

## **These are our responses to comments from Reviewer #2**

We are grateful to the anonymous reviewer for their careful review and valuable comments on this manuscript. The constructive feedback provided has been instrumental in strengthening the manuscript, and we appreciate the opportunity to address the reviewer's suggestions during the revision process. We have carefully considered all comments and revised the manuscript accordingly. Reviewer comments and our detailed responses are provided below.

**L 117-119:** "The basin spans the full permafrost gradient, from continuous to discontinuous and sporadic permafrost zones with approximately 13 % underlain by continuous permafrost and 42 % by continuous and discontinuous permafrost combined, of which approximately 80 % is underlain by permafrost". This is unclear, please re-word to clearly depict what percentage of the watershed is underlain by continuous permafrost, discontinuous permafrost, and no permafrost. Currently, it reads as 42% of the watershed contains some form of permafrost (presumably, 13% continuous, 29% discontinuous). The 80% conflicts with the other values provided, but presumably represents the total coverage of all permafrost types.

### **Response:**

To make the area of permafrost zones clearer but also provide some numbers to complement Figure 1, the text has been updated to: "Approximately 42% of the basin is covered by continuous and discontinuous permafrost (Holmes et al., 2012)."

### **L 120-121:**

"This broad permafrost transition exerts strong controls on hydrology, sediment delivery, and organic carbon composition entering the delta-shelf system." What type of controls? Even if you reference, rather than explicitly state, it is beneficial to indicate how each permafrost type would control hydrology, sediment delivery, and OC composition briefly to emphasize how this transition will manifest in observable dynamics from satellites.

### **Response:**

The text has been updated to: "This broad permafrost transition exerts strong controls on hydrology, sediment delivery, and organic carbon composition entering the delta-shelf system. Zones of continuous permafrost are characterized by surface-dominated, flashy runoff with strong seasonal pulses and episodic sediment delivery. The shallow active layer in continuous permafrost soils can also be characterized by more labile inputs of carbon from recent plant material and the surface area. As permafrost becomes more patchy in discontinuous and sporadic zones or the active layer thickens, there is more surface-subsurface connectivity, which can lead to older, more processed carbon inputs (Vonk et al., 2019)."

### **Line 228:**

This should be "overestimate" rather than "underestimate" – if salts remained on the SPM filters, they would have a greater weight. This uncertainty, while not quantified, sometimes appears in the replicate agreement, so you may point to that rather than indicating you don't believe it impacted the results. This may also be true for POC (line 209).

### **Response:**

Thank you for catching this error. The text has been updated to read: "For PeCaBeau, the sample filters were not washed for salts after filtration, which may overestimate the resulting measurement, but we do not believe this has a significant impact."

### **Lines 231:**

I recommend splitting this sentence into two sentences, and ensuring it is in the past tense.

### **Response:**

Thank you for this suggestion. The text has been updated to: "Inherent optical properties (IOPs) such as light absorption, beam attenuation, and scattering coefficients, define apparent optical properties (AOPs), including  $R_{rs}$ , which is often used synonymously with ocean color. To relate water sample properties to radiometric measurements, absorption at 443 nm was analyzed alongside DOC and POC concentrations from co-located samples collected during all campaigns."

**Lines 233:**

"The total light absorption ( $a_t(\lambda)$ ) and attenuation ( $ct(\lambda)$ ) coefficients were measured by filling the optical path of the AC-s (10 cm) with the unfiltered water sample." The AC-S was used as a benchtop unit, correct? If so, can you describe how samples were debubbled, or otherwise provide a brief sentence on if/how measurement noise was addressed. These types of measurements tend to be quite noisy. I am assuming these were measured in the field? If not, how was the whole water maintained?

**Response:**

Thank you for bringing this to our attention so we can provide better clarification for the reader. In the first manuscript version, we were using both indirect AC-s measurements and direct measurements of aCDOM (with spectrophotometer (PSICAM) in lab) and aP (with QFT-ICAM in lab) in our analysis. To keep things consistent between datasets, we have removed the AC-s measurements from this analysis and are only using direct measurements as described in the methods section. The methods section (in addition to Figure 5 and the Results) has been updated to reflect this. The text in question here has been updated to read: "Inherent optical properties (IOPs) such as light absorption, beam attenuation, and scattering coefficients, define apparent optical properties (AOPs), including  $R_{rs}$ , which is often used synonymously with ocean color. To relate water sample properties to radiometric measurements, absorption at 443 nm was analyzed alongside DOC and POC concentrations from co-located samples collected during all campaigns. This is a commonly used wavelength in ocean-color remote sensing due to its sensitivity to multiple optically active constituents and its widespread availability across satellite missions."

**Line 236:**

ap was determined by subtracting aCDOM from  $a_t$ ?

**Response:**

Yes, for the first version of the manuscript, this is correct, however, please see answer above (AC-S measurements were replaced by PSICAM and QFT-ICAM measurements where aCDOM and aP is directly measured and this calculation is not needed anymore.

**Line 240:**

No "-" between "ocean" and "color"

**Response:**

The text has been updated to: "This is a commonly used wavelength in ocean color remote sensing due to its sensitivity to multiple optically active constituents and its widespread availability across satellite missions."

**Table 2:**

Table 2 indicates that C-OPS radiometry was collected above-water. Was this through the sky block approach? If so, it would be beneficial to indicate this in the table.

**Response:**

C-OPS radiometry was used for in-water measurements as described in Juhls et al., 2022. Please find details about the measurements and processing of the C-OPS measurements in the related paper.

**Line 272:**

OCRS needs to be defined, and the definition later in the manuscript can be removed from that instance.

**Response:**

The acronym has been added, but Ocean Color Remote Sensing (OCRS) is defined in the introduction section (line 87) -- which now reads: "Across fluvial-marine gradients, changes in organic matter and sediment composition are closely linked to shifts in optical properties of the water. The absorption of colored dissolved organic matter  $a_{CDOM}(\lambda)$  and particulates  $a_P(\lambda)$  provide measurable proxies for DOC and POC concentrations, and form the basis for Ocean Color Remote Sensing (OCRS) applications, or how constituents in water absorb and scatter incident light at different wavelengths, in Arctic waters (Gonçalves-Araujo et al., 2015; Juhls et al., 2019; Matsuoka et al., 2012; Matsuoka et al., 2017; Pugach et al., 2018; Juhls et al., 2022). "

**Line 277:**

The classification scheme aims to a broad applicability" - needs to be reworded

**Response:**

Thank you for catching this. The text has been updated to be more straightforward and clear: "The classification scheme is designed to apply to inland, coastal, and ocean waters, as well as for various hyper- and multispectral band settings of in situ measurement methods and satellite missions."

**Line 338:**

I would avoid describing  $a_{CDOM}(443)$  in marine waters as "near-zero". CDOM absorption is quite low in the open ocean relative to river values, but this does not mean it is not an important component of ocean biogeochemistry. Framing this end member value (e.g., 0.1) provides meaningful biogeochemical context while not offering a phrasing that implies it is absent from the system or otherwise unimportant. This comment is true for all of the Results – indicate the average or global minimum for your dataset. All of these values will be close to zero relative to river values, but the value itself is still important for interpretation of the data.

**Response:**

The text has been updated to better describe  $a_{CDOM}$  in marine waters: "Fig. 4b depicts  $a_{CDOM}(443)$  showing a similar inverse relationship with salinity ( $R^2=0.74$ ), with values decreasing from  $>4 \text{ m}^{-1}$  in freshwater to much lower values ( $<0.5 \text{ m}^{-1}$ ) in marine waters (approx.  $>20 \text{ psu}$ ). POC and SPM concentrations also generally declined with increasing salinity, although with greater scatter relative to dissolved components. POC concentrations were highest at low salinities ( $>5 \text{ mg L}^{-1}$ ) and decreased to much lower concentrations in marine waters (Fig. 4c)."

**Figure 4:**

(a) Why are negative  $a_{CDOM}(443)$  values present in the dataset? Where are these data sourced from? This is surprising for freshwaters and indicates issues with sampling or sample handling and processing. I would suggest these data be excluded from analysis. This is particularly troublesome when the DOC values are  $>2 \text{ mg/L}$  for these same samples.

(b) Why are relationships and fits not presented for c and d? Even if the relationship is poor, this is helpful for interpreting the data and understanding system dynamics across these variables and relative to each other.

**Response:**

The negative  $a_{CDOM}(443)$  values plotted in Figure 4 resulted from a baseline correction that we applied on published ArcticGRO river water samples. We have removed these negative values from the dataset so as to not produce negative  $a_{CDOM}$  data used in the analysis. An updated Fig. 4 is provided with relationships given for all four parameters in addition to annual mean at 0 psu and a freshet mean (for months May-June as defined in Holmes et al., 2012) at 0 psu. The campaign and sampling periods have

also been noted by different symbols to address related reviewer comments (see below). These additions were made to address following comments.

Methods for the baseline correction were added to line 197:

“A baseline correction was applied by calculating the mean absorption between 690 and 710 nm and subtracting this value from the  $a_{\text{CDOM}(443)}$  measurements.”

Paragraph 334-344 has been updated to:

Concentrations of dissolved and particulate constituents decreased markedly with increasing salinity along the fluvial-marine transition (Fig. 4). DOC exhibited a strong negative linear relationship with salinity (0.2-35 psu) ( $r^2=0.79$ ), with the highest concentrations ( $>10 \text{ mg L}^{-1}$ ) occurring at very low salinities and declining to  $<1 \text{ mg L}^{-1}$  at salinities above 30 psu (Fig. 4a). Fig. 4b depicts  $a_{\text{CDOM}(443)}$  showing a similar inverse relationship with salinity ( $r^2=0.74$ ), with values decreasing from  $>4 \text{ m}^{-1}$  in freshwater to  $\leq 1 \text{ m}^{-1}$  in marine waters. POC and SPM concentrations also generally declined with increasing salinity, although with greater scatter relative to dissolved components ( $r^2=0.5$  and  $r^2=0.45$ , respectively). POC concentrations were highest at low salinities ( $>3 \text{ mg L}^{-1}$ ) and decreased to much lower concentrations in marine waters (Fig. 4). Similarly, SPM concentrations were highest in the freshwater endmember (up to  $400 \text{ mg L}^{-1}$ ) and declined substantially along the salinity gradient, with most marine samples exhibiting concentrations below  $20 \text{ mg L}^{-1}$  (Fig. 4d).

Red-outlined symbols represent water samples collected near the spring freshet (May through June) across different campaigns. The spring freshet mean for DOC ( $6.61 \text{ mg L}^{-1}$ ) is noticeably higher than the annual freshwater mean ( $5.12 \text{ mg L}^{-1}$ ) (Fig. 4a) and the slope of the DOC spring freshet theoretical mixing line ( $-0.18$ ) is higher and steeper than the annual theoretical mixing line ( $-0.14$ ). The marine endmember for these mixing lines is the interception of linear fit ( $0.326 \text{ mg L}^{-1}$ ). Similarly, for  $a_{\text{CDOM}(443)}$ , the spring freshet measurements draw the freshwater mean from ( $1.45 \text{ m}^{-1}$  annual mean) to ( $2.01 \text{ m}^{-1}$  spring freshet mean) (Fig. 4b). The slope of the spring freshet theoretical mixing line ( $-0.06$ ) is slightly steeper than for the annual theoretical mixing line ( $0.04$ ). The marine water endmember for  $a_{\text{CDOM}(443)}$  is  $0.058 \text{ m}^{-1}$ . Particulates exhibit a similar pattern between year-round and spring freshet freshwater endmembers. For SPM, the average freshwater freshet concentration is almost two times higher than the annual freshwater average ( $117.03 \text{ mg L}^{-1}$  and  $62.97 \text{ mg L}^{-1}$ , respectively) (Fig 4d), while the average freshwater freshet concentration for POC ( $1.62 \text{ mg L}^{-1}$ ) is also noticeably higher than the mean annual freshwater endmember ( $1.02 \text{ mg L}^{-1}$ ) (Fig 4c). The slope of the SPM spring freshet theoretical mixing line ( $-3.53$ ) is higher and much steeper than the slope of the annual theoretical mixing line ( $-1.98$ ) with a marine water endmember of  $-6.45 \text{ mg L}^{-1}$ . Slightly less pronounced but following a similar pattern, the slope of the POC spring freshet theoretical mixing line ( $-0.05$ ) is also steeper than that of the annual theoretical mixing line ( $-0.04$ ). The POC marine water endmember is  $-0.21 \text{ mg L}^{-1}$ . Overall, these relationships demonstrate pronounced decreases in both dissolved and particulate organic matter pools along the fluvial-marine mixing continuum with noticeable influences from the seasonal spring freshet from the Mackenzie River.

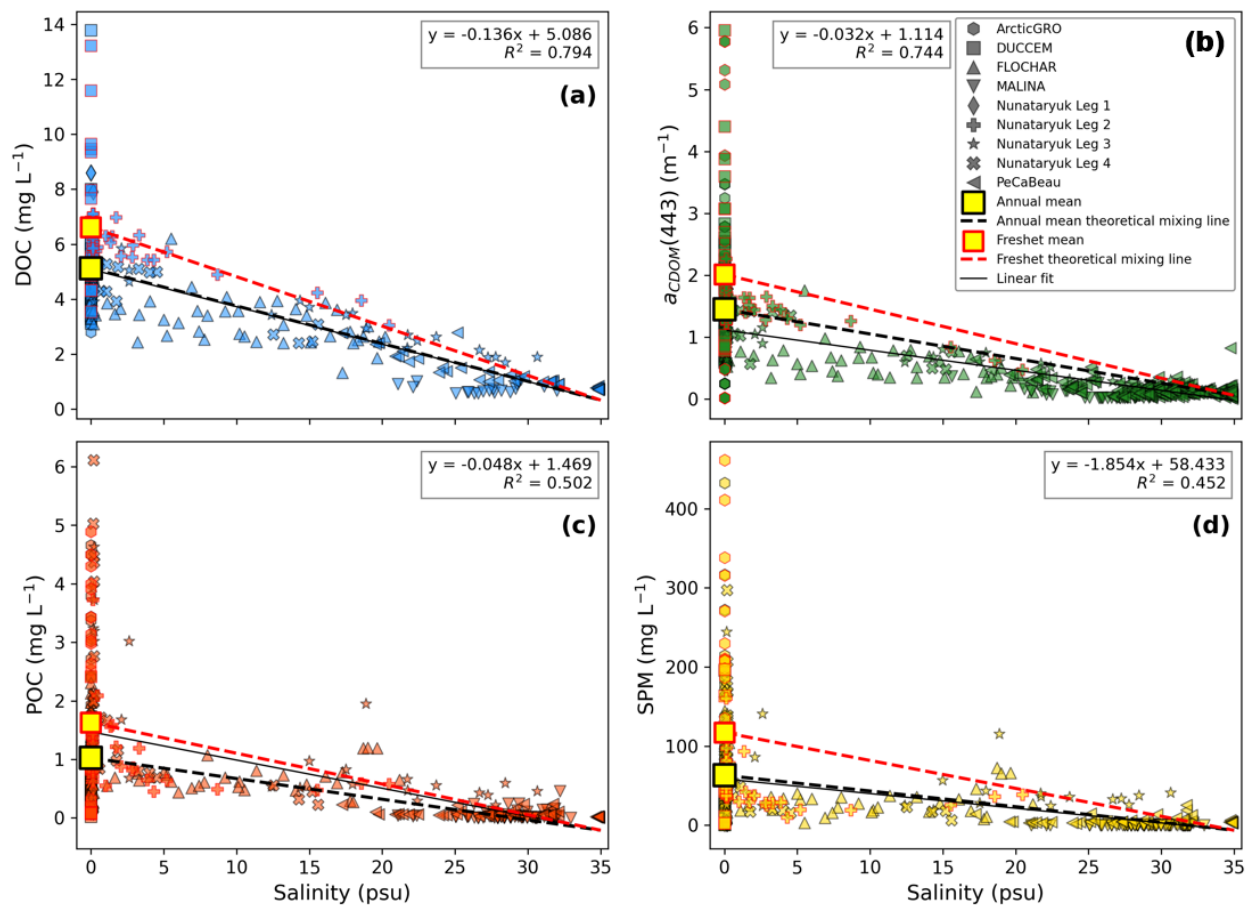


Figure 4. Linear regressions between salinity and (a) DOC, (b)  $a_{\text{CDOM}}(443)$ , (c) POC and (d) SPM across the fluvial-marine salinity gradient from all campaign data from 2009-2024. The solid black lines represent the linear fit. The linear regression analysis filtered observations for salinity  $>0.2$  psu for all four parameters to exclude the large seasonal variation of the river water. The yellow box outlined in black represents the annual mean for observations  $\leq 0.2$  psu and the black dashed line represents the annual mean theoretical mixing line. The yellow box outlined in red represents the freshet mean for observations  $\leq 0.2$  psu while the red dashed line represents the spring freshet theoretical mixing line (for months May-June, as described in Holmes et al., 2012). Observations outlined in red represent samples from May and June. Equations and coefficients of determination ( $r^2$ ) are shown for each plot.

**Figure 5:**

Are the  $a_{\text{CDOM}}(443)$  values in this figure averages? They diverge from what is shown in Fig. 4, presumably due to a wide range, and inclusion of incorrect (negative), absorption values for freshwater samples.

**Response:**

Yes, the data in Figure 5 are averaged across salinity bins. This data originally consisted of dissolved and particulate absorption values measured both directly (spectrophotometer (PSICAM) and QFT-ICAM) and indirectly (using AC-s). However, upon further review and to keep consistency across methods with our analysis, we have removed AC-s measurements and instead use only direct measurements. The figure and associated text have been updated to reflect these changes.

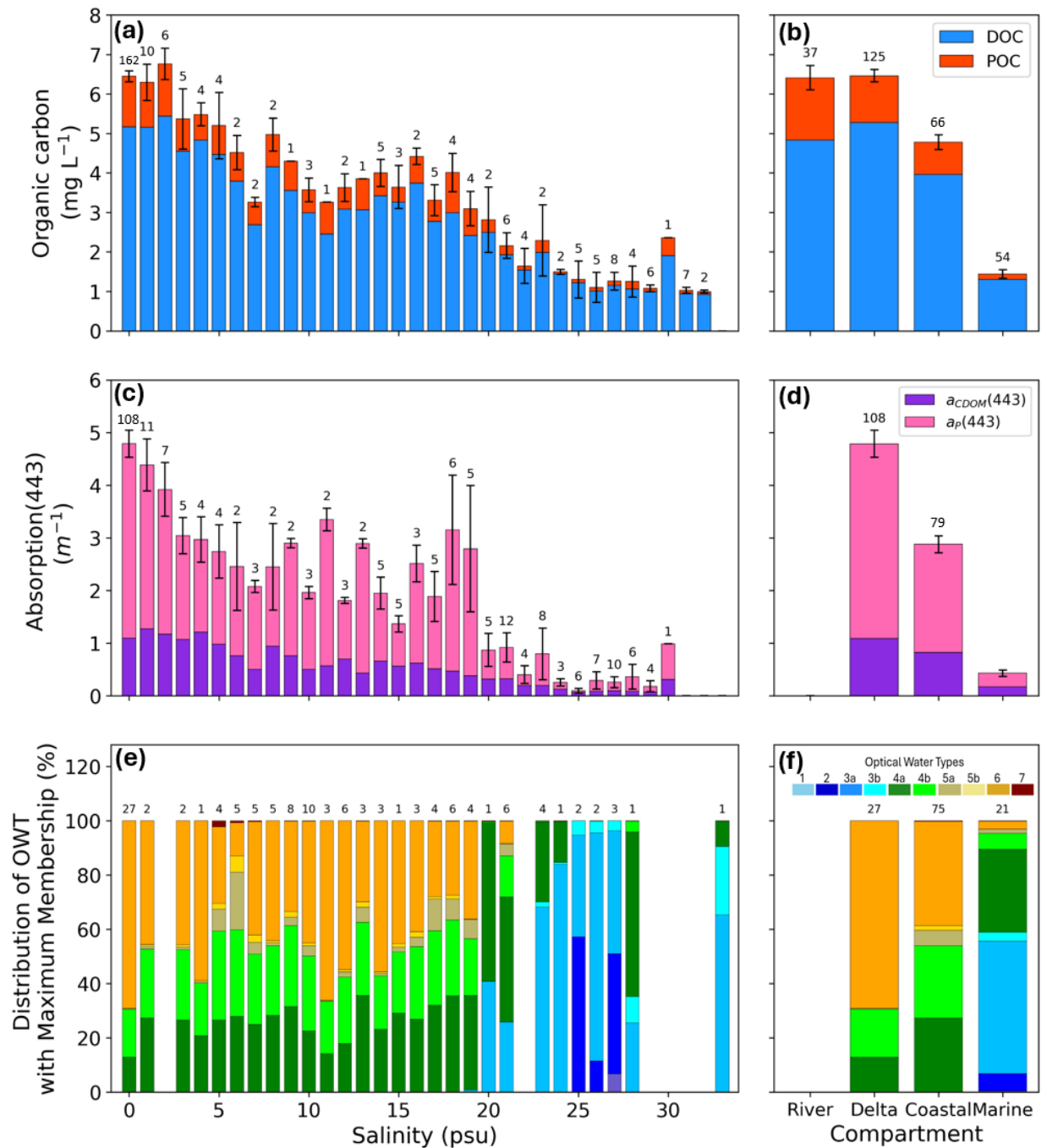


Fig. 5. (a) Changes in DOC (blue) and POC (red) concentration along the salinity gradient and (b) from river to delta to coastal to marine compartments for samples collected during the open-water season from the MALINA, Nunataryuk, PeCaBeau, FLOCHAR, ArcticGRO, and Mackenzie Monitoring campaigns during 2009-2024. The middle graphs (c, d) show the relative contributions to the light absorption coefficient of dissolved (purple) and particulate (pink) components from MALINA, Nunataryuk, PeCaBeau, and FLOCHAR campaign samples. The lower graphs (e, f) show the contributions of OWT memberships along the salinity gradient and along the freshwater-marine compartments from a subset of data where both radiometric

and optical data was available. Error bars represent standard error and the numbers above bars reflect the number of samples per salinity bin.

**L 362-373:**

Linked with the comment on Fig. 5, there is a wide discrepancy between organic carbon concentrations and optics, but this is presumably due to high inorganic particle loads. There is no indication of this in the Results, and it would be helpful to understand what is driving this significant difference between ap and aCDOM. Also – did the AC-S ever saturate?

**Response:**

We agree that the discrepancy between particulate optical properties and dissolved optical properties is likely related to the high load of mineral-rich suspended sediments in the Mackenzie Delta–Beaufort Sea system. Inorganic particles strongly influence particulate absorption and scattering signals, while being only weakly coupled to organic carbon concentrations. This is addressed in the Discussion 4.1 section (line 517) “Despite DOC representing the dominant fraction of OC, particulate material exerted a strong influence on optical absorption (Fig. 5c-d), indicating that particle-driven processes shape the optical properties in near-delta environments. This reflects differences in specific absorption efficiency, as suspended mineral and detrital particles exhibit higher absorption and scattering cross-sections than dissolved organic matter (Doxaran et al., 2012). Processes such as primary production and in situ POC generation via phytoplankton growth may also occur in deltaic waters, although are likely limited in these highly turbid waters due to reduced light penetration (Clark et al., 2022).”

(For clarification, the ACs did saturate at 2-3 stations while sampling FLO CHAR delta stations. We simply diluted the sample and corrected the measurements for the dilution. But the AC-s measurements have been removed from the analysis and replaced with direct measurements of aCDOM and aP.)

**L 375-376:**

These are repeat lines.

**Response:**

Thank you for catching this error. The sentence has been corrected to: "The distribution of optical water types (OWTs) classified by maximum membership shows a systematic shift along the salinity gradient and across fluvial-marine compartments (Fig. 5e–f)."

**Line 376:**

Is there another way to indicate “systematic shift”? This has appeared quite a few times, and appears to be a rhetorical device that hides a lack of interpretation of the data. The Results are descriptive, but do not elucidate the meaning of the data.

**Response:**

We agree with the reviewer and have replaced “systematic shift” with a more process-oriented description. The text has been updated to “The distribution of optical water types (OWTs) classified by maximum membership indicates a progressive transition from river-influenced, highly absorbing waters to optically clearer marine waters along the salinity gradient, accompanied by corresponding changes in organic carbon concentrations and the relative contributions of dissolved and particulate absorption (Fig. 5e–f).”

**L 398-406:**

“A strong, non-linear relationship was found between observed DOC concentrations and aCDOM(443) across the full salinity gradient, with an overall coefficient of determination of  $r^2=0.81$  (Fig. 6a). While compartment-specific relationships were generally linear, combining samples across compartments

resulted in a non-linear relationship. The overall regression reflects the combined variability of river and delta samples at higher aCDOM(443) values, while marine samples form a tightly clustered low-concentration group. The strength and type of this relationship vary markedly among compartments with the coastal compartment exhibiting the strongest linear relationship ( $r^2=0.86$ ), whereas the delta ( $r^2=0.54$ ) and marine ( $r^2=0.49$ ) compartments showed weaker relationships and narrower range of DOC variability. The compartment-specific regressions differed not only in strength but also in slope, with steeper relationships observed in coastal and marine compartments compared to river and delta samples, contributing to the non-linear cross-compartment scaling.”

What does the non-linear relationship indicate about CDOM absorption along the river to ocean continuum? Is the non-linear relationship expected? By considering and answering these questions, the authors should be able to address whether considering linear relationships within compartments is reasonable for analyzing this data, and what the within-water type relationships and “global” relationship represent about CDOM biogeochemistry across the salinity gradient.

**Response:**

The strong, non-linear relationship observed between DOC and aCDOM(443) across the fluvial-marine transition suggests that DOC and aCDOM are biogeochemically linked but may behave differently under changing environmental conditions, reflecting the varying inputs, dilutions, or transformation zones found across a land-sea gradient. This non-linearity across the four compartments reflects the system complexity, especially as water masses mix (Fig 5e&f). The non-linear relationship is generally expected, as it resembles the relationship previously found in the Mackenzie River-Beaufort Sea region (Juhls et al., 2022), and in the Lena River-Laptev Sea transitional zone (Juhls et al., 2019).

Additionally, when looking at specific UV absorbance (SUVA) and slope ratio (SR) of S275-295 / S350-400, key indicators of the quality and sources of DOM, we see a distinction across the fluvial-marine compartments. Higher SUVA values typically represent more terrestrial and more chemically complex DOM with high aromaticity, whereas low SUVA values are reflective of more marine and microbially processed, or degraded, DOM. The SR also points to DOM composition. A higher SR typically reflects DOM with lower molecular weight, indicative of sunlight exposure, microbial degradation and photobleaching processes. We see highest SR values observed in Fig. 7b while lowest SR values are from freshwater samples. These lower SR values reflect heavier molecules of DOM that can be of terrestrial origin and not as degraded. The non-linear relationship found between DOC-aCDOM(443) indicates that there are different processes (biogeochemical and dilution) at play across the river to sea continuum. We think it is important to show this non-linearity across compartments since it is very useful for remote sensing applications that naturally often go across compartments, due to the synoptic nature of remote sensing data.

A new figure has been added (Figure 7) at line 490 to show the relationship between DOC and SUVA + DOC and the slope ratio (SR) which addresses the question about non-linearity and potential biogeochemical processes occurring across the land-sea continuum. The new text to accompany new Fig 7 is presented in the next reviewer comment.

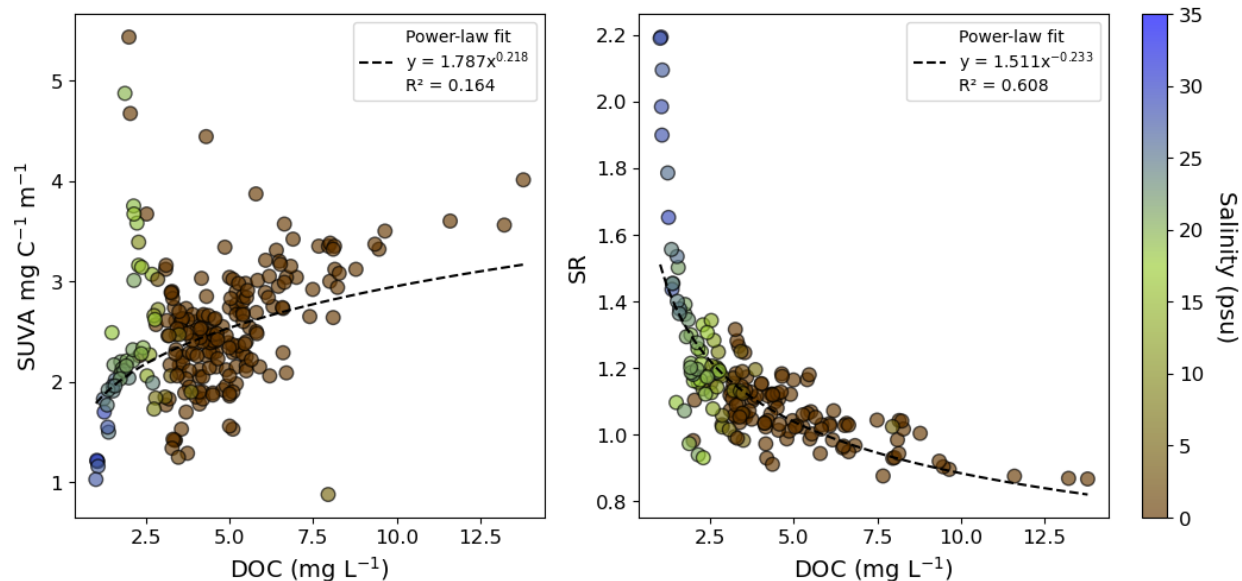


Fig. 7. Relationships between DOC and (a) Specific Ultraviolet Absorbance (SUVA) and (b) Slope Ratio of S<sub>275-295</sub> / S<sub>350-400</sub> along the freshwater-marine salinity gradient during 2009-2024. The black dashed line shows the power law fit of all samples (Lizotte et al., 2023, Bröder et al., 2022, this study, mackenzie-monitoring.awi.de) across all compartments.

The methods section (Section 2.3 line 204) has been updated to include text describing calculations for SUVA and SR used in Fig. 7. “Various parameters of CDOM absorption are used to derive the chemical characteristics, origin, and degradation processes that have altered DOM. These include the ratio of spectral slope of  $a_{\text{CDOM}}(\lambda)$  at different wavelengths and the specific ultraviolet absorbance (SUVA). These optical indices correlate aromaticity and molecular weight of bulk DOC (Weishaar et al., 2003; Helms et al., 2008; Coch et al., 2019). SUVA ( $\text{m}^{-2} \text{g C}^{-1}$ ) is calculated by dividing decadal absorption at 254 nm by the DOC concentration ( $\text{mg L}^{-1}$ ). The spectral slope of  $a_{\text{CDOM}}(\lambda)$  between 275 and 295 nm is an index for photodegradation and is calculated by fitting a regression for the wavelengths 275 – 295 nm to the exponential function in Helms et al. (2008). The spectral slope for the interval of 350 – 400 nm is determined by fitting the absorption spectra to a single exponential decay function by non-linear regression (Helms et al., 2008). The SR was calculated as the ratio of S<sub>275-295</sub> to S<sub>350-400</sub> nm.”

**L425-440:**

(a) There is no mention in the Results of specific attributes of the data presented that indicate processes such as flocculation, photodegradation, or other biogeochemical processing. As currently written, the Results present the data but do not extend into describing the data and linking with these processes. This paragraph also only indicates that this biogeochemical cycling occurs, but does not point to the emergence of these signals in the dataset presented here.

(b) You do not indicate any “hot spots” of DOM transformation in the dataset.

(c) Where are these processes “suggested” within the data? This is not presented or highlighted in the Results.

**Response:**

We think it is best to describe the additional analytical methods used to interpret the results in the Discussion section of this paper where they are presented (Fig. 7). The Discussion text has been updated to include at Line 432:

“While concentration gradients alone cannot uniquely distinguish dilution from biogeochemical processing, shifts in SUVA and SR along the salinity gradient indicate changes in DOM composition and molecular character, consistent with progressive photochemical and microbial alteration during transport from river to marine waters (Fig. 7). These results suggest that DOM transitions from terrestrially derived and chemically complex material (high SUVA) in low-salinity waters to more microbially processed and degraded material (low SUVA) in high-salinity waters, reflecting progressive transformations along the salinity gradient. While these observed shifts in SUVA and SR suggest that the compositional changes in DOM occur along the transport from freshwater to marine waters, these patterns cannot fully disentangle dilution from in-situ biogeochemical processing, as multiple factors influence the relationship, including overlapping seasonal mixing lines observed in Fig. 4.”

Fig. 7 has been added at the end of the paragraph following line 457.

**L 444-450:**

Again – does the data presented here show these processes? Concentrations alone do not belie biogeochemical processes. How are you interpreting the data to determine that flocculation and particle settling are driving POC concentration gradients, and not dilution? Is the shape of the relationship consistent with a particular biogeochemical process, or dilution? Are there residuals in relationships that emerge in specific locations or time periods (seasons) that indicate a specific process? Without this supporting interpretation, this is a data paper with significant speculation only.

**Response:**

Thank you for pointing towards this lack of interpretation. As you pointed out, using these compiled multi-year datasets it is difficult to identify processes that might happen in some years in some seasons and not during others. To determine if flocculation and particle settling are driving the POC concentration gradients, we tested POC/DOC vs. salinity. For an indication of DOC to POC conversion, we would expect an increase in POC/DOC at low salinities (5-10 psu), where fresh and saline waters mix, followed by a continual decrease at higher salinities. However, we do not see a clear and distinct increase of POC/DOC between 5-10 psu, but instead do observe an increase between 15-20 psu, followed by a gradual decrease into more saline waters. This could be indicative of some DOC to POC conversion and thus flocculation and particle settling, however it is not clear. Therefore, dilution is likely dominating with only localized or episodic deviations of flocculation and settling.

A new figure has been added to the Supplementary material and the following text added to line 445: “While abrupt concentration changes in the estuarine mixing zone point to flocculation and aggregation processes, testing POC/DOC vs. salinity revealed no clear indication of DOC to POC conversion and thus flocculation (Fig. A2). Instead of seeing an increase in POC/DOC at low salinity mixing zone (5-10 psu), followed by a continual decrease at higher salinities, we observe a slight increase at higher salinity (15-20 psu), followed by a gradual decline into saline waters. Therefore, dilution is likely dominating with only localized or episodic deviations of flocculation and settling. While concentration gradients alone cannot uniquely distinguish dilution from biogeochemical processing, shifts in SUVA and SR along the salinity gradient indicate changes in DOM composition and molecular character, consistent with progressive photochemical and microbial alteration during transport from river to marine waters (Fig. 7). While these observed shifts in SUVA and SR suggest that the compositional changes in DOM occur along the transport from freshwater to marine waters, these patterns cannot fully disentangle dilution from in-situ biogeochemical processing, as multiple factors influence the relationship, including overlapping seasonal mixing lines.”

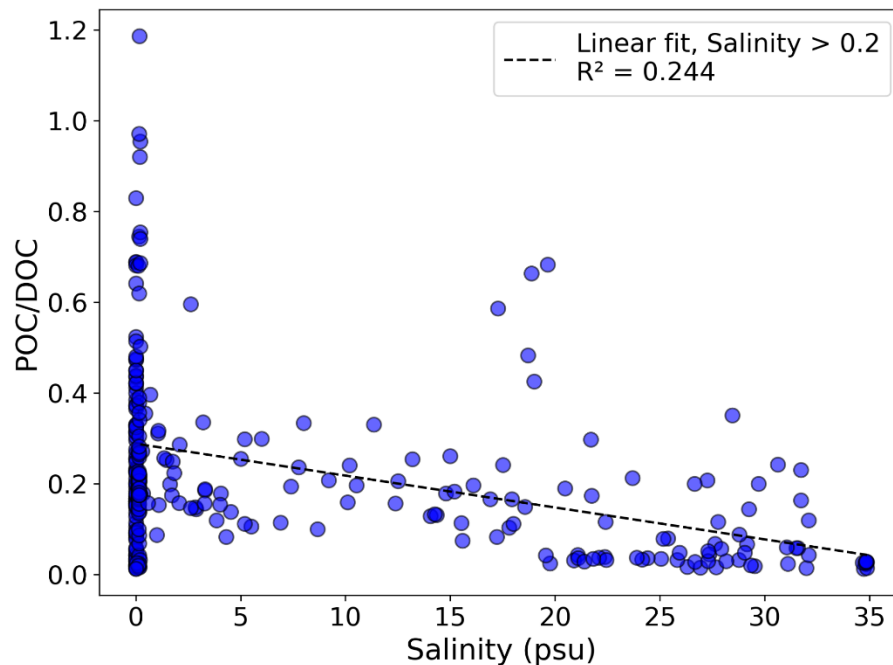


Fig. A2. POC/DOC vs salinity (psu). The black dashed line represents the linear fit.

**L 510-521:**

The non-linear relationship in Fig. 6 is driven largely by a few points. Additionally, there are a large number of river points that are bad data (negative CDOM absorption values at 443 nm, and even very low values that are likely indicating issues with analysis or sample handling). Without assessing the robustness of the fit when removing these values (e.g., ~6-8 delta values with elevated CDOM absorption), or considering why the delta values that display elevated carbon concentration relative to absorption (CDOM and particulate in Fig. 6), you lack the ability to interpret this data and extend the relevance of this dataset to remote sensing frameworks. If all river values with  $a_{CDOM}(443) < 0.5 \text{ m}^{-1}$ , and DOC values  $> \sim 3$  are removed, what does the relationship look like? If the delta values that fall significantly off a linear trend line are removed, what does the relationship look like? These questions need to be addressed to effectively assess this dataset and extend interpretation to implications for remote sensing.

**Response:**

Regarding the negative CDOM values from the river compartment, these data are from the ArcticGRO dataset. No mention of issues with sampling handling or processing were reported, and the negative value resulted from a baseline correction applied to the data. These negative values have been removed from this analysis and the Figure has been updated.

We chose not to exclude these samples from the regression analysis because they represent environmentally meaningful observations rather than statistical outliers. The elevated concentrations of delta samples represent spring freshet and breakup conditions that contribute disproportionately to annual carbon export and are often underrepresented in Arctic river-coastal datasets. Excluding these observations would bias the dataset toward lower-flow summer conditions, reduce its environmental representativeness, and limit our ability to improve remote sensing approaches that require robust performance across the complete range of naturally occurring concentrations and optical conditions. We therefore interpret the observed non-linearity not as a statistical artefact driven solely by a few points, but

as reflecting the integration of multiple hydrological and spatial regimes across the river–delta–coastal continuum. Additionally, the river and delta compartments show similar slopes (Fig. 6a), which contributes to the cross-compartment non-linearity and supports the argument that the pattern is not solely driven by a few high-value delta observations.

The delta compartment values with high DOC and low CDOM absorption are from the Nunataryuk sampling campaign Leg 1 (during April, sampling below the ice cover). Since the major aim of this study is to show implications for ocean color remote sensing applications that can be done only during the open water period, these data, as well as data from DUCCEM monitoring and ArcticGRO monitoring, collected during winter months (November - April) from under the ice have been removed from the analysis of bio-optical relationships. These data are still plotted in Fig. 6, but are colored grey and not included in the regression analyses. Figure 6 has also been updated to remove data points that were negative and those collected during winter months.

This has been added to the methods section at line 456:

“Since the major aim of this study is to show implications for ocean color remote sensing applications that can be done only during the open water period, data collected during winter months (November - April) from under the ice have been removed from the analysis of bio-optical relationships. This includes observations from Nunataryuk (Leg 1), DUCCEM monitoring and ArcticGRO monitoring. These data are still plotted in Fig. 6 but are noted in grey and not included in the regression analyses.”

Figure 6 in the manuscript and the figure caption included below have been updated in the manuscript. Associated  $R^2$  values have also been updated in the text.

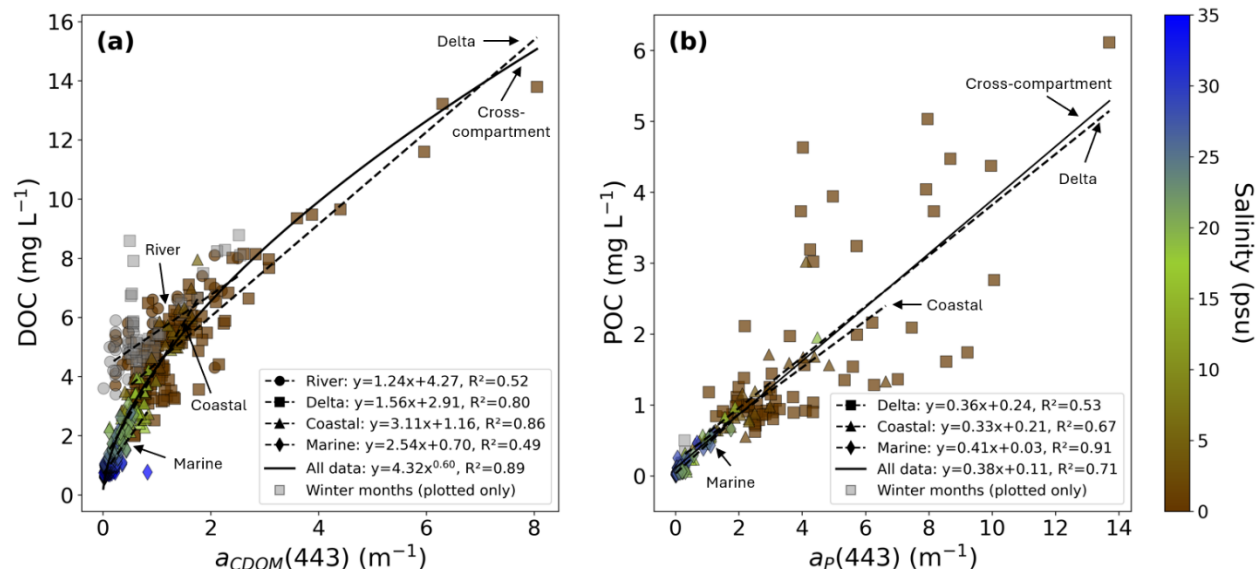


Fig. 6. Bio-optical relationships for measured in-situ (a) DOC and  $a_{CDOM}(443)$  and (b) POC and  $a_p(443)$  along the freshwater-marine salinity gradient during 2009-2024. The black solid line shows the regression of all samples (Massicotte et al., 2021, Lizotte et al., 2023, Bröder et al., 2022, this study, mackenzie-monitoring.awi.de) across all compartments. The dashed black lines show the relationship per compartment. Observations in grey are plotted but are not included in the statistical analysis.

**L 514-517:**

Linear relationships have been observed across river-delta-plume-ocean transects within the same period. There is interpretation of these dynamics in Clark et al. (2022), widely cited here, and not directly but observations, which are associated with the work in Clark et al. (2022), in Grunert et al. (2021) (see Supplementary Info). There is also more general discussion of these dynamics across a number of papers by Cedric Fichot and Maria Tzortziou. One of the issues with this study is a lack of spatiotemporal context within the dataset. Overlapping multiple conservative mixing relationships may offer the appearance of emergent biogeochemical processing when applying a global relationship, when in fact singular relationships representing a temporally fixed space state (spring freshet in 2017, for example) would display predominantly conservative mixing. There is a need to consider seasonal dynamics, and spatial dynamics, within this dataset and how these overlap to inform the extent of conservative vs. nonconservative processes. Additionally, deviations from relationships can be informative to determine. One key dynamic that is not addressed here, but is mentioned throughout papers cited, is the role that spring discharge plays in largely conservative mixing, while nonconservative processes occur more in summer months when flow rates are slower, solar irradiance is higher and often penetrates deeper, and temperatures are relatively warmer, enhancing microbial metabolic rates.

**Response:**

We agree with the reviewer that the integration of samples across seasons and hydrological regimes complicates the interpretation of DOC and aCDOM(443) behavior along the salinity gradient. Previous studies from Arctic river–shelf systems have shown that temporally constrained river–plume transects, particularly during spring freshet, can exhibit near-conservative mixing relationships between DOC, CDOM, and salinity (e.g., Clark et al., 2022; Grunert et al., 2021; Hölemann et al., 2021). When combining observations from multiple seasons, years, and spatial compartments, overlapping seasonal mixing trajectories may produce more diffuse or non-linear annual relationships.

In our study, we therefore do not argue for uniformly non-conservative mixing across the Mackenzie River Delta–southern Beaufort Sea continuum. Instead, we interpret the observed annual-scale variability as reflecting the superposition of multiple seasonal and spatial mixing regimes. During spring freshet, high discharge and rapid transport likely favor predominantly conservative mixing behavior, whereas during lower summer discharge periods, longer residence times, enhanced light penetration, warmer temperatures, coastal erosion, and marine production may increase the relative influence of photochemical, microbial, and particle-related processes on DOC and CDOM distributions.

To better illustrate these dynamics, theoretical seasonal mixing trajectories were added to the revised Fig. 4 for DOC and aCDOM(443) along with annual mean and freshet mean at 0 psu. The campaign and sampling periods are denoted by point symbols. Since processes such as degradation, flocculation, coastal erosion, sea-ice meltwater input, and seasonal variability in freshwater endmembers overlap spatially and temporally, it remains difficult to attribute deviations from conservative mixing to a single mechanism. In the Yukon River–coastal ocean continuum, Grunert et al. (2021) attributed rapid transformation of DOM composition with increasing salinity to photochemical and microbial alteration, however observation from this study were based on data collected during only two sampling periods (spring freshet and June), potentially limiting the representation of broader seasonal variability. Given the temporal uniqueness of our dataset for this study, we interpret the observed patterns as reflecting a combination of conservative mixing and seasonally variable biogeochemical processing across the fluvial–marine continuum.

The reviewer comment points to lines 514-517 in the manuscript, however based on the comment we assume the reviewer is referencing conservative vs. non-conservative mixing, which is discussed in the

previous sub-section of the Discussion. We have added the following text as a response to the reviewer comment but at line 469 in the manuscript:

“Previous studies from Arctic river–shelf systems have shown that temporally constrained river–plume transects can exhibit near-conservative mixing relationships between DOC, CDOM, and salinity (e.g., Clark et al., 2022; Hölemann et al., 2021; Grunert et al., 2021). However, due to the complex dynamics and biogeochemistry of the seasonal freshet, more intensive sampling during and between under-studied high flow conditions are imperative to improve our understanding of OC composition and reactivity across the land-ocean scale (Burns et al., 2024). When combining observations from multiple seasons, years, and spatial compartments, overlapping seasonal mixing trajectories may produce more diffuse or non-linear annual relationships. Fig. 4a demonstrates the influence of the seasonal spring freshet on DOC conservative mixing, where observations collected during the May-June freshet result in a freshwater endmember of 6.61 mg L<sup>-1</sup> compared to the year-round mean freshwater endmember (5.21 mgL<sup>-1</sup>). Similarly,  $a_{CDOM}(443)$  illustrates a similar relationship along the salinity gradient (Fig. 4b), where measurements collected during the spring freshet shift the theoretical mixing lines, visible by the changing slopes (-0.06 m<sup>-1</sup> psu<sup>-1</sup> during the May-June freshet to -0.04 m<sup>-1</sup> psu<sup>-1</sup> including year-round observations). Since processes such as degradation, flocculation, coastal erosion, sea-ice meltwater input, and seasonal variability in freshwater endmembers overlap spatially and temporally, it remains difficult to attribute deviations from conservative mixing to a single mechanism. We therefore interpret the observed patterns as reflecting a combination of conservative mixing and seasonally variable biogeochemical processing across the fluvial–marine continuum.”