Koseff, J.R., Lucas, L.V., Cloern, J.E., & Schoellhamer, D.H. (2003). Effects of
- spatial and temporal variability of turbidity on phytoplankton blooms. *Marine Ecology Progress Series*, 254, 111-128. doi:10.3354/meps254111
- 1277 Mayer, L.M. (1994). Relationships between mineral surfaces and organic carbon concentrations
- in soils and sediments. *Chemical Geology*, 114, 347-363. https://doi.org/10.1016/0009-2541(94)90063-9
- 1280 Mietta, F., Chassagne, C., Manning, A.J., & Winterwerp, J.C. (2009). Influence of shear rate,
- organic matter content, pH and salinity on mud flocculation. Ocean Dynamics, 59, 751–763.
   https://doi.org/10.1007/s10236-009-0231-4
- 1283 Mikkelsen, O., Curran, K., Hill, P., & Milligan, T. (2007). Entropy analysis of in situ particle
- 1284 size spectra, Estuarine Coastal and Shelf Science, 72, 615–625.
- 1285 https://doi.org/10.1016/j.csr.2006.11.004
- 1286 Mikkelsen, O., Hill, P., & Milligan, T. (2006). Single-grain, microfloc and macrofloc volume
- variations observed with a LISST-100 and a digital floc camera. *Journal of Sea Research*, 55,
- 1288 87–102. https://doi.org/10.1016/j.seares.2005.09.003

- 1289 Milliman, J.D., Quichun, X., & Zuosheng, Y. (1984). Transfer of particulate organic carbon and
- nitrogen from Yangtze river to the Ocean. American Journal of Science, 284, 824-835.
- 1291 https://doi.org/10.2475/ajs.284.7.824
- 1292 Milliman, J.D., Yun-Shan, Q., Mei-E, R., & Saito, Y (1987). Man's influence on the erosion and
- transport of sediment by Asian rivers: The yellow river (Huanghe) example. *Journal of Geology*,
  95, 751-762. https://doi.org/10.1086/629175
- 1295 Morelle, J., Schapira, M., Françoise, S., Courtay, G., Orvain, F., & Claquin, P. (2018). Dynamics
- 1296 of exopolymeric carbon pools in relation with phytoplankton succession along the salinity
- 1297 gradient of a temperate estuary (France). Estuarine Coastal and Shelf Science, 209, 18-29.
- 1298 https://doi.org/10.1016/j.ecss.2018.05.008
- 1299 Muylaert, K., Gonzales, R., Franck, M., Lionard, M., Van der Zee, C., Cattrijsse, A., et al.
- (2006). Spatial variation in phytoplankton dynamics in the Belgian coastal zone of the North Sea
   studied by microscopy, HPLC-CHEMTAX and underway fluorescence recordings. *Journal of*
- studied by microscopy, HPLC-CHEMTAX and underway fluorescence recor
   *Sea Research*, 55, 253–265. https://doi.org/10.1016/j.seares.2005.12.002
- 1303 Neukermans, G., Ruddick, K., Loisel, H., & Roose, P. (2012). Optimization and quality control
- 1304 of suspended particulate matter concentration measurement using turbidity measurements.
- 1305 Limnology and Oceanography Methods, 10, 1011–1023.
- 1306 https://doi.org/10.4319/lom.2012.10.1011
- 1307 Neumann, A., Hass, H.C., Möbius, J., & Naderipour, C. (2019). Ballasted flocs capture pelagic
- 1308 primary production and alter the local sediment characteristics in the coastal German Bight
- 1309 (North Sea). *Geosciences*, 9, 344. https://doi.org/10.3390/geosciences9080344
- 1310 Nohe, A., Goffin, A., Tyberghein, L., Lagring, R., De Cauwer, K., Vyverman, W., & Sabbe, K.
- 1311 (2020). Marked changes in diatom and dinoflagellate biomass, composition and seasonality in
- 1312 the Belgian Part of the North Sea between the 1970s and 2000s. *Science of the Total*
- 1313 Environment, 716, 136316. https://doi.org/10.1016/j.scitotenv.2019.136316
- 1314 Nosaka, Y., Yamashita, Y., & Suzuki, K. (2017). Dynamics and origin of Transparent
- 1315 Exopolymer Particles in the Oyashio region of the Western Subarctic Pacific during the spring
- diatom bloom. Frontiers in Marine Science, 4, 79. <u>https://doi.org/10.3389/fmars.2017.00079</u>
- 1317 Ortega-Retuerta, E., Marrasé, C., Muñoz-Fernández, A., Sala, M.M., Simó, R., & Gasol, J.M.
- 1318 (2018). Seasonal dynamics of transparent exopolymer particles (TEP) and their drivers in the
- coastal NW Mediterranean Sea. *Science of the Total Environment*, 631–632, 180-190.
  https://doi.org/10.1016/j.scitotenv.2018.02.341
- 1320 <u>https://doi.org/10.1010/j.schotenv.2018.02.341</u>
- Passow, U. (2000). Formation of transparent exopolymer particles, TEP, from dissolved precursor material. *Marine Ecology Progress Series*, 192, 1-11. doi:10.3354/meps192001
- precursor material. *Marine Ecology Progress Series*, 192, 1-11. doi:10.3354/meps192001
- Passow, U. (2002). Transparent exopolymer particles (TEP) in aquatic environments. *Progress in Oceanography*, 55, 287–333. <u>https://doi.org/10.1016/S0079-6611(02)00138-6</u>
- 1325 Passow, U., & Alldredge, A.L. (1995). A dye-binding assay for the spectrophotometric
- 1326 measurement of transparent exopolymer particles. Limnology and Oceanography, 40, 1326-
- 1327 1335. <u>https://doi.org/10.4319/lo.1995.40.7.1326</u>

- 1328 Pietrzak, J.D., de Boer, G.J., & Eleveld, M.A. (2011). Mechanisms controlling the intra-annual
- mesoscale variability of SST and SPM in the southern North Sea. *Continental Shelf Research*,
  31, 594–610. https://doi.org/10.1016/j.csr.2010.12.014
- 1331 Ramaiah, N., Yoshikawa, T., & Furuya, K. (2001). Temporal variations in transparent
- 1332 exopolymer particles (TEP) associated with a diatom springbloom in a subarctic ria in Japan.
- 1333 Marine Ecology Progress Series, 212, 79-88. doi:10.3354/meps212079
- 1334 Regnier, P., Friedlingstein, P., Ciais, P. Mackenzie, F.T., Gruber, N., Janssens, I.A., et al. (2013).
- 1335 Anthropogenic perturbation of the carbon fluxes from land to ocean. *Nature Geoscience*, 6, 597–
- 1336 607. <u>https://doi.org/10.1038/ngeo1830</u>
- 1337 Röttgers, R., Heymann, K., & Krasemann, H. (2014). Suspended matter concentrations in coastal
- 1338 waters: methodological improvements to quantify individual measurement uncertainty.
- 1339 Estuarine, Coastal and Shelf Science, 151, 148–155. <u>https://doi.org/10.1016/j.ecss.2014.10.010</u>
- 1340 Rousseau, V., Leynaert, A., Daoud, N., & Lancelot, C. (2002). Diatom succession, silicification
- and silicic acid availability in Belgian coastal waters (southern North Sea). *Marine Ecology*
- 1342 Progress Series, 236, 61–73. doi:10.3354/meps236061
- 1343 Schartau, M., Engel, A., Schröter, J., Thoms, S., Völker, C., & Wolf-Gladrow, D. (2007).
- Modelling carbon overconsumption and the formation of extracellular particulate organic carbon.
   *Biogeosciences*, 4, 433–454. https://doi.org/10.5194/bg-4-433-2007
- 1346 Schartau, M., Riethmüller, R., Flöser, G., van Beusekom, J.E.E., Krasemann, H., Hofmeister, R.,
- 47 & Wirtz, K. (2019). On the separation between inorganic and organic fractions of suspended
- matter in a marine coastal environment. *Progress in Oceanography*, 171, 231-250.
- 1349 https://doi.org/10.1016/j.pocean.2018.12.011
- 1350 Schlünz, B., & Schneider, R.R. (2000). Transport of terrestrial organic carbon to the oceans by
- rivers: Re-estimating flux- and burial rates. *International Journal of Earth Science*, 88, 599-606.
- 1352 <u>https://doi.org/10.1007/s005310050290</u>
- 1353 Schwarz, C., Cox, T.J.S., Van Engeland, T., Van Oevelen, D., Van Belzen, J., van de Koppel, J.,
- et al. (2017). Field estimates of floc dynamics and settling velocities in a tidal creek with
- 1355 significant along-channel gradients in velocity and SPM. Estuarine, Coastal and Shelf Science,
- 1356 197, 221-235. <u>https://doi.org/10.1016/j.ecss.2017.08.041</u>
- 1357 Shen, X., Toorman, E.A., Lee, B.J., & Fettweis, M. (2018). Biophysical flocculation of
- suspended particulate matters in Belgian coastal zones. *Journal of Hydrology*, 567, 238-252.
  https://doi.org/10.1016/j.jhydrol.2018.10.028
- 1360 Shen, X., Toorman, E.A., Lee, B.J., & Fettweis, M. (2019). An approach to modeling biofilm
- 1361 growth during the flocculation of suspended cohesive sediments. *Journal of Geophysical*
- 1362 Research Ocean, 124, 4098-4116. https://doi.org/10.1029/2018JC014493
- 1363 Skinnebach, K.H., Fruergaard, M., & Andersen, T.A. (2020). Biological effects on flocculation
- of fine-grained suspended sediment in natural seawater. *Estuarine, Coastal and Shelf Science*,
  228, 106395. <u>https://doi.org/10.1016/j.ecss.2019.106395</u>
- 1366 Smith, D.C., Simon, M., Alldredge, A.L., & Azam, F. (1992). Intense hydrolytic enzyme activity
- on marine aggregates and implications for rapid particle dissolution. *Nature*, 359, 139–141.
   https://doi.org/10.1038/359139a0

- 1369 Stavn, R.H., Rick, H.J., & Falster, A.V. (2009). Correcting the errors from variable sea salt
- 1370 retention and water of hydration in loss on ignition analysis: Implications for studies of estuarine
- 1371 and coastal waters. *Estuarine, Coastal and Shelf Science*, 81, 575-582.
- 1372 <u>https://doi.org/10.1016/j.ecss.2008.12.017</u>
- 1373 Tang, F.H.M., & Maggi, F. (2016). A mesocosm experiment of suspended particulate matter
- 1374 dynamics in nutrient- and biomass-affected waters. *Water Research*, 89, 76–86.
- 1375 <u>https://doi.org/10.1016/j.watres.2015.11.033</u>
- 1376 Tran, D., & Strom, K. (2017). Suspended clays and silts: Are they independent or dependent
- 1377 fractions when it comes to settling in a turbulent suspension? *Continental Shelf Research*, 138,
- 1378 81-94. <u>http://doi.org/10.1016/j.csr.2017.02.011</u>
- 1379 Van Beusekom, J.E.E., Buschbaum, C., & Reise, K. (2012). Wadden Sea tidal basins and the
- mediating role of the North Sea in ecological processes: Scaling up of management? Ocean &
   *Coastal Management*, 68, 69–78, https://doi.org/10.1016/j.ocecoaman.2012.05.002
- 1382 Van Engeland, T., Soetaert, K., Knuijt, A., Laane, R.W.P.M., & Middelburg, J.J. (2010).
- Dissolved organic nitrogen dynamics in the North Sea: A time series analysis (1995–2005).
- *Estuarine, Coastal and Shelf Science*, 89, 31-42. https://doi.org/10.1016/j.ecss.2010.05.009
- 1385 Van Hoey, G., Vincx, M., & Degraer, S. (2005). Small- to large-scale geographical patterns
- within the macrobenthic Abra alba community. *Estuarine, Coastal and Shelf Science*, 64, 751 <u>763. https://doi.org/10.1016/j.ecss.2005.03.022</u>
- 1388 Van Maren, D.S., van Kessel, T., Cronin, K., & Sittoni, L. (2015). The impact of channel
- deepening and dredging on estuarine sediment concentration. *Continental Shelf Research*, 95, 1–
   14. <u>https://doi.org/10.1016/j.csr.2014.12.010</u>
- 1391 Verdugo, P. (2012). Marine microgels. Annual Review of Marine Science, 4, 375–400.
- 1392 https://doi.org/10.1146/annurev-marine-120709-142759
- 1393 Verney, R., Lafite, R., & Brun-Cottan, J. (2009). Flocculation potential of estuarine particles:
- 1394 The importance of environmental factors and of the spatial and seasonal variability of suspended
- 1395 particulate matter. *Estuaries and Coasts*, 32, 678–693. <u>https://doi.org/10.1007/s12237-009-9160-</u>
- 1396 <u>1</u>
- 1397 Wang, Y.P., Voulgaris, G., Li, Y., Yang, Y., Gao, J., Chen, J., & Gao, S. (2013). Sediment
- resuspension, flocculation, and settling in a macrotidal estuary. *Journal of Geophysical Research Oceans*, 118, 5591–5608. https://doi.org/10.1002/jgrc.20340
- 1400 Winterwerp, JC. (1998)., A simple model for turbulence induced flocculation of cohesive
- sediment. Journal of Hydraulic Research, 36, 309-326.
- 1402 https://doi.org/10.1080/00221689809498621
- 1403 Zhang, J., Liu, G., Wang, R., & Huang, H. (2017). Polycyclic aromatic hydrocarbons in the
- 1404 water-SPM-sediment system from the middle reaches of Huai River, China: Distribution,
- partitioning, origin tracing and ecological risk assessment. *Environmental Pollution*, 230, 61-71.
   https://doi.org/10.1016/j.envpol.2017.06.012
- 1407 Zhang, Y., Ren, J., Zhang, W., & Wu, J. (2021). Importance of salinity-induced stratification on
- 1408 flocculation in tidal estuaries. *Journal of Hydrology*, 596, 126063.
- 1409 https://doi.org/10.1016/j.jhydrol.2021.126063

- 1410 Zhou, J., Mopper, K., Passow, U., 1998. The role of surface-active carbohydrates in the
- 1411 formation of transparent exopolymer particles by bubble adsorption of seawater. *Limnology and*
- 1412 Oceanography, 43, 1860–1871. https://doi.org/10.4319/lo.1998.43.8.1860