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# The influence of sediment-derived dissolved organic matter in the Vistula River Estuary/Gulf of Gdansk

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**Key Points:**

- The Vistula river supplies large amounts of terrestrial dissolved organic matter to the Gulf of Gdansk
- Sediment-derived dissolved organic matter has a unique fluorescent signature
- Fluorescent dissolved organic matter in the Gulf of Gdansk is dominated by pelagic sources



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**Abstract**

Dissolved organic matter (DOM) concentrations in sediment porewaters are often orders of magnitude higher than in the overlying water column resulting in a diffusive flux of DOM from sediments. The intensity and fate of this DOM flux is poorly understood. The Gulf of Gdansk in the Southern Baltic Sea is dominated by the Vistula River, one of the largest and most anthropogenically impacted rivers in the Baltic Sea catchment. The sediment characteristics of the region are varied, from mixed sandy conditions near shore to mud sediments in the Gdansk Deep. We investigated the significance of sediment-derived DOM in the Gulf of Gdansk in comparison to that supplied by the river. Sediment-derived DOM in the region was found to have an organic matter fluorescence signature distinct from the DOM in the water column. The visible wavelength fluorescence could be used to distinguish organic matter from near shore sediments influenced by riverine sources and organic matter from deeper offshore sediments, influenced by more pelagic sources. UVA wavelength fluorescence dominated the sediment flux but was rapidly removed in bottom waters suggesting that it may contribute to bottom water oxygen consumption. While there is potential for DOM fluxes from sediments in the Gulf of Gdansk, the high background pelagic concentration of DOM in these waters and the much stronger influence of the Vistula River can mask the contributions from sediments.



## 1 Introduction

Coastal sediments have high organic matter content and act as a considerable storage reservoir for organic carbon in marine systems (Burdige & Komada, 2015; Hedges & Keil, 1995). Particulate organic carbon flocculates and settles to sediments as detritus, salt-induced flocculates of organic matter in estuaries, and by the association of organic matter with metal minerals (Burd & Jackson, 2009; Eckert & Sholkovitz, 1976; Sholkovitz, 1978). The gradual degradation and dissolution of this organic matter results in high porewater concentrations of dissolved organic matter (DOM), often orders of magnitude higher than concentrations in the water column (Burdige et al., 1992; Burdige & Komada, 2015). The large concentration gradient between porewaters and overlying water results in a persistent diffusive flux and suggests that the sediments should be a significant source of DOM to the water column (Burdige et al., 2004). Studies have shown that DOM inputs from global marine sediments should be comparable to the input of DOM from rivers (Burdige et al., 1992; Burdige & Komada, 2015), with coastal and shelf sea sediments being a significant diffusive source of DOM. Furthermore, re-suspension events, which are common in coastal areas have the potential to release large amounts of DOM from the porewaters of surface sediments (Komada & Reimers, 2001). These can be driven by storm events and sustained wind conditions, depending on water depth (Osburn et al., 2012).

The Baltic Sea is a relatively shallow semi-enclosed basin that is highly terrestrially influenced, with salinities ranging from 0-2 in the northern regions to between 5-10 in the Baltic Proper, increasing out through the Danish Straits to the North Sea. The Danish Straights are particularly shallow and this hinders frequent exchange of saline waters from the North Sea with bottom waters of the Baltic. The restrictive nature of circulation in the Baltic Sea, and high loads of terrestrial nutrients result in zones of both periodic and permanent hypoxic and anoxic conditions throughout the Baltic Sea, the extent of which have increased over the past century (Carstensen et al., 2014; Conley et al., 2011).

Sedimentation of DOM by association with iron minerals, a process documented to occur in the Baltic (Kritzberg et al., 2014; Lalonde et al., 2012; Riedel et al., 2013), has been speculated to be an effective mechanism for the removal of biologically labile DOM from the water column (Lalonde et al., 2012). Though most of the DOM in the Baltic Sea appears to be terrestrially sourced (Alling et al., 2008; Deutsch et al., 2012), the potential addition of DOM from sediments could represent a heretofore understudied pool of DOM in the region. Early studies have detected evidence for systematically elevated DOM concentrations in waters directly overlying sediment (Kowalczuk et al., 2010, 2015; Skoog et al., 2011). If bioavailability of this material is high, sediment-sourced DOM could represent a further stressor on the oxygen conditions of the Baltic Sea, by supporting higher bacterial respiration rates.

In this study, we investigated the Vistula river outflow in the Gulf of Gdansk, to better understand the sources of DOM in the Southern Baltic. The Vistula is one of the largest rivers in the Baltic Sea and is also one of the most anthropogenically impacted rivers (Łysiak-Pastuszak et al., 2004; Voss et al., 2006), due to large amounts of agricultural land in its catchment (Buszewski et al., 2005). The study area covered a variety of sediment-types, ranging from sand in more shallow waters to mud in deeper waters roughly separated by the 50m depth line. While sandy sediments can experience more advective flow in interstitial porewaters, muddy sediments tend to experience strictly diffusive conditions (Huettel et al., 1998). We hypothesize that the influence of sediment DOM fluxes on water column DOM will be identifiable using fluorescence fingerprinting, and further that sediments will be a significant source of DOM to the water column in this region.

## 2 Materials and Methods

### 2.1 Study site and field campaigns

Two sampling campaigns were carried out in the Gulf of Gdansk, in the outflow of the Vistula River (Figure 1a on board the R/V Elisabeth Mann Borgese (July 4 – 17, 2014 campaign) and the R/V Alkor (January 31 - February 13, 2015 campaign). The first campaign was performed during low flow, summer conditions (blue dots Figure 1b). The second campaign was performed during relatively high flow conditions on the Vistula River (red dots Figure 1b). Peak flow of the river normally occurs in March, however, the winter 2014/2015 of was relatively mild and an extensive river plume was found and traced for part of the campaign. The Vistula River is a highly anthropogenically impacted river, the catchment covers 194,424 sq. km, and largely flows through farmland (39.5 – 79.2%) (Buszewski et al., 2005). Sampling sites for both campaigns ranged from near coastal sandy sediments out to the muddy sediments in the Gdansk Deep, a permanently anoxic basin at the mouth of the Gulf of Gdansk.

Water column properties were sampled using a Seabird 911plus CTD - rosette water sampling system. Conductivity sensors were calibrated using an AUTOSAL 8400 salinometer and OceanScientific seawater standards at appropriate salinity ranges (5-6) to an accuracy of 0.001 mS/cm.

### 2.2 Dissolved organic matter sampling and analysis

Samples were taken for dissolved organic carbon (DOC), chromophoric and fluorescent dissolved organic matter (CDOM, FDOM). A total of 197 samples were collected from both campaigns. Sixteen stations were sampled in July 2014 and 13 were sampled in February 2015. Typically, 6 depths were sampled (surface, 5, 7.5, 10, 15 m and just above the seafloor) and at some deeper stations the 7.5 m sample was sacrificed for covering a deeper

intermediate depth (between 15m and the sea floor). At the deepest stations (on the shelf break, VE38, VE39, VE43 (only July), TF0233) samples were taken every 10 m to the bottom in July, and every 30 m until below the thermocline and then every 10 m to the bottom in February. The number of samples taken in February at the deeper stations was truncated due to storm weather, which cut sampling short. The samples in July were filtered directly from the Niskin bottles using 0.2 µm Millipore Opticap XL cartridge filters, samples in February were filtered from clean glass bottles using rubber-free plastic syringes (NORM-JECT®, Henke Sass Wolf GMBH) and 0.2 µm Acrodisc syringe filters. Samples for DOC were stored in acid washed HDPE bottles and preserved immediately either by acidification and storage at 4 ºC (July) or freezing (-18 ºC) (February). Samples for C/FDOM were stored in ashed brown glass vials and stored at 4 ºC until analysis.

Upon return to the laboratory in Denmark (within 2 weeks), DOC and TN were analysed on a Shimadzu TOC-V CPH, which was calibrated with using an acetanilide standard (Cauwet, 1999) and referenced to deep sea standard DOC (Hansell Lab, RSAMS Miami). Absorbance and fluorescence characteristics were measured on a Horiba Aqualog, and calibrated to Raman units (Lawaetz & Stedmon, 2009). Emission spectra were collected (240-600 nm) across a range of excitation wavelengths, from 240-450 nm in 5 nm increments, resulting in an excitation-emission matrix (EEM) for each sample. Absorbance was measured simultaneously across the same wavelength range as fluorescence emission spectra. The spectral fluorescence measurements were corrected for instrument bias and inner filter effects according to the recommendations in (Murphy et al., 2010) and subsequently characterized using parallel-factor analysis (Murphy et al., 2013). The modeled dataset contained samples collected from the water column, the overlying water from cores and from the sediment-slurry experiments. As there were considerable differences in the fluorescence intensities between the sample types the EEMs were normalized to total fluorescence intensity prior to PARAFAC analysis using the drEEM toolbox (Murphy et al., 2013). The PARAFAC analysis separated the fluorescence signal recorded in the EEMs into 7 underlying components (Figure 2), which were validated using split half-validation. The components are labeled according to the wavelength position of their emission maximum.

### 2.3 Sediment sampling and analysis

Sediment samples were taken with either a multicorer, equipped with eight 10 cm diameter cores for softer sediment or with a HAPS sediment corer (KC Denmark) equipped with a single 25 cm metal core, for the harder coarser grain size sediments. Water samples for DOM analysis were taken by syringe from the water overlying the cores (~5-10 cm from sediment surfaces) and filtered using 0.2 µm Acrodisc filters, storage and analysis was identical as for water column samples from the CTD-rosette. To ensure an undisturbed water column above we only sampled cores that were intact had clear waters on top and with undisturbed surface sediments. Samples for organic content analysis of sediments was taken for the surface layer (0.5 cm slice thickness). Samples were frozen until analysis. Samples were thawed, weighed, and then dried overnight at 100 ºC. After samples were thoroughly dried, they were weighed and ashed at 500 ºC overnight, and re-weighed. The porosity of the sample was determined from its water content (i.e. difference between wet weight and dry weight), while the loss on ignition (LOI, i.e. the difference between the dry weight and ashed weight) was taken as an approximation of the organic content of the sediment; the two were found to be highly correlated in this area.

### 2.4 Sediment resuspension experiments

During the February campaign, additional sediment samples were taken to assess the character of the DOM associated with sediments, as porewater and/or loosely bound organic

matter. As with the sampling for benthic boundary layer water, only undisturbed cores were sampled, resulting in a total of 10 samples. An 10 cm diameter circular slice of the top 1 cm of surface sediment (total 78.5 $cm^3$ of sediment) was collected and placed in a 250 mL jar, which was then filled with bottom water from the same site. The samples were stirred for 18 hours at 4 ºC and then left to settle for 6 hours, before filtering for DOC, CDOM and FDOM analysis, which were then processed in the same manner as the water column samples. DOM released in these experiments (i.e. sediment-associated DOM) is defined as the difference between the final sample and the original bottom water used in the experiments.

## 3 Results

### 3.1 Hydrographic conditions

The Gulf of Gdansk is characterized by two regions, the inshore shallow waters and offshore deeper waters towards the Gdansk Deep (110 m) both clearly separated at a depth of roughly 50m. Moreover, LOI and grain size clearly distinguished inshore and offshore sediments with higher LOI and larger grain sizes closer to the coast. In the winter, the extension of the plume of Vistula River is clear from the lower surface water salinities and temperature below 5˚C (Figure 1b, box 4a, red dots). In summer the plume-influenced water is less distinct due to lower river flow conditions, but is still distinguishable by lower salinities (<7) and temperatures above 5˚C (Figure 1b, box 4a, blue dots). The shallow in-shore waters have salinities typically between 7 and 8 (Figure 1b, box 4b), while the deeper waters of the Gdansk Deep are characterized with higher salinities (<8) and temperatures between 5-8˚C (Figure 1b, box 4c).

Station depths ranged from 20-105 m, with the deepest three stations being the most saline and with lowest oxygen concentrations (depths below 60m, Figure 2b and c). With the exception of the surface layer, the majority of water column parameters are consistent across the sampling seasons. Surface waters showed a pronounced warming during summertime (Figure 2a) and the presence of a clear river plume in February. The river plume is also reflected in higher winter surface TN concentrations while DOC concentrations did not show very pronounced seasonality (Figure 2d and e, Figure 3).

### 3.2 FDOM character and distribution

Figure 2f-l shows the fluorescent components from PARAFAC modeling and their respective depth profiles. $C_{405}$, $C_{449}$, $C_{498}$, and $C_{412}$ all have broad visible wavelength emission maxima while $C_{354}$, $C_{337}$ and $C_{300}$ have UVA emission maxima similar to that of aromatic amino acids (Table 1). The components aligned well with peaks previously identified in sediment DOM and could be grouped into three categories based on their vertical profiles (Figure 2) and mixing diagrams (Figure 3). The vertical profiles and mixing plots of the visible wavelength fluorescence $C_{405}$, $C_{449}$, and $C_{498}$ were very similar with high fluorescence intensities associated with low salinity plume waters and little variability with depth (>20 m). The fluorescence signal of $C_{412}$ had a very broad emission peak and in contrast to the other visible wavelength components its fluorescence intensity was much less variable in surface waters (Figure 2i). Samples from deeper than 70 m, with salinities >8 had slightly lower fluorescence intensity. This profile pattern matched that for observed for DOC (Figure 2d). Additionally, the $C_{412}$ mixing plots for February 2015 and July 2014 differed with a linear trend in February across the salinity gradient as opposed to a three point mixing curve in July (Figure 3).

In contrast to the visible fluorescence, the UVA components ($C_{354}$, $C_{337}$, $C_{300}$) fluorescence intensity in surface waters was generally lower and decreased with depth. At depth there is very little difference in the profiles between the two cruises for all fluorescent components, except for $C_{337}$ which had elevated deepwater fluorescence during the winter

cruise. None of the UV components were correlated with total nitrogen, despite being in the ranges typically defined as "protein-like" (Table 1).

The mixing plots for DOC and the fluorescent components (Figure 3) reveal a general picture of mixing of three water bodies with differing DOM and salinity character that is retained across both seasons. The high DOM low salinity plume influenced waters at the very surface, intermediate salinity inshore waters where DOM concentrations are much lower, and high salinity deep waters with comparable DOM concentrations to intermediate waters.

Figure 4 shows the mean component intensities from the three different water types. In the surface plume-influenced water fluorescent intensities of the three components associated with organic matter in the river plume ($C_{405}$, $C_{449}$ and $C_{498}$) are more variable than the other components as evident from the greater standard deviations (error bars) (Figure 4a). The in-shore non plume-influenced water and the deep water (Figure 4b and 4c) largely have the same FDOM fingerprint with little differences in fluorescent intensities for all components, and a relative decrease in the contribution of $C_{405}$ and $C_{449}$.

### 3.3 Effects of sediments on DOM characteristics

The sediment characteristics in the Vistula River estuary and Gulf of Gdansk are variable. Closest to shore sediments are largely characterized as sandy mud, muddy sand, or coarse sand. The near shore stations were also generally low in porosity and LOI, but that pattern is not consistent (Figure 1c and 1d). The deeper stations, on the transect out to the Gdansk Deep, are characterized as coarse silt and as can be seen in Figure 1c and 1d have higher porosities and LOIs. Sediment cores from this region were black in colour, with some clay content particularly on the shelf.

DOM fluorescence results, i.e. Fmax values for each component (both with the whole dataset and BBL alone, as well as bottom water differences see following paragraph), were analyzed with respect to gradients in LOI and sediment porosity using regression analysis, however, no significant trends were apparent. Similarly, grouping stations into high and low LOI or onshore – offshore did not result in any significant differences between groups (1-way ANOVA). As a result, the data are presented as averages in proportional changes (percentages) across stations for water masses defined by temperature and salinity.

Sediment resuspension experiments showed the potential for large amounts of DOM release from both sandy and muddy sediments. To be able to identify the influence of sediment in the water column, DOM fluorescence was used as an indicator. Figure 5 presents the FDOM fingerprints of the sediment resuspension in relation to FDOM fingerprints in the benthic boundary layer and bottom water (defined as the lowest depth that was sampled using the CTD-rosette). Firstly, we compared the FDOM signature from the two deepest water samples from each profile. If the salinity difference between samples was <0.5 it was assumed that the FDOM signature should be identical as the samples came from a very similar water mass. If the bottom water sample had higher fluorescence it would be evidence for a flux from sediments. Similarly, a negative value would indicate consumption of FDOM in bottom waters. To facilitate comparison between depths these changes are plotted as percentages in Figure 5a. Our results show a decrease in $C_{337}$ and $C_{300}$ (0-8%), and decrease (~2%) in $C_{412}$, while the rest of the components and DOC reveal essentially no systematic difference.

In a similar fashion, Figure 5b shows the difference between the water collected from the top of the cores and the "bottom" water sampled with the CTD-rosette (i.e. the deepest CTD depth). In these samples, there is evidence for systematically higher fluorescence intensities for all components, except $C_{412}$, in the water in direct contact with sediment. The pattern is strikingly similar for the FDOM fingerprint released in the sediment resuspension experiments (Figure 5c), although the relative changes are an order of magnitude greater. The

largest signals in the resuspension experiments was recorded for the UVA fluorescent signals, $C_{337}$ by ~400% and $C_{300}$ by ~200%. $C_{405}$, $C_{449}$ $C_{354}$ and $C_{498}$ show small increases, while $C_{412}$ is largely unaffected. The change in fluorescence between the sediment overlying water and bottom water (i.e. Figure 5b) were investigated for correlations to physico-chemical parameters (i.e. oxygen, temperature, salinity, LOI, TN), but no significant correlations were found.

Figure 6 shows a mixing plot for the ratio of C449:C405 and indicates qualitative changes in FDOM across the salinity gradient. The low salinity river plume organic matter has a high ratio (>0.7), while the mid-depth waters have lower values similar to that found in the deep high salinity offshore samples. The FDOM released from the sediment resuspension experiments could be grouped into two categories depending on depth and C449:C405. The organic matter released from shallow sediments (<25 m) had similar ratios to plume influenced water samples, while that released from deeper sediment (>35 m) grouped with the FDOM characteristics of pelagic waters (ratio <0.7).

## 4 Discussion

### 4.1 Water column DOM

The most distinct source of DOM to the Gulf of Gdansk is the Vistula River. The Vistula River is highly anthropogenically impacted, and is a significant source of terrestrial nitrogen to the southern Baltic Sea (Łysiak-Pastuszak et al., 2004; Voss et al., 2006). It is clear from the DOC and TN depth profiles that during the late winter months with high river flow, large amounts of DOM are delivered to the Gulf of Gdansk. The chemically distinct influence of the river DOM is also clear from the strong influence and variability of the visible wavelength fluorescence components in the surface plume-influenced waters in both campaigns compared the non-plume influenced waters. High visible wavelength fluorescence such as this is often associated with terrestrial DOM sources and anthropogenically influenced sources (Coble, 2007; Osburn et al., 2012). While the majority of the visible wavelength fluorescent components were sourced to both river water and surface sediments (see discussion later), $C_{412}$ appeared to be more specific to the river plume. There was no evidence of a contribution from sediments (Figure 5) and during the winter sampling the mixing line was comparatively linear across the whole salinity range.

Organic matter fluorescence measurements can also be used to distinguish between river and sediment derived DOM. There is a distinct signal of sediment-derived FDOM in the water overlying the sediment cores. The strongest signals seen in the sediment overlying water, as well as in the sediment resuspension experiments, show an increase in two of the UVA fluorescence components ($C_{337}$ and $C_{300}$), while the visible components experience small changes, or no changes.

It should be noted that because of the sampling technique used here, i.e. withdrawing water from the top of sediment cores, it is not possible to determine whether this DOM diffused naturally from the sediments, or was influenced by the intrusion of the corer into the sediments during sampling. The multi-corer is designed for a “soft-landing” to minimize disturbance of the benthic boundary layer and porewaters, while the HAPS corer is designed to core into much coarser sediment and uses a more aggressive coring approach. Samples from both types of cores showed this sediment fingerprint in the overlying water, and a distinction between a true benthic boundary layer and artificially expelled porewater DOM cannot be made. The similarity between the organic matter fluorescence fingerprint between the sediment resuspension experiments and the core-overlying water strongly suggests the sediment source of this DOM (Figure 5b and 5c).

### 4.2 Sources of sediment DOM

Co-precipitation of DOM and iron oxides is a well-recognized phenomenon (Lalonde et al., 2012; Riedel et al., 2013; Skoog et al., 1996) and is particularly of interest in the Baltic Sea where iron concentrations are high and iron has been shown to have potential to be transported into open waters by association with DOM (Kritzberg et al., 2014). It has been suggested that the association of iron oxides and DOM preferentially precipitates biologically available fractions, such as protein-like DOM with high nitrogen content, through association with iron oxides (Lalonde et al., 2012). Under the anoxic conditions present in porewaters, iron oxides are reduced to free iron and the association with organic matter is thus broken, and the organic matter returned to the dissolved phase. UVA DOM fluorescence, like that of $C_{337}$ and $C_{300}$, has been associated with aromatic amino acid structures and bioavailable DOM (Yamashita & Tanoue, 2003), and prevalence of this signal in the sediment resuspension experiments and the benthic boundary layer samples lends (Figure 5b and 5c) support to the theory that biologically labile DOM is preferentially removed to the sediments in environments like the Baltic Sea.

On the other hand, this signal could also suggest early diagenetic processes in the sediment porewaters, as particulate organic matter reaching the sediment in these shallow areas is relatively fresh and has not undergone significant degradation in the water column. The microbial community located in the surface layers of sediment use particulate organic matter as an electron receptor and by their metabolism release large amounts of DOM to the sediment porewaters (Arndt et al., 2013), lending a potential biological source to these fluorescent components. UVA fluorescent signals similar to those identified here have also been shown to be produced in conjunction with phytoplankton blooms in the water column (Stedmon & Markager, 2005).

The organic matter supplied in the plume had a distinct fluorescence signature which was dominated by two visible wavelength components, $C_{449}$ and $C_{405.}$ The ratio of these two decreased with mixing reflecting the change in composition occurring. The ratio could also separate the sediment resuspension fluorescence into two distinct groups by depth (Figure 6). This ratio is similar to the ratio between peak C and peak M described first by (Coble, 1996) and later by others (Burdige et al., 2004), and can show a shift between terrestrially sourced material and marine material. Although these fluorescent signals are not source specific, their relative ratios can vary depending diagenetic state or source of organic matter (Burdige et al., 2004; Stedmon & Nelson, 2014). The organic matter released from shallow inshore sediments grouped with the surface plume-influenced waters, suggesting a more terrestrial source of organic matter to the sediments coming from the Vistula River, while the deep stations grouped with the deeper waters, possibly indicating a pelagic source of sediment organic matter. There has been some evidence of the enhancement of visible fluorescent peaks at depth in marine sediment porewaters, and in particular the ratio $C_{449}$:$C_{405}$ being associated with diagenetic processes (Burdige et al 2004, M:C ratio therein), though in the current study these signals are better indicators of source material. This could be due the limited sediment depth sampled (i.e only the top 1 cm of sediment was sampled), or it could indicate potential water column diagenetic processes prior to settling in the sediments.

### 4.3 Fluxes of sediment derived DOM to the water column

Sediment influenced waters clearly have a unique signature as illustrated by the similarity of the fluorescent fingerprints of the sediment re-suspension experiment and that of the overlying water of cores (Figure 5b and 5c). The similarity of these two DOM fingerprints, and the fact that both sampling and sediment resuspension experiments were performed under oxic conditions indicates that the difference between redox conditions in the sediments and the bottom water are not influencing the results. Furthermore, limiting the sampling to the top 1 cm of sediment rules out deeper diagenetic sources of the DOM

associated with the processing of organic matter in sediment at depth. Thus, the experiment results can be considered to represent the fingerprint of sediment associated DOM as it would be in the largely oxic water column, rather than the in-situ porewater.

The contribution of UVA fluorescent DOM fractions in sediment-influenced samples suggests that this DOM should be highly bioavailable when released to the water column by either diffusive fluxes or by resuspension events (i.e. winter storms). The distinct sediment-derived DOM fingerprint was not evident in the bottom water samples, instead a slight decrease in the UVA components was observed (Figure 5a). The lack of this sediment fingerprint in the bottom water CTD sample suggests that the sediment fingerprint is either transient in nature or rapidly diluted against the high DOM background present in the Gulf of Gdansk. It is likely that $C_{337}$ and $C_{300}$ represent biologically available substrate which when remobilized from the sediment are rapidly degraded.

In the current study the station most likely to have experienced the kind of stability necessary for sediment-derived DOM to be detectable in bottom water from CTD-rosette sampling would be the Gdansk Deep station, where circulation is restricted and semi-permanent anoxic conditions exist thereby lowering rates of biological degradation of DOM. A large influx of North Sea water to the Baltic Sea in winter 2014/2015 disturbed the bottom waters in the Gdansk Deep at the time of sampling (Mohrholz et al., 2015) leaving only the July 2014 set of samples where the bottom water was undisturbed, and conditions were anoxic so that release of biologically available sediment-derived DOM would be expected. However, even at this station, the DOM fingerprint found in the sediment overlying water is not seen in the bottom water sampled with the CTD, and in comparison with the next deepest water sample, the deeper waters show virtually no difference in these UVA fingerprints of $C_{337}$ (-1.73 % change) and $C_{300}$ (0.57 % change). The total DOM contribution diffused from sediments sampled in this study (i.e. sampled in the benthic boundary layer) appears to be small compared to the variability from mixing between river plume, coastal and deeper waters. However the spectral characteristic of the organic matter released and the fact that it is rapidly removed suggests that the material is labile and likely influences oxygen consumption in bottom waters.

## 5 Conclusions

The Vistula River is by far the largest source of DOM to the Gulf of Gdansk, at peak flow, the plume of the river had DOC concentrations twice that of the surrounding water. Sediment-sourced DOM has a unique signal compared to the highly terrestrial DOM that dominates the water column of the region, and based on the fluorescence fingerprint of this DOM, is likely to be readily biologically available. However, the signal is not readily measureable in the water column, likely due to a combination of high background levels of DOM from the Vistula River, relatively rapid mixing, and microbial degradation. Although sediments are a weak source of DOM with limited influence on local carbon budgets, the diffusion of bioavailable DOM from sediments will contribute to the oxygen demand of bottom waters and warrants further experimental investigation.

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Environmental Database http://www.balticnest.org/bed. Sediment data can be found in the supplemental information of Thoms et al (2018).

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**Table 1.** Position of the excitation and emission maxima of the seven fluorescent components identified by the PARAFAC analysis. Also listed are matches found with components in previous sediment organic matter studies available in openfluor.org database (Murphy et al., 2014) and peaks labeled A, M, C, T, B and SR in Burdige et al (2004) and Coble (1996).

| Component | Excitation maxium (nm) | Emission maxium (nm) | Identification from other studies |
|---|---|---|---|
| $C_{405}$ | <250,310 | 405 | M peak (Ex302-357/Em410-436)<br>C3 in Osburn et al 2012 |
| $C_{449}$ | 259, 365 | 449 | C peak (Ex360/450-467)<br>C4 in Osburn et al 2012 |
| $C_{498}$ | 270,400 | 498 | |
| $C_{412}$ | <250 | 412 | A/A' peak (Ex220-261/Em419-466)<br>C3 in Osburn et al 2012 |
| $C_{354}$ | <250, 295 | 354 | Burdige SR (EX220-250/Em304-354)/ T peak, tryptophan-like (Ex275/Em340) |
| $C_{337}$ | 280 | 337 | T peak, tryptophan-like (Ex275/Em340)<br>C5 in Osburn et al 2012 |
| $C_{300}$ | 280 | 300 (minor 390) | B peak, tyrosine-like (Ex275/Em305) |

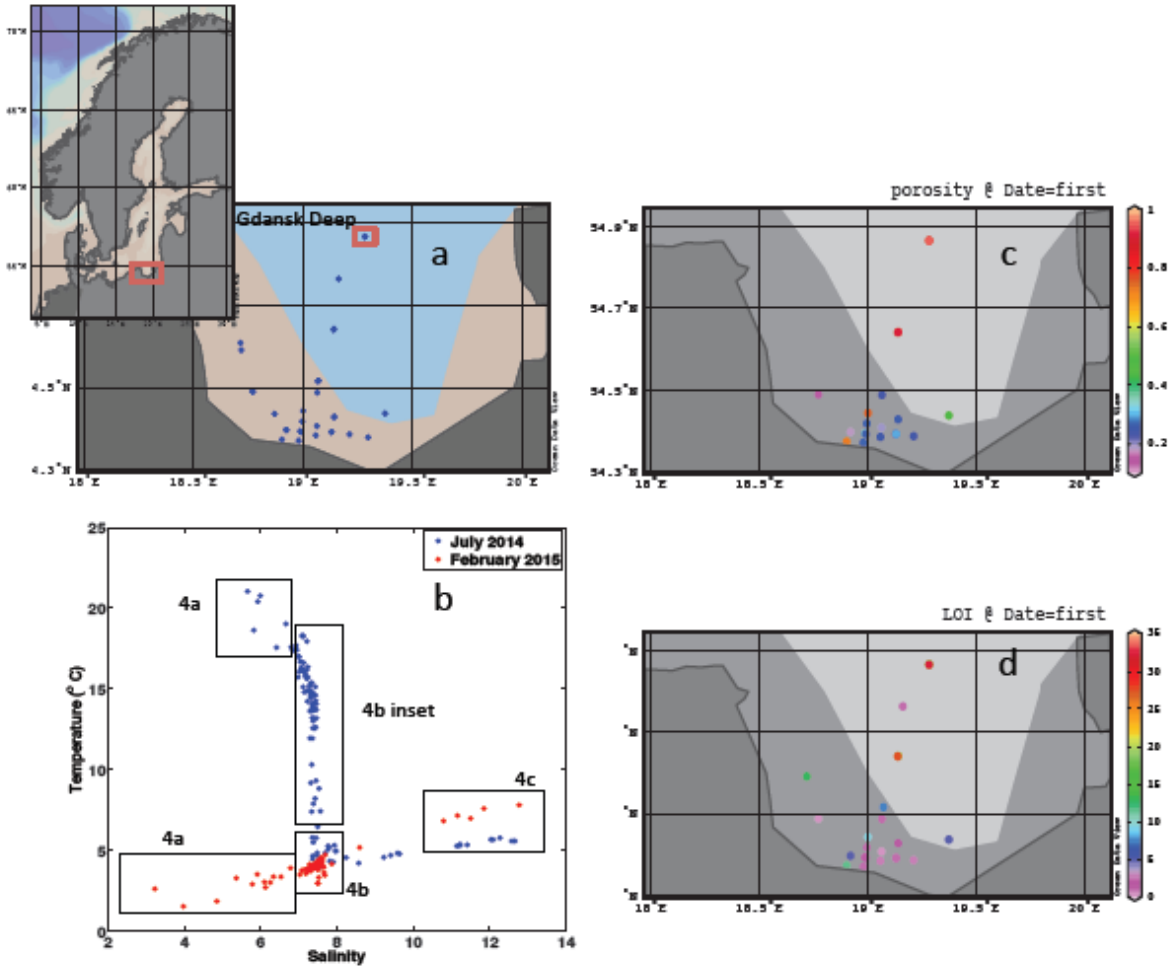


**Figure 1**. a) map of cruise stations, b) Temperature-Salinity plot of all water column data from both cruises, inset boxes refer to the water mass groupings in Figure 4, used to separate surface, mid-depth, and deep samples based on temperature and salinity, c) porosity data for top 0-2cm of sediment for both cruises, d) loss on ignition (% organic C) for all stations.

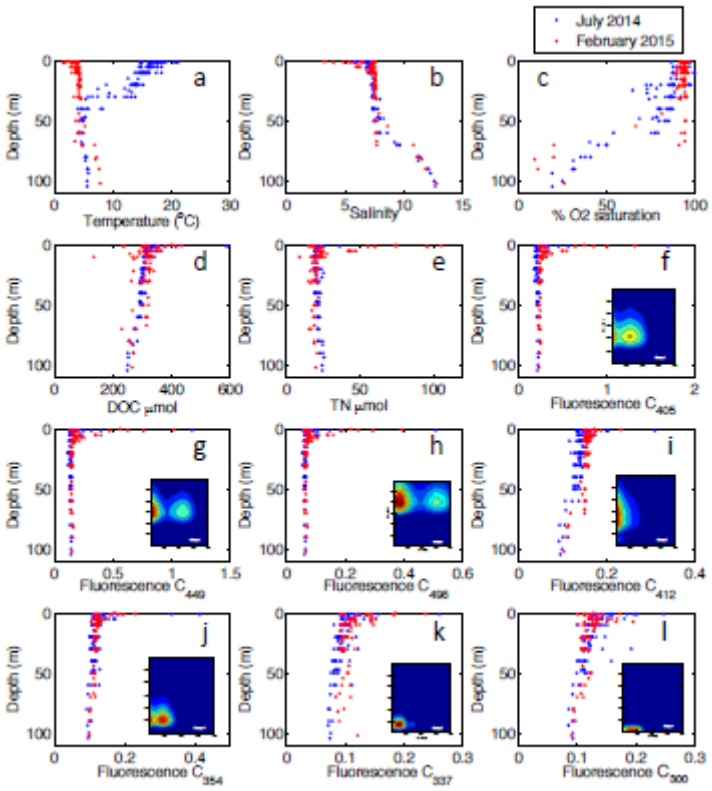


**Figure 2.** Profiles of water column properties for both cruises. In all plots, blue represents July 2014, red represents February 2015. a) Temperature, b) Salinity, b) Oxygen, d) Dissolved organic carbon, e) total dissolved nitrogen, f – l) Fluorescent components from PARAFAC model, with insets of the fluorescent fingerprints. On the insets, excitation (260 nm - 450 nm) is on the x-axis, emission (300 nm – 600 nm) is on the y-axis.

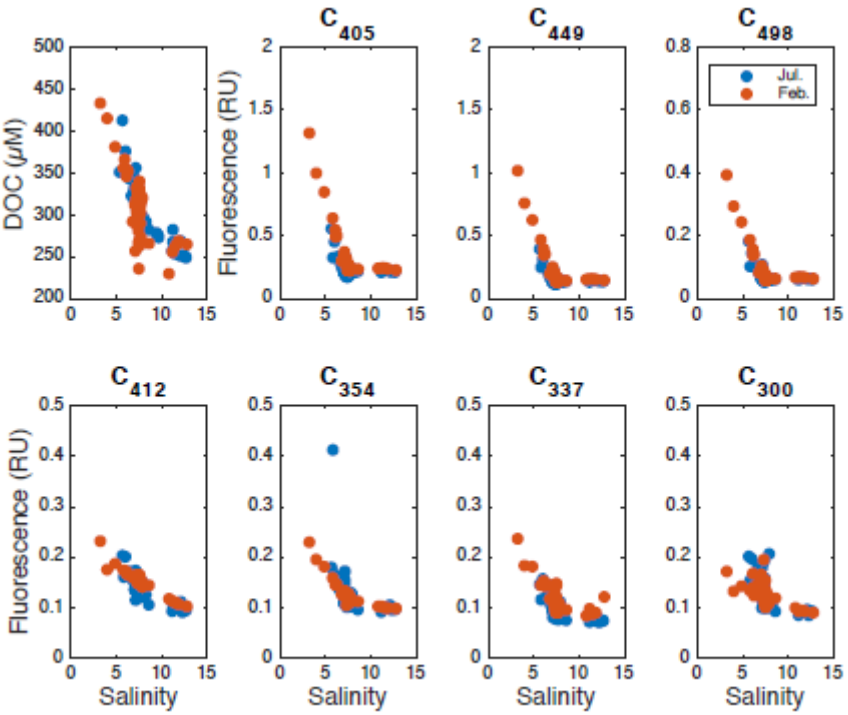


**Figure 3.** DOM-salinity mixing plots: Dissolved organic carbon (DOC, top left panel) and the fluorescence intensity of each component identified by the PARAFAC analysis.

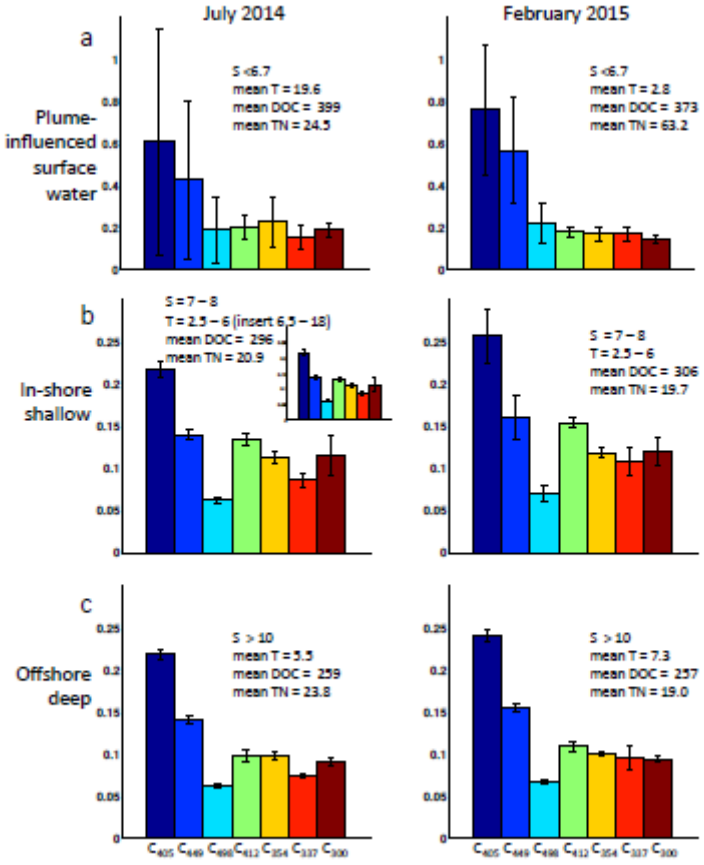


**Figure 4.** a) Fluorescent components from surface water for July (left) and February (right). b) Mid-depth water column fluorescence components for July (left) and February (right), inset, warmer water in July. c) Deep water fluorescent components for July (left) and February (right). Refer to boxes in 1a) for the identification of water masses. The fluorescent components are ordered in the same order as in Figure 2 and Figure 3, i.e.: $C_{405}$, $C_{449}$, $C_{412}$, $C_{354}$, $C_{498}$, $C_{337}$, $C_{300}$.

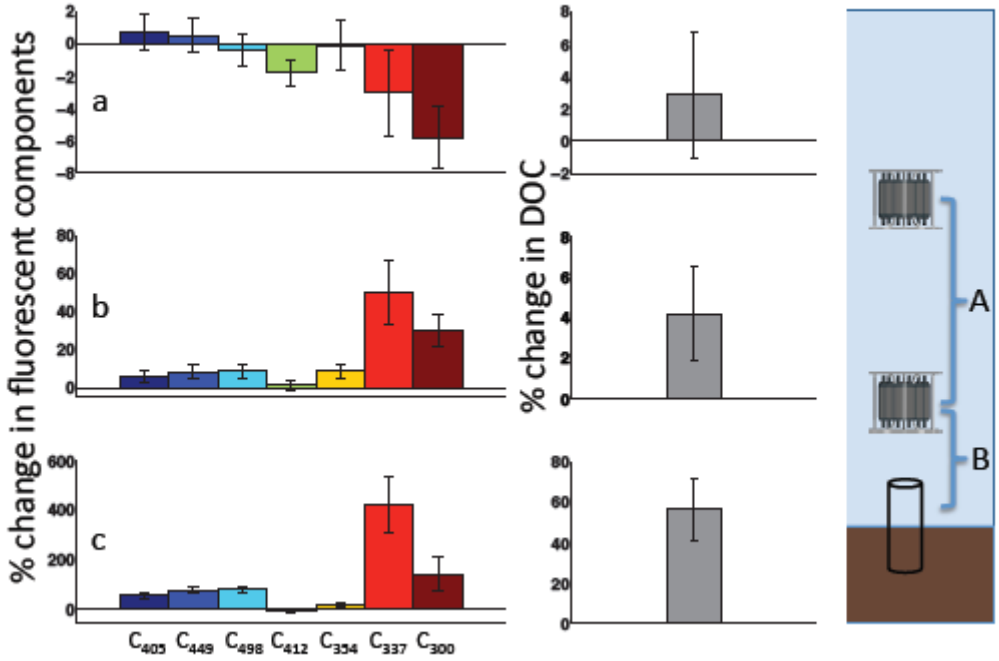


**Figure 5.** a) % change in fluorescence and DOC between the bottom bottle from the rosette and the water sample immediately above it. b) % change in fluorescence and DOC in water overlying sediment core (5-10cm from sediment surface) from bottom water from the Niskin bottle. b) sediment-derived fluorescence and DOC from the sediment resuspension experiment.

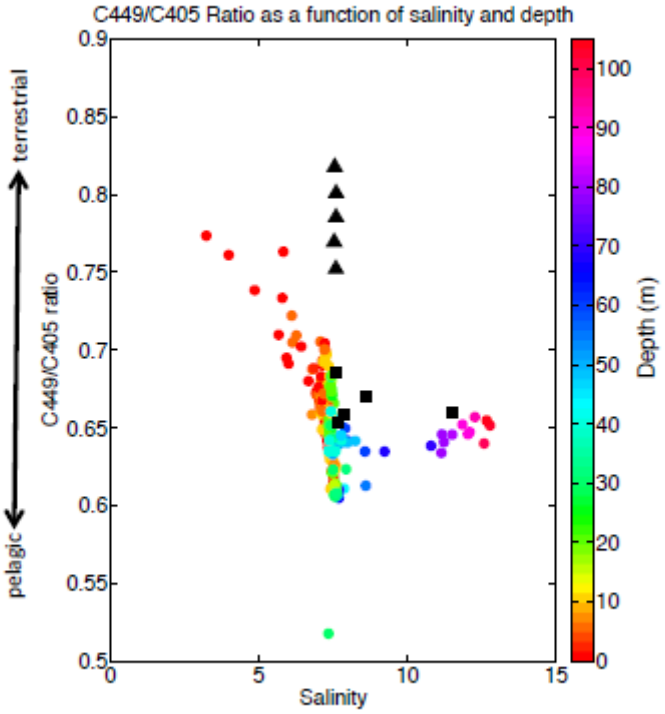


**Figure 6.** Mixing plot of the ratio between C449:C405, illustrating the riverine – pelagic distribution of DOM. Coloured circles are water column samples, black triangles are from sediment resuspension experiments at shallow stations (<25 m), black squares are from sediment resuspension experiments at deep stations (>35 m).