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Spatial variability of organic matter degradability in tidal Elbe sediments

Florian Zander¹ · Timo Heimovaara¹ · Julia Gebert¹

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Abstract

Purpose The microbial turnover of sediment organic matter (OM) in ports and waterways impacts water quality, sonic depth finding and presumably also rheological properties as well as greenhouse gas emissions, especially if organic carbon is released as methane. As a consequence, sediment management practices as a whole are affected. This study aimed to discern spatial OM degradability patterns in the Port of Hamburg and investigated correlations with standard analytical properties as a basis for future predictive modelling.

Materials and methods Sediments in the Port of Hamburg were repeatedly sampled at nine locations along an east-west transect using a 1-m corer. In a stratified sampling approach, layers of suspended particulate matter (SPM), fluid mud (FM), pre-consolidated sediment (PS) and consolidated sediment (CS) were identified and individually analysed for long-term aerobic and anaerobic degradation of organic matter, DNA concentration, stable carbon isotope signature, density fractions and standard solids and pore water properties.

Results and discussion The investigation area was characterised by a distinct gradient with a 10-fold higher OM degradability in upstream areas and lower degradability in downstream areas. Concomitantly, upstream locations showed higher DNA concentrations and more negative $\delta^{13}\text{C}$ values. The share of bulk sediment in the heavy density fraction as well as the proportion and absolute amount of organic carbon were significantly larger at downstream locations. A depth and hence age-related gradient was found at individual locations, showing higher degradability of the upper, younger material, concomitant with higher DNA concentration, and lower OM turnover in the deeper, older and more consolidated material. Deeper layers were also characterised by higher concentrations of pore water ammonium, indicative of anaerobic nitrogen mineralisation.

Conclusions Organic matter lability is inversely linked to its stabilisation in organo-mineral complexes. The observed degradability gradient is likely due to the different OM quality in relation to its origin. Downstream OM enters the system with the tidal flood current from the direction of the North Sea whereas upstream locations receive OM originating from the catchment, containing more autochthonous, plankton-derived and more easily degradable components. At individual sampling points, depth-related degradability gradients reflect an age gradient, with easily degradable material in top layers and increasing stabilisation of OM in organo-mineral compounds with depth.

Keywords Dredging · Fluid mud · Organic matter degradation · Organo-mineral complexes

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1 Introduction

Sources of organic matter in riverine sediments can be natural or anthropogenic. Examples of natural sources are eroded terrestrial topsoils and plant litter, supplying allochthonous organic matter, or planktonic and pelagic biomass, yielding autochthonous organic matter, whereas urban sewage and surface runoff reflect anthropogenic allochthonous sources. Under aerobic conditions, the microbial degradation of organic matter with oxygen as terminal electron acceptor releases carbon dioxide (CO_2), whereas under anaerobic conditions organic carbon is additionally

released as methane (CH₄). Estuarine systems emit CO₂ into the atmosphere at rates that are quantitatively significant for the global carbon cycle (Borges and Abril 2012). Streams and rivers are responsible for the dominant share of global CO₂ emissions from inland waters (Raymond et al. 2013). Intense aerobic turnover of organic matter can cause oxygen minimum zones in the water body. Because of the poor solubility of methane in water, methanogenesis results in the formation of gas bubbles which are either entrapped within the sediment or released by ebullition through the overlying water column. Gas bubbles produced from anaerobic degradation of organic matter in sediments are assumed to decrease sediment density, viscosity and shear strength and to delay sedimentation and consolidation. Gas bubbles may obstruct sonic depth finding and therefore maintenance of the navigable depth and increase dredging costs by requiring the operation of degassing units on trailer suction hopper dredgers (Wurpts and Torn 2005). Lastly, anaerobic degradation of organic matter in sediments leads to the release of the potent greenhouse gas methane. The magnitude and rate of anaerobic organic matter degradation depend on the organic matter content and degradability as well as the prevailing environmental (e.g. temperature) and geochemical (e.g. types of electron acceptors) conditions (Arndt et al. 2013).

The water depth in the Port of Hamburg, one of the biggest ports in Europe, is strongly affected by a tidal range of approximately 3.6 m. The port receives sediments, suspended and sediment-bound organic matter both from the upstream catchment and from the North Sea, the latter due to tidal pumping (Boehlich and Strotmann 2008). The resulting sediment load in combination with the presence of low-flow areas within port basins or the formation of eddies at turn-offs causes hotspots of sedimentation and hence respective dredging efforts to maintain the nautical depth. Due to the possible effects of sediment organic matter turnover highlighted above, quantification of the lability of organic matter at focal points of sedimentation plays an important role for optimising sediment management. In light of this, the aim of this study was to investigate the spatial variability of organic matter degradability in the Port of Hamburg and to examine possible correlations with standard analytical geochemical properties as prerequisite for the prediction of location-specific behaviour of organic matter, supporting spatially differentiated management of sediments. It was hypothesised that:

1. Stabilisation of sediment organic matter in organo-mineral complexes increases with age and therefore with depth as well as along a transportation gradient.
2. Ageing of sediments decreases organic matter lability and therefore changes biodegradation kinetics as well as the distribution of organic matter over different density fractions.
3. An upstream-downstream decreasing gradient of organic matter degradability exists as labile organic matter enters the harbour mainly from upstream through algal biomass, adding a more rapidly degradable pool.

2 Investigation area and sampling strategy

2.1 Investigation area

The Port of Hamburg (Fig. 1) is a tidal port located approximately 100 km inland from the North Sea. The sampling points (P1 to P9) mostly reflect key locations of maintenance of the nautical depth, with high sedimentation rates and hence increased dredging effort. Further, the sampling points represent a gradient from upstream to downstream. They feature different hydromorphological properties with respect to their distance to the main fairway, the geometry of the harbour basin and the extent of flow-through of water (see Table 1).

2.2 Sampling strategy

In 2018, sediment samples were taken with a core sampler (volume ca. 10 l) at nine locations in the Port of Hamburg (Fig. 1) in June, August, September and November. The goal of the sampling strategy was to include the most upstream and most downstream locations as well as the major sedimentation areas in the Port of Hamburg. Additionally, sampling aimed at analysing variability with depth (see Section 4.3) and time (not presented in this study). In a vertical cut, four layers were distinguished between the upper (water) and lower (riverbed) boundaries: suspended particulate matter (SPM), fluid mud (FM), pre-consolidated sediment (PS) and consolidated sediment (CS). While SPM layers still fully represent the aqueous phase, FM is the first layer below the lutocline, still showing fluidic but already non-Newtonian properties. This layer is not always present. The lutocline was identified visually, seconded by on-board measurements of density (Anton Paar density meter DMA 35). Below the FM layer follows pre-consolidated sediment (PS) which can be described as a non-fluidic sediment layer in the initial stages of consolidation, representing the topmost, freshly settled material. This layer is most pronounced in areas of high sedimentation rates. Below follows the consolidated sediment (CS) layer, defined as a firm, aged sediment layer of reduced water content. The described stratification was accompanied by a pronounced redox gradient with SPM still in an oxidised state but FM, PS and CS material usually in a reduced state with values decreasing with depth (see Fig. 7). In the core sampler, the depth of each layer was determined with reference to the lutocline (Wolanski et al. 1988), located between suspended particulate matter and fluid mud. In a stratified sampling approach, several cores were taken at each location, and layers were separated, homogenised and stored cool in air-tight containers until they were processed. Suspended particulate matter was pumped from the top of the core on the vessel and centrifuged in the laboratory.

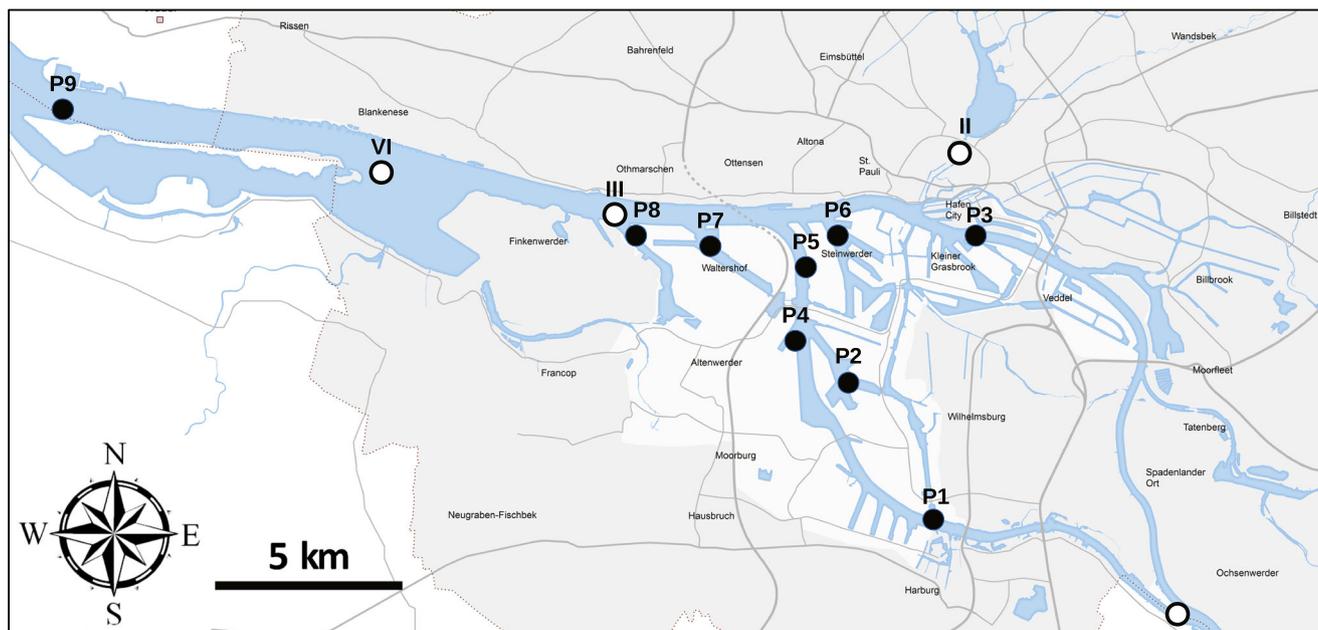


Fig. 1 Investigation area (Port of Hamburg) with sampling locations (small dots) between river km 616 (P1, upstream) and 643 (P9, downstream); the big dots show the sampling location of the Hamburg

Serviceportal (compare Sect. 4.2) (source: adapted from Hamburg Port Authority)

3 Methods

3.1 Anaerobic degradation of organic matter

Depending on the available sample mass, the water content and the expected gas production rate, 20 g (SPM), 100 (FM) and 200 g fresh sample (PS and CS) were placed in triplicates into 100-ml (SPM), 250-ml (FM) or 500-ml glass bottles (PS and CS). The bottle headspace was flushed with 100% N₂ to establish anaerobic conditions and incubated at 36 °C in dark. For quantification of gas production, an automated low gas flow measuring device (Gas Endeavour, Bioprocess Control, Sweden) was used for samples from PS and CS layers and a pressure gauge for samples from SPM and FM layers. After gas production had reached a level of below 2 ml day⁻¹, considered

as the lower limit for measurements with the Gas Endeavour device, the long-term gas production for pre-consolidated and consolidated layers were continued with the pressure gauge.

The anaerobic (anoxic) degradation of organic matter was quantified based on the release of carbon into the gas phase. According to the oxidation-reduction reactions taking place with decreasing redox potential and decreasing enthalpy, organic carbon is first released as CO₂ from the reduction of nitrate, manganese, iron and sulphate. After the depletion of these terminal electron acceptors (TEAs), carbon is additionally released as CH₄. Gas phase carbon was quantified applying the ideal gas law using the gas composition, the headspace volume, the incubation temperature and the pressure inside the bottle. The total amount of generated gas equals the sum of CO₂ and CH₄ produced and was expressed as mass unit of

Table 1 Characterisation of sampling points

Number	River-km km	Coordinates (WGS 84)		Length of basin m	Distance to centre of main fairway m
		°N	°E		
P1	616	53.477625	9.984925	300	300
P2	619	53.511615	9.949098	2300	1000
P3	620	53.538433	10.000369	1400	200
P4	621	53.516918	9.935416	600	400
P5	623	53.529945	9.938585	–	0
P6	624	53.538188	9.949979	2300	400
P7	627	53.533910	9.905856	2400	700
P8	629	53.538894	9.881215	2700	700
P9	643	53.567833	9.679490	–	0

carbon released per mass unit of organic carbon (as present in the original sample), hence indicating the degradability of the organic carbon independent of its absolute amount. Gas chromatographic analyses did not detect any other gases. Values measured after 21 days (G_{21}) and after 100 days (G_{100}) were used as standard benchmarks.

3.2 Aerobic degradation of organic matter

To determine the degradation of organic matter under aerobic (oxic) conditions, in this paper also referred to as ‘respiration’, 15 g of homogenised fresh sample was incubated in 1-l glass bottles at 20 °C in the dark with a headspace consisting of atmospheric air. The sample was distributed on the bottom of the bottles in a layer of only a few millimetre thickness in order to minimise limitations to the diffusion of oxygen into the sample. To avoid the limitation of OM degradation by elevated CO_2 levels, the bottle headspace was flushed with synthetic air after CO_2 concentrations had reached three vol.% in the gas phase, then measurements were resumed. Applying the ideal gas law, the amount of degraded carbon was calculated using the concentration of CO_2 as measured by gas-chromatographic analysis and the bottle headspace volume. Respiratory C-release was related to mass unit organic carbon present in the sample at the beginning of the incubation and calculated for the benchmark times of 21 days (R_{21}) and 100 days (R_{100}).

3.3 Carbon stable isotopes

The $\delta^{13}\text{C}$ values of the sediment organic matter were determined with an isotope-ratio mass spectrometer (Delta V; Thermo Scientific, Dreieich, Germany) coupled to an elemental analyser (Flash 2000; Thermo Scientific). Prior to analysis, samples were treated with phosphoric acid (43%, 80 °C for 2 h) to release inorganic carbon. Values are expressed relative to Vienna Pee Dee Belemnite (VPDB) using the external standards IAEA IAEA-CH7 (−31.62‰ vs. VPDB) and IVA soil 33,802,153 (27.46‰ vs. VPDB).

3.4 DNA concentration

Isolation of genomic DNA was performed using the ‘Quick-DNA Fungal/Bacterial Microprep’ kit (<https://www.zymoresearch.eu/quick-dna-fungal-bacterial-kit>) following the procedure indicated by the supplier, with the following minor modifications: for better cell lysis, 5 μl lysozyme (2000 $\mu\text{g ml}^{-1}$) and 5 μl proteinase K (200 $\mu\text{g ml}^{-1}$) were added to the sample. Genomic DNA was eluted in 27 μl distilled water into a 1.5-ml reaction tube. The eluate was passed through the same filter a second time. Isolated DNA was suspended overnight at 4 °C. DNA concentrations were

measured using an Implen NanoPhotometer NP80 (Implen GmbH, München, Germany) at 260 nm (Cryer et al. 1975).

3.5 Density fractionation

Density fractionation was carried out using LUDOX® HS-40 colloidal silica suspension in water (Sigma-Aldrich) with a cut-off density of 1.4 g cm^{-3} . The procedure is based on the method first presented by van den Pol-van Dasselaar and Oenema (1999), adapted from Meijboom et al. (1995), and also applied by Gebert et al. (2006) on riverine sediments in a previous study. In brief, fresh sediment samples were placed in glass beakers, mixed with an excess of Ludox® at a density of 1.4 g cm^{-3} and stirred thoroughly. Light material < 1.4 g cm^{-3} accumulated at the surface and was separated from heavy material > 1.4 g cm^{-3} , sinking to the bottom, by decantation. The two fractions were washed with distilled water and oven-dried at 105 °C for subsequent physical and chemical analyses (see Section 3.6).

3.6 Standard properties of solids and pore water

The analysis of solid properties included total nitrogen (TN, DIN EN 16168 2012), total organic carbon (TOC, both DIN ISO 10694 1995), water content (WC, DIN ISO 11465 1993), redox potential (Eh, DIN 38404 2012), particle size distribution (DIN ISO 11277 2009), oxygen consumption after 3 h ($\text{AT}_{3\text{h}}$, TV-W/I 1994), phosphorus (P) and sulphur (S, both DIN ISO 11885 2007), pH value (pH, DIN EN 15933 2012) and electrical conductivity (EC, DIN EN 27888 1993). The following parameters were measured in filtrated pore water: dissolved organic carbon (DOC, DIN EN 1484 1997), ammonium (NH_4^+ , DIN ISO 11732 2005), phosphate (PO_4^{3-} , DIN ISO 6878 2004) and sulphate (SO_4^{2-} , DIN ISO 10304 2009).

3.7 Statistical evaluation of data

Linear regression analyses were carried out to detect possible interrelations between sediment properties and parameters of organic matter degradation. Statistical significance of Pearson’s coefficient r was accepted for a probability of error $p < 0.01$ for a two-sided test. The time course of carbon release from anaerobic and aerobic organic matter degradation was described by exponential fitting. The number of considered phases was increased until the coefficient of determination no longer improved and was highest for a two- or three-phase system, depending on the degradation state of the sample. For most of the samples, a three-phase exponential fit best described the data (Eq. 1).

$$y = A1 * \exp(-x/t1) + A2 * \exp(-x/t2) + A3 * \exp(-x/t3) + y0 \quad (1)$$

with A1, A2, A3 = initial value in each phase
 x = time in days
 t1, t2, t3 = degradation rate constant
 y0 = total cumulative anaerobically degraded organic matter

For the comparison between samples and for the correlation with sediment properties, benchmark values of carbon release under aerobic (R) and under anaerobic (G) conditions after 21 days (R₂₁, G₂₁) and 100 days (R₁₀₀, G₁₀₀) were used.

4 Results

4.1 Sediment properties

The thickness of the investigated pre-consolidated layer PS, the first freshly deposited material below the lutocline, was between 15 and 30 cm (Table 2). Except for the most downstream point P9, all samples showed a very high content of fines < 63 µm (sum of clay and silt) of up to 97% of the total mass. Sediment texture varied between clay (P4, most clay) to sandy clay loam (P9, most sand; FAO 2006). The sand-dominated texture at P9 and high sand contents at P5 reflect the fact that both are situated within the main flow channel (Table 1) where flow rates are higher, limiting sedimentation of fines. Correspondingly, these locations showed the lowest TOC contents. Concentrations of nitrogen (TN) and organic carbon (TOC) varied strongly between 0.2 and 1.0% (TN) and

2.0 and 7.6% (TOC) and were highest upstream and lowest downstream. The TOC-to-TN ratio was 10-fold higher at the downstream location (P9). The water content, phosphorus and electric conductivity showed similar patterns with increased values upstream and lower values downstream. NH₄⁺ in the pore water was strongly increased at upstream point P1 (up to 70 times) compared with other locations; PO₄³⁻ was increased two-fold. Inversely, the sulphate concentration was around five-fold higher at downstream location P9 compared with upstream location P1.

Organic matter degradation leads to transformation and stabilisation of the remaining organic matter in organo-mineral complexes with silt and clay, which causes a shift in the distribution of organic carbon towards higher density fractions. Compared with the bulk sediment (Table 2), the light fraction was enriched in organic matter, showing TOC contents of up to 14%. By contrast, TOC contents in the heavy fraction only reached up to 1.6% (data not shown). Between 40 and 50% of the total mass was found in the light fraction at upstream sampling point P1, comparing to only 5 to 20% at downstream sampling point P9 (Fig. 2, upper panel). In combination, between 80 and 90% of the organic carbon were found in the light density fraction at upstream point P1, whereas at downstream point P9 this share was 30–80% (Fig. 2, lower panel). Although the fractionated mass was often enriched in the heavy fraction, the share of TOC was always higher in the light fraction, with one exception for location P9 (CS layer from November 2018).

Table 2 Abiotic properties of pre-consolidated (PS) layers (solids) and the corresponding pore water by example of the sampling campaign from June 2018

	P1	P2	P3	P4	P5	P6	P7	P8	P9
Depth b.l. (cm)	5–25	5–35	5–20	5–30	0–30	10–30	0–25	0–20	10–30
TN (%)	1.0	0.6	0.6	0.6	0.3	0.5	0.5	0.5	0.2
TOC (%)	7.6	4.4	4.4	4.3	2.2	3.9	3.6	3.8	2.0
TOC/TN (% % ⁻¹)	7.6	7.6	7.2	7.4	8.5	8.3	7.7	8.4	10.0
WC (% DM)	495	371	359	342	169	299	293	366	158
Eh (meV)	-226	-280	-315	-280	-256	-300	-280	-360	-173
Clay (< 2 µm, %)	50	51	48	56	23	47	43	46	20
Silt (2–63 µm, %)	44	46	48	36	45	45	45	47	27
Sand (> 63 µm, %)	6	3	4	8	32	8	12	7	53
P (mg g _{DM} ⁻¹)	2120	1650	1640	1610	930	1510	1500	1510	840
S (mg g _{DM} ⁻¹)	4540	4750	4660	4530	2850	4630	4560	4590	2620
pH (-)	7.5	7.4	7.5	7.6	7.6	7.5	7.6	7.7	8.0
EC (µS cm ⁻¹)	2250	1945	1817	2020	1768	1792	1680	1627	1371
DOC (mg l ⁻¹)	41	27	56	37	21	23	15	17	20
NH ₄ ⁺ (mg l ⁻¹)	200	23	39	29	9	10	6	6	3
PO ₄ ³⁻ (mg l ⁻¹)	0.15	0.10	0.12	0.12	0.09	0.15	0.08	0.10	0.07
SO ₄ ²⁻ (mg l ⁻¹)	23	9	5	5	100	19	100	100	120

Italics = min. and max. values

TN total nitrogen, TOC total organic carbon, WC water content, Eh redox potential, LOI loss on ignition, P phosphorus, S sulphur, EC electric conductivity, DOC dissolved organic carbon, NH₄⁺ ammonium, PO₄³⁻ ortho-phosphate, SO₄²⁻ sulphate, b.l. below lutocline

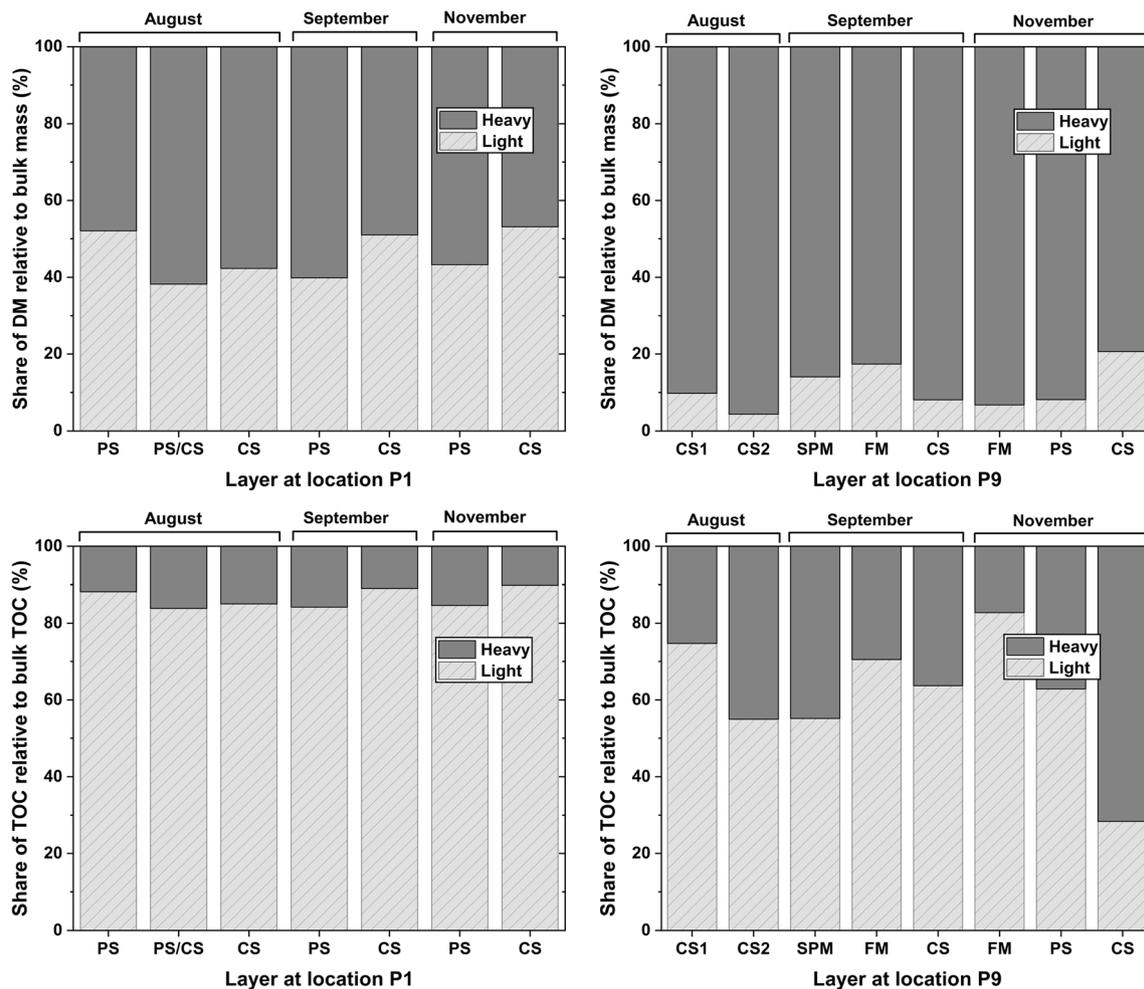


Fig. 2 Share of total dry mass (DM, upper panel) and of total organic carbon (TOC, lower panel) in the light ($< 1.4 \text{ g cm}^{-3}$) and heavy ($> 1.4 \text{ g cm}^{-3}$) density fraction at points P1 (upstream, left) and

(downstream, right). FM = fluid mud, PS = pre-consolidated sediment, CS = consolidated sediment, samples taken in August, September and November

The contrast between upstream and downstream properties was also reflected by the stable isotope signature and the concentration of DNA. The organic matter at the downstream location P9 was enriched in ^{13}C (Fig. 3, left panel); moreover, at all locations the heavy density fraction was enriched in ^{13}C compared with the light density fraction (Fig. 3, right panel). Also, an increased concentration of DNA was found in the sediment at upstream point P1 (location RV at river-km 616) compared with downstream point P9 (location SW at river-km 643) (Fig. 4). While for the $\delta^{13}\text{C}$ values no clear differentiation with depth could be identified, DNA concentrations showed a clear depth-related gradient with highest values in the youngest layers (fluid mud) and the lowest values in the oldest material (consolidated sediment).

4.2 Degradation of organic matter

An example of cumulated release of carbon from the anaerobic degradation of organic matter is shown in Fig. 5 for the

most upstream (P1) and the most downstream (P9) location for pre-consolidated (PS) layers with averages of three parallel measurements. In spite of the significant differences in absolute levels of carbon release (about four times higher at P1 after 160 days), the time course for both the samples shown here and all other samples followed the same asymptotic pattern with decreasing rates over time. The time course of carbon release by aerobic respiration followed the same pattern over time: however, the amount of carbon released when oxygen was available as terminal electron acceptor was threefold compared with carbon release under anaerobic conditions (Fig. 6).

Both the degradation (carbon release normalised to dry mass) and the degradability (carbon release normalised to mass unit TOC) of organic matter followed a marked gradient with higher values upstream and lower rates downstream (Fig. 6). The following key differences were observed between the sampling locations regarding degradation and degradability of organic matter (Table 3):

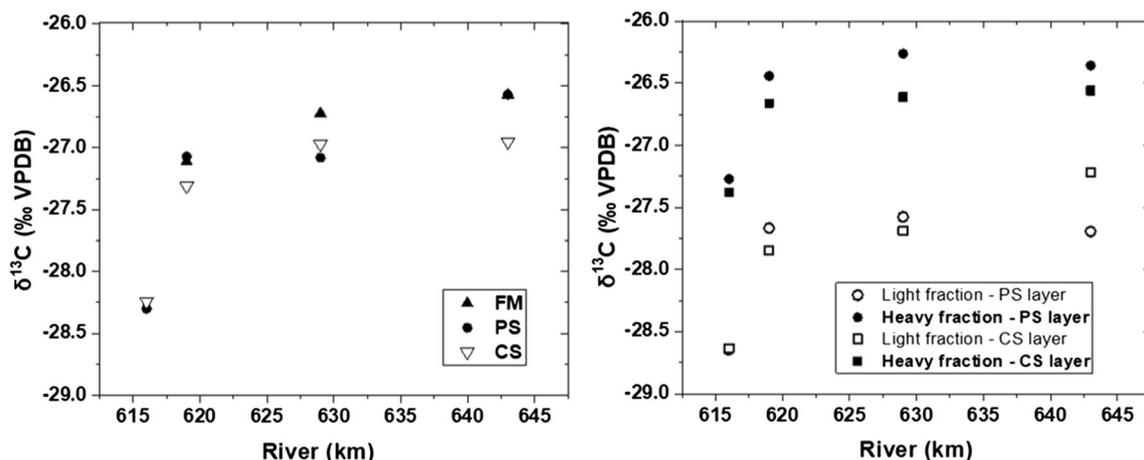


Fig. 3 $\delta^{13}\text{C}$ signature of fluid mud (FM), pre-consolidated (PS) and consolidated sediment (CS) on the original sample (left panel) and on the density-fractionated samples (only PS and CS, right panel) over the

sampling transect East (km 616)–West (km 643) for the locations P1, P2, P8 and P9, samples taken in November 2018. Left: bulk sample, right: light ($< 1.4 \text{ g cm}^{-3}$) and heavy ($> 1.4 \text{ g cm}^{-3}$) density fractions

- 10 to 30 times higher carbon release (per g DW) from anaerobic organic matter degradation (G_{21} , G_{100}) and up to 10-fold increased carbon release (per g DW) from aerobic degradation (R_{21} , R_{100}) related to dry mass at the upstream location P1 compared with the downstream location P9.
- The consumption of oxygen within 3 h was higher at location P1 compared with P9 by the factor of seven ($\text{AT}_{3\text{h}}$, P1: $2.0 \text{ g O}_2 \text{ kg}_{\text{DW}}^{-1}$, P9: $0.4 \text{ g O}_2 \text{ kg}_{\text{DW}}^{-1}$).
- Higher degradability of organic matter at location P1, with a factor of 2.5 to 7 compared with location P9 for both aerobic (R_{21} , R_{100}) and anaerobic (G_{21} , G_{100}) conditions.

Besides the upstream-downstream gradient of organic matter degradability, a depth- and therefore age-related gradient

was also observed at the individual sampling points (Fig. 7). Both anaerobic and aerobic (not shown) degradation of carbon per unit TOC decreased with increasing depth and hence age, coinciding with increased in situ concentrations of pore water ammonia (Fig. 8, left panel) and more negative redox potentials (Fig. 8, right panel) in deeper layers.

4.3 Relationship between abiotic sediment properties and organic matter degradation

Correlation analyses showed strong relationships between parameters reflecting carbon release by aerobic and anaerobic degradation of organic matter (R and G) and individual sediment properties (Table 5). Both processes were strongly positively related to TN and TOC contents as well as to water content and inversely related to the ratio of TOC to TN. Further, organic matter degradation was positively related to clay content, total phosphorus, total sulphur, dissolved organic carbon and pore water ammonium, but negatively to sand content and pore water sulphate. Aerobic and anaerobic degradability of organic matter were correlated well with each other, with values for Pearson’s r of 0.85 or greater, both for short-term (after 21 days) and long-term (100 days) periods, indicating the same principal governing factors behind the two processes.

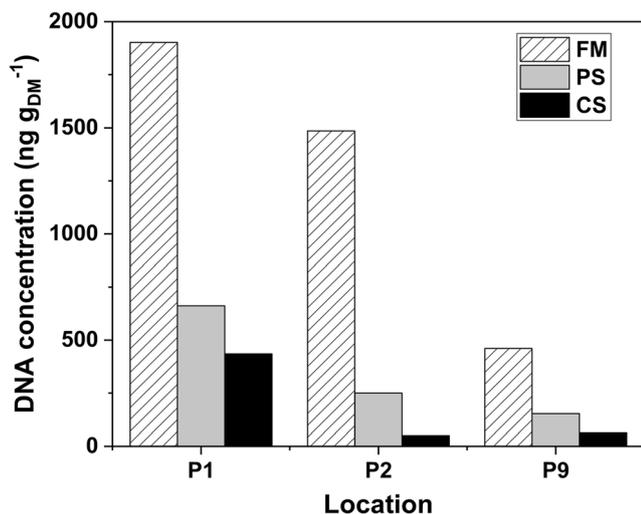


Fig. 4 DNA concentration in fluid mud (FM), pre-consolidated (PS) and consolidated sediment (CS) for locations RV, RT and SW in June 2018

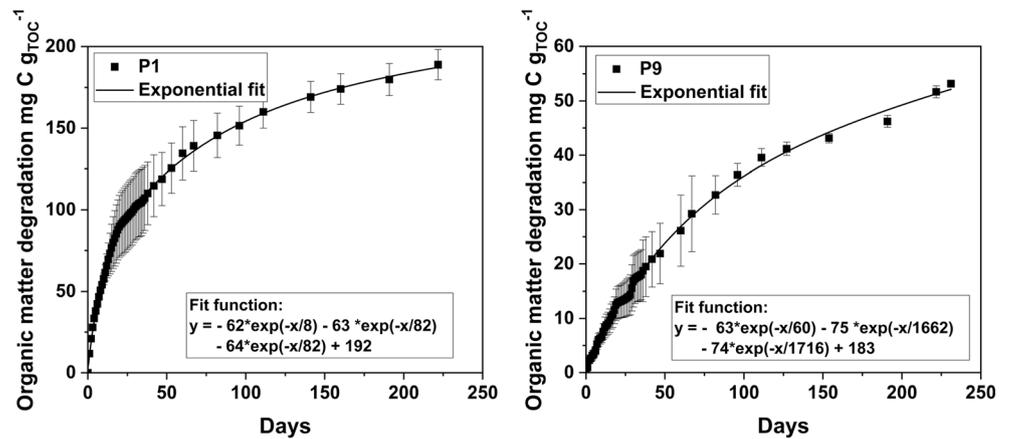
5 Discussion

5.1 Sediment properties and degradation of organic matter

5.1.1 Sediment properties

Both the abiotic sediment properties as well as organic matter degradation and degradability and DNA content in the

Fig. 5 Time course of organic matter degradation under anaerobic conditions by example of pre-consolidated samples from location P1 (left) and P9 (right) taken in June 2018, line: exponential fit with equation. Data points = average of three parallels, error bars = maximum and minimum



investigation area were subject to a pronounced spatial gradient. In general, upstream sediments featured a higher organic matter content (reflected by higher TOC and TN contents) with a lower TOC-TN-ratio, higher total sulphur and phosphorus and higher concentrations in pore water of dissolved organic carbon, ammonium and phosphate. The higher solute concentration was reflected by a higher electric conductivity

upstream, while downstream samples showed higher sulphate content, indicating increase of marine influence. The sulphate concentration in the sediment pore water can be influenced by two processes: the input of sulphate from marine origin through the stream water and the reduction of pore water sulphate under anaerobic conditions. Oxygen saturation of the water and hence higher redox potentials can be promoted by

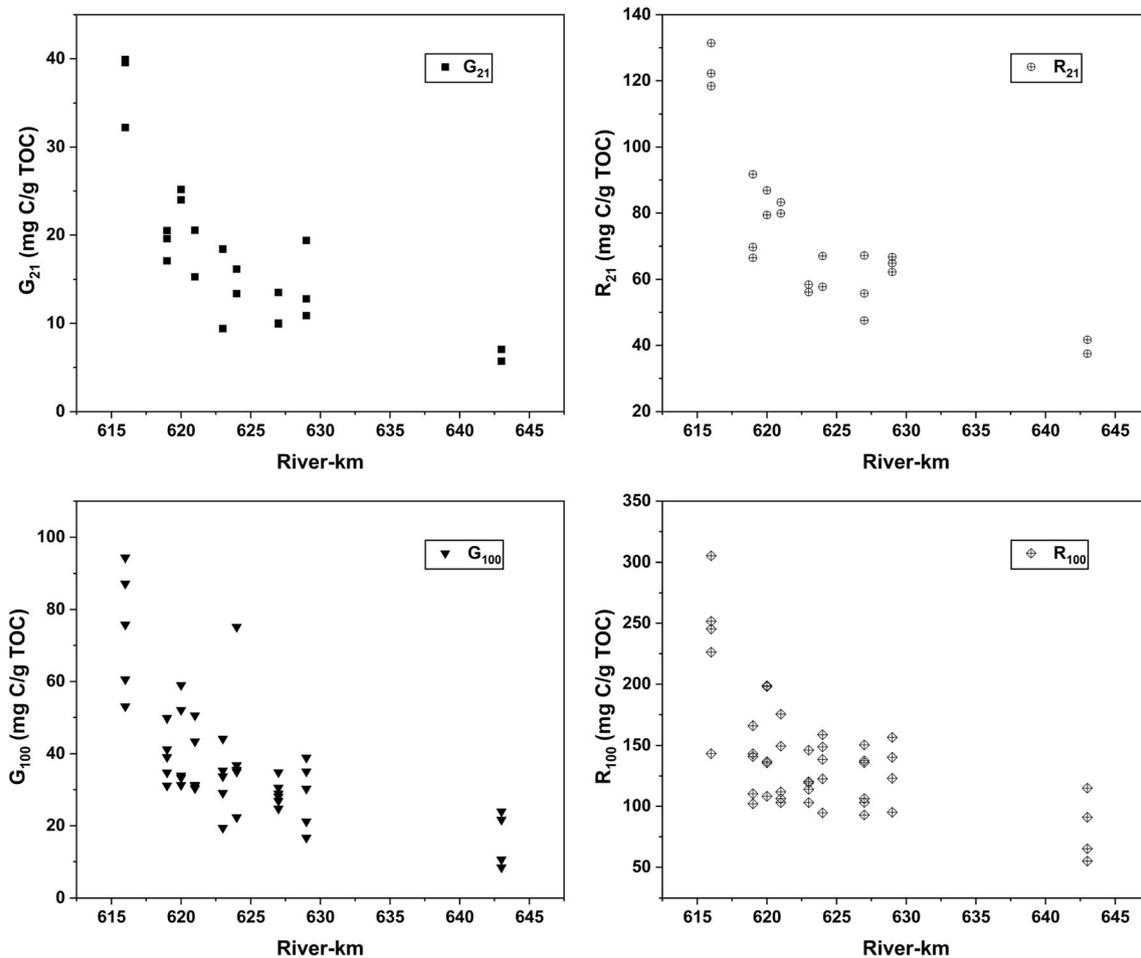


Fig. 6 Cumulative C release from pre-consolidated sediment, measured over 21 and 100 days under aerobic (R) and anaerobic (G) conditions shown over the sampling transect East (km 616)–West (km 643), data from campaign 1 to 5

Table 3 Cumulative carbon release from anaerobic (*G*) and aerobic (*R*) degradation of organic matter of pre-consolidated (PS) layers after 21 and 100 days by example of the sampling campaign from June 2018

	P1	P2	P3	P4	P5	P6	P7	P8	P9
<i>R</i> ₂₁ (mg C g _{TOC} ⁻¹)	118	92	87	83	56	58	56	67	42
<i>R</i> ₁₀₀ (mg C g _{TOC} ⁻¹)	245	110	199	106	120	149	136	140	91
<i>G</i> ₂₁ (mg C g _{TOC} ⁻¹)	40	20	25	21	9	13	10	11	6
<i>G</i> ₁₀₀ (mg C g _{TOC} ⁻¹)	87	50	59	51	29	36	29	30	22
<i>R</i> ₂₁ (mg C g _{DM} ⁻¹)	9.0	4.0	3.8	3.6	1.2	2.3	2.0	2.5	0.8
<i>R</i> ₁₀₀ (mg C g _{DM} ⁻¹)	18.6	4.9	8.7	4.6	2.6	5.8	4.9	5.3	1.8
<i>G</i> ₂₁ (mg C g _{DM} ⁻¹)	3.0	0.9	1.1	0.9	0.2	0.5	0.4	0.4	0.1
<i>G</i> ₁₀₀ (mg C g _{DM} ⁻¹)	6.6	2.2	2.6	2.2	0.6	1.4	1.0	1.2	0.4
<i>AT</i> _{3h} (g O ₂ kg _{DM} ⁻¹)	2.0	1.6	1.6	1.5	0.7	1.2	0.3	1.1	0.4

Italics = min. and max. values

*R*₂₁/*R*₁₀₀ and *G*₂₁/*G*₁₀₀ cumulative C release by aerobic and anaerobic organic matter degradation after 21/100 days, *AT*_{3h} oxygen consumption after 3 h, *DM* dry matter

turbulence as induced by a stronger current (location P9 in the main fairway; Fig. 7). This can be seen from also higher turbidity values (Table 4, position IV), showing three-times higher turbidity values than at location P1 (compare position I). The water temperature, affecting organic matter decay by its influence on the biological activity, did not vary between the locations. The influence of tributaries (Alster: 6 m³ s⁻¹ runoff, Bille: 4 m³ s⁻¹) to the total flow (on average in 2017 around 500 m³ s⁻¹) is negligible.

Concurrent with the gradient in sediment properties, both the mass-related release of carbon from the anaerobic and aerobic degradation of sediment organic matter and the degradability of the organic matter also decreased in the downstream direction. In terms of possible greenhouse gas emissions, this gradient means that sediments from the upstream location P1 can, within 21 days, produce up to 30 times the amount of methane and carbon dioxide per unit dry mass of dredged sediment than sediments from the downstream location P9. Carbon release under aerobic conditions was around

three to five times higher compared with anaerobic conditions (Fig. 6), one reason being the higher energy gain when oxygen is available as terminal electron acceptor. Cumulative oxygen consumption values in this study, normalised to 20 °C, were in agreement with Spieckermann et al. (2018) who sampled at a similar location (near location P2) in 20 to 40 cm sediment depth.

5.1.2 Correlation between sediment properties and organic matter degradability

Statistically significant correlations were found between standard analytical sediment parameters and the degradation and degradability of organic matter (Table 5). Organic matter degradability (*R* and *G* are expressed in carbon release per unit TOC) correlated most strongly with total organic carbon, indicating that in the investigated system higher organic matter content also means a higher share of degradable organic matter. Degradability was inversely related to the ratio of TOC to

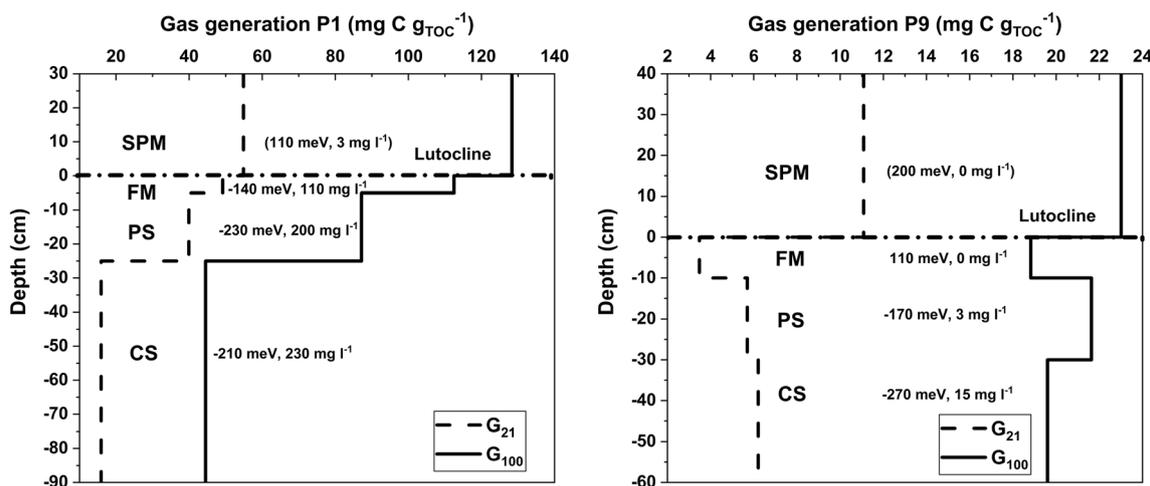


Fig. 7 Cumulative organic matter degradation under anaerobic conditions (*G*) over depth for 21 days (*G*₂₁) and 100 days (*G*₁₀₀) with redox potential (meV) and ammonium concentration in pore water

(mg l⁻¹) at location P1 and P9 per layer (SPM - CS), depth below lutocline, samples taken in June 2018, values in brackets calculated from other campaigns

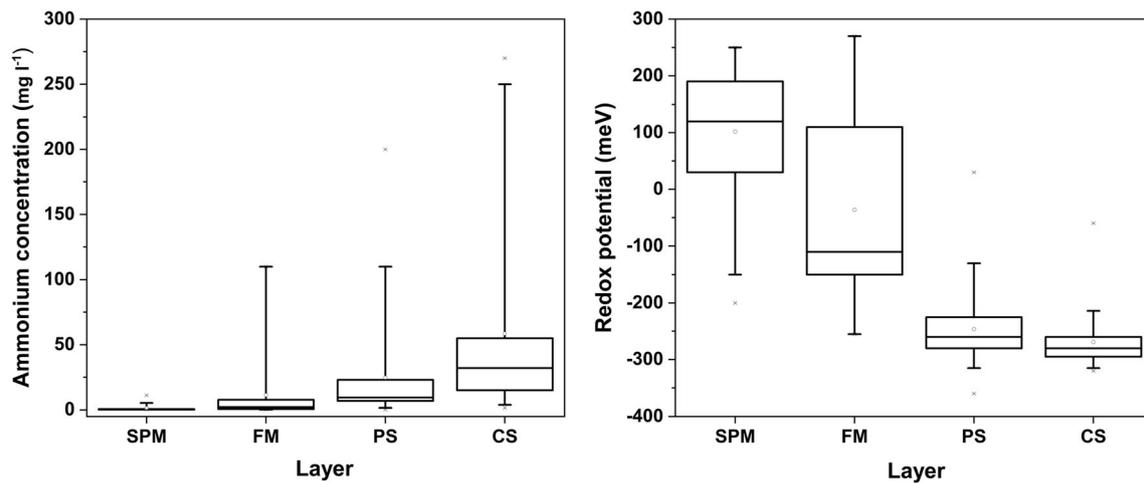


Fig. 8 Depth profiles of redox potential and pore water concentration of ammonia (NH_4^+) at the time of sampling for selected sampling points, samples taken in June 2018. Square symbol = mean, line = median,

box = 25th–75th percentile, whisker = 5th–95th percentile, cross = 1st–99th percentile, line symbol = minimum and maximum

TN, confirming the findings of Gebert et al. (2019) for degradation of organic matter in landfilled dredged sediment, suggesting lower degradability with decreasing contents of nitrogen per unit organic carbon. An inverse relationship can be expected because the nitrogen-to-carbon ratio in the decomposer biomass is higher than in soil (sediment) organic matter and litter, creating a constant demand for nitrogen (Berg and McLaugherty 2003). In terrestrial soils, decomposition rates for litter were thus also found to be positively linked to the TN/TOC ratio (Manzoni et al. 2008) and negatively to the TOC/TN ratio (e.g. van Dijk 1980). The strong correlation between sediment water content (WC) and TOC ($r = 0.95$) and TN ($r = 0.93$) contents reflects the fact that the youngest, most freshly settled material is the least consolidated one (highest water content) and at the same time the one with the least extent of organic matter decomposition, featured by (still) higher TOC and TN contents. From thermodynamic considerations (for a review see Arndt et al. 2013) it appears plausible that pore water sulphate correlated negatively with organic matter degradability, as the reduction of sulphate is energetically favourable compared with methanogenesis. In a study investigating gas production of sediments from ten

federal German waterways, Gebert et al. (2006) found the lag phase until methane production commenced to be strongly correlated to the concentrations of inorganic electron acceptors such as sulphate in the pore water.

5.1.3 Organic matter quality

All systems with high organic carbon sedimentation rates, high internal primary production and anoxic bottom waters have a high CH_4 emission potential (Grasset et al. 2018). Indeed, the strongest CH_4 production potential was found for the sediments at the highly anoxic locations of this study (e.g. location P1; Fig. 7). Grasset et al. (2018) attributed low CH_4 production from sediment to a low availability of labile compounds, comparable with downstream location P9 showing low concentrations in the light density fraction (Fig. 2) and high CH_4 to the addition of fresh organic carbon to anoxic sediments. The same study showed that planktonic biomass (autochthonous organic carbon) was faster degradable than terrestrial biomass (allochthonous organic carbon). This suggests that, as also shown by Schoel et al. (2014, see Section 5.2), the organic carbon input at more upstream locations in the

Table 4 Water parameters at the date of the sampling in June 2018 with location and river-km of this study and the sampling positions of Hamburg Serviceportal (2019)

This study		HH-Service		WT	O_2	TB	CH	pH
Location	River-km	Position	River-km	$^\circ\text{C}$	mg l^{-1}	FNU	$\mu\text{g l}^{-1}$	–
P1	616	I	610	<i>18</i>	<i>9.0</i>	19	<i>118</i>	<i>8.4</i>
P3	620	II	622	25	3.8	12	20	7.8
P8	629	III	629	19	4.3	39	13	7.6
P9	643	IV	636	20	4.9	57	nd	7.5

Italics = min. and max. values

WT water-temperature, O_2 oxygen concentration, TB turbidity, CH total chlorophyll concentration, nd not determined

Table 5 Pearson's coefficient *r* for correlations between aerobic and anaerobic organic matter degradation referred to g TOC and material properties for pre-consolidated layers (*n* ≥ 25). Italics = Pearson's coefficient *r* significant on a confidence level of 99.99%, bold: Pearson's coefficient *r* > 0.85

	TN	TOC	TOC/ TN	R ₂₁	R ₁₀₀	G ₂₁	G ₁₀₀	WC	Eh	Clay	Silt	Sand	Al _{3h}	P	S	EC	DOC	NH ₄ ⁺	PO ₄ ³⁻	SO ₄ ²⁻		
TN	-	0.99	-0.72	0.92	0.87	0.85	0.84	0.95	-0.33	0.67	0.30	-0.68	0.81	0.89	0.65	0.56	0.51	0.82	-0.16	-0.16	-0.64	
TOC		-	-0.68	0.91	0.88	0.85	0.85	0.93	-0.30	0.68	0.30	-0.68	0.77	0.91	0.65	0.53	0.54	0.81	-0.16	-0.16	-0.59	
TOC/TN			-	-0.71	-0.65	-0.63	-0.62	-0.78	0.57	-0.77	-0.42	0.80	-0.62	-0.67	-0.72	-0.42	-0.29	-0.43	0.26	0.64	0.64	
R ₂₁				-	0.91	0.86	0.87	0.92	-0.40	0.63	0.21	-0.60	0.75	0.79	0.52	0.43	0.60	0.76	-0.14	-0.64	-0.64	
R ₁₀₀				-	-	0.83	0.85	0.85	-0.40	0.53	0.27	-0.55	0.71	0.72	0.50	0.31	0.73	0.72	-0.10	-0.61	-0.61	
G ₂₁				-	-	-	0.98	0.80	-0.40	0.55	0.21	-0.53	0.74	0.73	0.50	0.36	0.58	0.72	-0.13	-0.63	-0.63	
G ₁₀₀				-	-	-	-	0.79	-0.38	0.51	0.21	-0.50	0.74	0.72	0.47	0.31	0.64	0.72	-0.07	-0.62	-0.62	
WC				-	-	-	-	-	-0.37	0.78	0.32	-0.77	0.78	0.87	0.73	0.46	0.42	0.69	-0.17	-0.57	-0.57	
Eh				-	-	-	-	-	-	-0.50	-0.55	0.61	-0.32	-0.38	-0.52	-0.16	-0.38	-0.08	0.45	0.46	0.46	
Clay				-	-	-	-	-	-	-	0.23	-0.92	0.56	0.81	0.88	0.28	0.33	0.29	-0.18	-0.41	-0.41	
Silt				-	-	-	-	-	-	-	-	-0.60	0.33	0.50	0.60	0.17	-0.01	0.12	-0.10	-0.32	-0.32	
Sand				-	-	-	-	-	-	-	-	-	-0.57	-0.83	-0.92	-0.29	-0.25	-0.28	0.18	0.45	0.45	
Al _{3h}				-	-	-	-	-	-	-	-	-	-	0.67	0.60	0.42	0.44	0.57	-0.09	-0.67	-0.67	
P				-	-	-	-	-	-	-	-	-	-	-	0.81	0.54	0.35	0.68	-0.29	-0.56	-0.56	
S				-	-	-	-	-	-	-	-	-	-	-	-	0.27	0.20	0.24	-0.24	-0.50	-0.50	
EC				-	-	-	-	-	-	-	-	-	-	-	-	-	0.14	0.67	-0.40	-0.42	-0.42	
DOC				-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.43	-0.05	-0.45	-0.45	
NH ₄ ⁺				-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-0.14	-0.51	-0.51	
PO ₄ ³⁻				-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.22	
SO ₄ ²⁻				-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

TN total nitrogen, TOC total organic carbon, R₂₁(R₁₀₀)/G₂₁(G₁₀₀) aerobic and anaerobic organic matter degradation after 21(100) days, WC water content, Eh redox potential, Al_{3h} oxygen consumption after 3 h, LOI loss on ignition, P phosphorus, S sulphur, EC electric conductivity, DOC dissolved organic carbon, NH₄⁺ ammonium, PO₄³⁻ phosphate, SO₄²⁻ sulphate

investigation area is dominated by autochthonous (phytoplankton, zooplankton) organic carbon, complementing the already mineral-phase bound and hence less degradable organic carbon pool. Other studies also related carbon release to organic matter quality and hence degradability, using different indicators. For example, White et al. (2002) described different classes of organic matter compounds that correlated positively (primary and secondary polysaccharides) or negatively (phenolic precursors, lignin, proteins and lipids) to the cumulative respiration. Further, Dai et al. (2002) could link carbon emission to the presence of easily degradable components such as polysaccharides. Straathof et al. (2014) found the concentration of the hydrophilic DOC fraction to correlate positively with respiration rates measured for compost. In this study, higher chlorophyll concentrations, indicative of higher phytoplankton biomass, are assumed to explain the higher degradability of organic matter seen at the downstream location P1.

5.2 Source and stabilisation of organic matter in sediments

Organic matter in soils and sediments is stabilised by formation of organo-mineral complexes which reduce its accessibility to biological degradation and hence to mineralisation (Baldock and Skjemstad 2000; Six and Paustian 2014; Gao et al. 2019). Conversely, non-complexed organic matter is more labile, i.e. prone to mineralisation, and has been found to be associated with microbial biomass C and N (Bu et al. 2012). The increased share of light fraction organic carbon upstream was seconded by a markedly higher concentration of DNA, indicative of a higher biomass content, as shown by Agnieszka et al. (2012) and Rehman et al. (2016). The gradient in DNA content supports the assumption a higher share of biomass-based degradable organic matter in the upstream area, as also suggested by the higher chlorophyll values in the water phase (Table 4). The chlorophyll concentration was nine times higher near the upstream location P1 (position I) compared with the more downstream location P8 (near position III; Hamburg Serviceportal 2019). It is assumed that at individual sampling locations the lower contents of DNA in deeper layers result from the mineralisation (decay) of the increasingly buried organisms without new biomass being introduced. The lower biomass levels are then maintained over time as the conditions such as scarcity of terminal electron acceptors (more negative redox potentials; Fig. 8) and poor rates of diffusive exchange of metabolites pose boundaries to biological activity.

A markedly higher share of light fraction organic carbon was found at the upstream location P1, while the downstream location P9 was dominated by heavy fraction organic carbon (Fig. 2). This suggests that the lower degradability of downstream organic matter results from a higher level of association

with the mineral phase and that upstream organic matter was characterised by a higher share in light-fraction, easily accessible biogenic share of organic matter. The latter is corroborated by the aforementioned elevated levels of chlorophyll and therefore an increased share of biomass-based degradable organic matter in the upstream area. For landfilled Elbe sediment that had undergone several years to decades of organic matter degradation, Gebert et al. (2019) found over 93% of the bulk mass and over 80% of the organic carbon to be associated with the heavy fraction. Together, these data suggest a transition of organic carbon from the more accessible (light) to the less accessible (heavy) fraction and hence progressive stabilisation of organic matter in organo-mineral complexes with increasing mineralisation and hence age.

The findings were supported by the carbon isotopic signature, with a greater share of ^{12}C in the bulk sample from upstream and an enrichment in ^{13}C downstream. Organic matter components containing the lighter isotope ^{12}C are degraded at a higher rate than those containing ^{13}C , causing an enrichment of ^{13}C and therefore an increase in the $\delta^{13}\text{C}$ signature with age (overview in Wang et al. 2015) and hence an increased level of organic matter stabilisation. Together with the distribution of TOC over the light and heavy density fractions, this again points at aged, more stabilised organic matter at the downstream location. However, the isotopic signature is also influenced by the origin of the organic matter. For example, plant species following the C3-assimilation pathway have an average $\delta^{13}\text{C}$ value of -27‰ , species assimilating via the C4 pathway an average $\delta^{13}\text{C}$ value of -14‰ , whereas marine organic matter typically has $\delta^{13}\text{C}$ values varying between -20 and -22‰ (Schulz and Zabel 2006). Lammers et al. (2017) found $\delta^{13}\text{C}$ values between 10.5 and 23.5‰ for eukaryotic phytoplankton in a shallow Dutch lake. The observed isotopic gradient can therefore reflect a higher age of the downstream sediment organic matter or a different origin. As point P9 (PS-layer -26.6‰ ; Fig. 3) is characterised by input of downstream sediments carried in direction of the harbour with the flood tide and point P1 (PS-layer -28.3‰ ; Fig. 3) is dominated by input from the upstream catchment with higher algal biomass in the water phase (see chlorophyll concentrations in Table 4), a source-based gradient over the investigation area is likely.

The $\delta^{13}\text{C}$ signature was expected to increase with depth due to a preferred consumption of ^{12}C by microorganisms. Likewise, it was expected that the share of carbon in the heavy density fraction would increase with depth. Both were only partly found, for example for the samples from November 2018 at location P9 (Fig. 2, lower right panel). It is assumed that the absence of a clear depth-related trend is due to the naturally dynamic hydro-morphological situation (variable current, tide, dredging activities, etc.), confounding depth gradients that would be visible if they reflected an age gradient of exactly the same original material. However, the assumption

that heavy fraction organic carbon reflects the older, more stabilised and therefore less degradable pool was supported by the fact that heavy density fraction organic carbon showed an enrichment in ^{13}C compared with the organic carbon found in the light density fraction (Fig. 3, right panel).

Schoel et al. (2014) showed that phytoplankton plays an important role for the concentration of dissolved oxygen in the Elbe. Also, Thorp and Delong (2002) described phytoplankton as the main driver of heterotrophic organic carbon cycling for eutrophic rivers. In line with the river continuum concept (Vannote et al. 1980), Schoel et al. (2014) demonstrated supersaturation with oxygen due to enhanced net primary production in the shallow and eutrophic upstream parts of the Elbe and light deficiency-induced decay of algal biomass by zooplankton grazing in the significantly deeper waters of the Hamburg Port area, inducing oxygen minimum zones. Concurrent to phytoplankton biomass, biological oxygen demand (BOD) and oxygen saturation plummeted within the Hamburg Port area, a trend is seen in the gradient of decreasing degradability of organic matter in downstream direction demonstrated in this study (Fig. 6). Within the harbour area, the river continuum concept is difficult to apply due to the strong tidal influence, additional urban afflux from streets, creeks, sewages or surface runoff as well as massive interventions like the removal of entire habitats (organisms, organic matter, etc.) by dredging.

Spatial variability of organic matter (degradation) with location and/or depth were also found in several other environments, for example in estuaries (Middelburg et al. 1996), mineral soils (Fang et al. 2005), intertidal sediments (Beck et al. 2008), lakes (Natchimuthu et al. 2015) and coastal wetlands (Yousefi Lalimi et al. 2018). Middelburg et al. (1996) found the spatial variability of organic matter mineralisation in intertidal sediments to be mainly caused by differences in the organic matter lability. As in our study, Yousefi Lalimi et al. (2018) and Fang et al. (2005) found a depth gradient of decreasing decomposition rates in (marsh) soil layers. The results from Fang et al. (2005) indicated that soil basal respiration rate is closely related to variations in available carbon pools occurring at different soil depths, also hypothesised in our study. Beck et al. (2008) described that products of organic matter remineralisation (e.g. DOC, NH_4^+ , PO_4^{3-}) increased with depth in pore waters of intertidal flat sediments, which can be also seen in this study (e.g. NH_4^+ ; Fig. 8).

The higher upstream degradability can be caused by a higher degradability of the organic matter itself, reflecting an intrinsic chemical property, or by more favourable environmental conditions such as increased availability of nutrients or both. In this study, the longitudinal gradient of organic matter degradability correlates with a gradient in decreasing nutrient concentrations, as seen from the contents in pore water phosphate and also total phosphorus (Table 2).

5.3 Transformation of nitrogen

Upstream locations showed stronger accumulation of NH_4^+ in the pore water (Table 2; Fig. 7), reflecting nitrogen mineralisation under anaerobic conditions, in line with higher degradability of upstream organic matter. The advanced state of organic matter degradation in deeper lying and therefore older layers was also seen by a depth gradient of increasing ammonium concentrations in the pore water (Fig. 8). This was most pronounced at point P1, where also both the highest organic matter turnover (related to dry weight of sample) and the highest degradability (related to mass unit organic carbon) were found.

Sanders et al. (2018) measured dissolved inorganic nitrogen in water samples of the stream along a gradient within the Elbe River in May 2013. Sampling locations included points near to points P1, P3, P6, P8 and P9 of this study. When comparing the two data sets, it is found that ammonium (NH_4^+) concentrations in the pore water (Table 2; layer PS) were 20 to 240 times higher compared with the concentrations in the water column, while nitrite concentrations (NO_2^-) were increased by only 2.5- to 12-fold and nitrate concentrations (NO_3^-) were partly even lower in the pore water compared with the water column (0.1- to 1.4-fold difference). Altogether, this indicates the dominance of anaerobic nitrogen mineralisation in the sediment, leading to the observed accumulation of ammonium, with denitrification being less relevant. Brockmann (1994) found decreased concentrations of dissolved organic nitrogen and dissolved organic phosphorus between Elbe river kilometres 630 and 770 towards the sea, mainly due to dilution with sea water. The decrease of the particulate organic matter concentration and the turbidity-organic matter-ratio in downstream direction was explained with organic matter degradation in the upper estuary and dilution with inorganic suspended particulate matter (SPM) from the lower estuary.

6 Conclusions and outlook

The time-course of organic matter degradation in long-term experiments showed the presence of differently available pools whose increasing depletion leads to an exponential decay of organic matter reactivity. The investigation area was characterised by a distinct gradient of sediment abiotic properties and organic matter lability, with higher degradability upstream and lower degradability downstream. Upstream locations were characterised by a higher concentration of DNA, a higher share of organic carbon in the light density fraction (i.e. not stabilised in organo-mineral complexes) and lower (more negative) $\delta^{13}\text{C}$ values. This supports the hypothesis of sediment and organic matter properties being determined by a spatial stratification of the source organic matter and the conditions impacting sediment properties at any individual location along the stream. Data suggest that at downstream locations, organic matter is mainly of

allochthonous origin (e.g. eroded soils, plant litter), entering the port mainly with the tidal flood current from the direction of the North Sea whereas upstream locations receive sediments and organic matter predominantly originating from the Elbe catchment, with an additional greater share of autochthonous organic matter (planktonic biomass), earmarked by a lighter organic carbon (less ^{13}C). In between, sediments are of mixed origin, the magnitude of the individual upstream and downstream shares depending on the prevalent hydrodynamic conditions. Upstream, the suspended particulate matter feeding sedimentation contains more easily degradable components such as algal biomass, already suggested by higher chlorophyll concentrations in the water column, and reflected by a higher share of total mass in the sediment's lighter density fraction. Downstream, a higher level of mineralisation and therefore of stabilisation of the input organic matter is evidenced by an increased share of organic carbon bound to the mineral phase and lower aerobic and anaerobic degradability. Whether the observed gradient is solely due to the assumed differences in input organic matter or whether an age gradient from upstream to downstream overlays the source pattern, cannot be determined at this moment. Ongoing clay mineralogical analyses of downstream and upstream sediments shall help to further elucidate the question.

Density fractionation appears to be a promising qualitative tool which can explain the presence of differently degradable organic matter pools in sediments. Future chemical fractionation will show whether these pools can be related to intrinsic organic matter chemical quality. While it became clear that degradability and density distribution are closely linked, the hypothesis that ageing (and hence increased mineralisation and stabilisation) leads to a shift towards increasing association of organic matter with the mineral phase could not be directly verified by the depth and hence age profiles at the individual sampling locations of this study. This is assumed to be due to depth profiles not representing a chronosequence of the very same settled material. Future experiments investigating the change in density distribution on one sample with ongoing incubation shall help to investigate this hypothesis.

The good correlation of organic matter degradability with standard analytical parameters such as TN and TOC may allow predictions of turnover using data on simple abiotic sediment properties. Additionally, the chlorophyll concentration might play an important role in the organic matter degradation. The significantly higher degradability of organic matter under aerobic compared with anaerobic conditions in combination with the marked spatial stratification of degradability provides the basis for the assessment of climate impact of dredging and relocation measures, but also for the quantification of potential greenhouse gas emissions from port areas without intervention.

Upcoming investigations will reveal the temporal variability of organic matter quality (fractions of dissolved organic carbon) and degradability in greater detail. All of the above will feed into the development of a process-based model predicting organic

matter turnover in the Port of Hamburg in time and space. Benefits of this study will include increased process knowledge on organic matter degradation behaviour as a basis for implementing adaptive sediment management, positively impacting the water quality and possibly reducing greenhouse gas emissions.

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