REPLY TO REVIEWERS' COMMENTS

Manuscript entitled *Seasonal Contrast in Rare Earth Elements Concentration in Sediment of the Mackenzie Delta* submitted to *Biogeosciences*

Ms. No.: **EGUSPHERE-2026-266**

Authors: Thomas Bossé-Demers, Bennet Juhls, Martine Lizotte, Santiago Mareque, Audrey Gaudy, and Raoul-Marie Couture*

REVIEWER #2

2.1

> **This manuscript presents a compelling and well-executed investigation of seasonal contrasts in rare earth element (REE) concentrations in sediments, porewaters, and overlying waters across the Mackenzie River Delta. The nearly two-order-of-magnitude enrichment of dissolved ∑REE in winter porewaters relative to fall conditions represents a striking and scientifically important observation in Arctic fluvial–marine transition systems. While REE dynamics in Arctic freshwater and coastal environments have been examined previously (e.g., Johannesson and Lyons, 1995; Johannesson and Zhou, 1999; MacMillan et al., 2017), the magnitude of seasonal porewater enrichment documented here appears unusually large and is clearly demonstrated through a well-constrained dataset. I encourage the authors to temper any claim of being the first to report seasonal REE variability in Arctic systems, as related studies exist; however, they are justified in emphasizing the scale, clarity, and statistical robustness of the seasonal contrast observed in this deltaic transition zone. The integration of REE concentrations with dissolved organic carbon (DOC), chromophoric DOM indices ($SUVA_{254}$, HIX, BIX), Fe and Mn, and multivariate statistical analyses (PCA and MANOVA) provides a coherent and well-supported analytical framework. Overall, the manuscript is thoughtfully structured and scientifically sound, and I support publication following minor revisions aimed at strengthening mechanistic clarity, methodological transparency, and internal consistency.**

We thank the reviewer for the kind words. We agree that seasonal REE variability has been investigated in Arctic surface waters. Our intention is not to claim the first observation of seasonal variability, but rather to emphasize the magnitude, consistency, and porewater-specific nature of the seasonal contrast observed here. We will refine the wording accordingly in the revised manuscript.

2.2

> **The central result of winter porewater ∑REE concentrations averaging ~217 nmol L^{-1} compared to ~3 nmol L^{-1} in fall is robust and statistically well supported. The PCA explains 83% of the total variance in the first two components and clearly separates seasonal datasets, while MANOVA (Pillai's trace = 0.883, $p < 0.0001$) confirms statistically distinct multivariate profiles between seasons. These analyses convincingly demonstrate that seasonal forcing dominates over spatial heterogeneity within the dataset. However, the discussion would benefit from a more explicit hierarchical framing of the mechanisms controlling winter enrichment. The manuscript invokes enhanced DOM accumulation, temperature-dependent carbonate complex stability, and Fe/Mn competition for ligands, yet these processes are presented largely qualitatively and without prioritization. A short integrative paragraph ranking the likely dominant control (for example, ligand abundance) relative to secondary modifiers (such as carbonate speciation shifts or competitive metal binding) would strengthen the mechanistic narrative and clarify the interpretation of seasonal drivers.**

We agree that clearer prioritization of mechanisms would strengthen the discussion. The revised manuscript will include a short integrative paragraph identifying DOC ligand abundance as the primary control on winter REE enrichment, with carbonate speciation and Fe/Mn competition as secondary modifiers, consistent with PCA loadings.

"The nearly two-order-of-magnitude enrichment of dissolved ΣREEs in winter porewaters is best explained by the effects of seasonal changes in dissolved organic matter, with potential contributions from carbonate speciation, and Fe/Mn redox cycling. DOC ligand abundance emerges as the primary control: winter porewaters accumulate DOC under ice-covered, hydrologically isolated conditions, providing a greater quantity of binding sites for REE complexation despite the lower aromaticity and humic character of winter DOM relative to fall. Secondary modifiers include temperature-dependent shifts in carbonate speciation, as lower temperatures favored carbonate complex stability and potentially reducing free REE availability, and competition between REEs, Fe, and Mn for organic binding sites, which is attenuated in winter as Fe and Mn are mobilized through reductive dissolution and may themselves complex with DOM. This ranking is consistent with the PCA structure, in which DOC and $SUVA_{254}$ *load most strongly on PC1, which accounts for the dominant seasonal separation in the dataset."*

2.3

The treatment of DOM quantity versus quality represents one of the manuscript's strongest conceptual contributions. Winter DOM is characterized by lower $SUVA_{254}$ and HIX values relative to fall, indicating lower aromaticity and humic character, yet dissolved REE concentrations are substantially higher in winter. The authors attribute this contrast to greater ligand abundance in winter overwhelming lower conditional binding strength relative to fall DOM. This interpretation is reasonable and consistent with established REE–organic complexation literature. Nevertheless, the argument would benefit from explicitly quantifying the seasonal DOC differences and briefly clarifying how increased ligand concentration can offset lower conditional stability constants. A concise conceptual framing of ligand concentration versus binding strength would render this interpretation more quantitatively grounded and prevent the explanation from appearing speculative.

We agree that a more quantitative treatment of quality vs quantity would strengthen the manuscript. Here, we propose to quantify seasonal DOC differences in terms of ligand concentrations in the revised manuscript and add a concise discussion of ligand concentration versus binding strength. Using carbon-normalized binding site densities for two contrasting DOM types from Mueller et al. (2023) as proxies, a higher site density (0.023 µmol mg C^{-1}) representative of our fall DOM and a lower site density (0.0105 µmol mg C^{-1}) representative of our winter DOM, and applying these to our measured seasonal DOC concentrations (~267 mg C/L in winter vs ~41 mg C/L in fall), we estimate the absolute concentration of binding sites available for REE complexation: ~0.94 µmol/L in fall vs ~2.80 µmol/L in winter. Despite fall DOM having higher binding site density per unit carbon, the ~6.5× higher DOC concentration in winter results in ~3× more binding sites in absolute terms. This order-of-magnitude estimate quantitatively support that ligand abundance dominates over conditional binding strength in controlling seasonal REE mobility.

2.4

Because the discussion references pKa values and logK differences in complexation strength, the Introduction would benefit from a short paragraph summarizing REE interactions with Fe oxyhydroxides, Mn oxides, and natural organic matter (including humic and fulvic substances). This would provide conceptual grounding for later references to binding site density and complex stability constants. Several prior studies have examined REE association with Fe–Mn phases and humic materials; briefly contextualizing this framework early in the manuscript would improve overall coherence and strengthen the mechanistic basis of the Discussion.

A short paragraph summarizing REE interactions with Fe/Mn oxyhydroxides and NOM will be added to the Introduction, citing relevant references (Davranche et al., 2004; Tadayon et al., 2023; Davranche et al., 2015; Sonke, 2006). The paragraph reads as follows:

"Rare earth elements in aquatic systems partition between dissolved, colloidal, and solid phases through competitive binding to Fe and Mn (oxy)hydroxides and natural organic matter (NOM). Iron oxyhydroxides exhibit strong REE affinity, but when REEs are complexed with humic

substances, the organic ligand rather than the metal ion interacts with the oxide surface, effectively suppressing direct REE mineral sorption (Davranche et al., 2004). In Fe-rich systems, REE association with Fe–organic matter colloids at circumneutral pH is primarily controlled by the organic component rather than the iron phase itself (Tadayon et al., 2024), with implications for REE mobility during seasonal redox oscillations. NOM binds REEs through heterogeneous sites: at high loading, carboxylic groups, while at low loading, phenolic and chelate groups control binding (Davranche et al., 2015; Sonke, 2006)."

2.5

With respect to sedimentary REE dynamics in cold regions, the manuscript suggests seasonal contrasts are understudied. While this is largely accurate for deltaic Arctic porewater systems, the phrasing should acknowledge prior Arctic REE investigations while emphasizing that coupled sediment–porewater seasonal contrasts in fluvial–marine transition zones remain comparatively poorly constrained. This refinement would maintain accuracy while preserving the manuscript's contribution. The study region description would benefit from inclusion of seasonal precipitation data or at least qualitative hydrological context. Seasonal REE concentrations may reflect dilution, flushing, organic matter mobilization, or restricted exchange processes, and precipitation variability could influence both DOM supply and REE mobility. Even a brief discussion of seasonal hydrologic regime would strengthen interpretation and situate the results within a broader environmental framework.

The manuscript already acknowledges prior Arctic REE investigations in surface waters and sediments, citing for instance MacMillan et al. (2017) and Pokrovsky et al. (2016), among others. While previous studies have examined REEs in Arctic waters and sediments, we maintain that seasonal dynamics of REE in Arctic sediment porewaters remain comparatively understudied, particularly in deltaic transition zones.

We will add hydrological context (Lizotte et al., 2023), noting that spring sampling occurred during baseflow (~4,000–5,000 $m^3 s^{-1}$), prior to the spring freshet, while fall sampling was conducted during the recession limb of the hydrograph (~10,000 $m^3 s^{-1}$).

2.6

Several methodological clarifications are required to improve transparency and reproducibility. Figure 1 would benefit from inclusion of river pathways or bathymetric context to better visualize potential fluid flow paths between sampling locations and to contextualize spatial variability. Table 1 should include salinity and pH values for each site, particularly because carbonate complexation and DOM interactions are invoked as mechanistic controls. The manuscript should clarify why different sampling containers were used in fall and winter and whether field blanks and container blanks were conducted to assess contamination or adsorption effects. A supplementary table reporting certified reference material (CRM) recoveries, relative standard deviations, and measured concentrations is strongly

recommended. Additionally, the manuscript should clarify how CRM analysis validates the porewater analytical method, as validation of solid CRMs does not necessarily confirm dissolved-phase matrix accuracy.

The requested methodological clarifications are provided below:
- Figure 1: We believe the current presentation is adequate; however, we are happy to revise this if the Associate Editor feels it would improve clarity.
- Table 1: Salinity values will be added to Table 1 in the revised manuscript. Salinity ranged from 0.002 to 1.429 across all sites, consistent with freshwater to very weakly brackish conditions, except for site 1030(F), which exhibited markedly higher salinity (22.79) indicative of marine influence. Station 1030(F) that is now removed from the analysis as it was only providing sediment data and no porewater data. As such, the system is therefore largely freshwater.
- pH was not measured during this campaign; this limitation is addressed in our response to comments 1.6 and 2.8.
- Sampling containers and field blanks: Different containers were used across the two campaigns because the first type (vacutainer tube, prewashed and vacuum sealed) proved a bit slow to retrieve porewater, which led us to switch to acid-washed syringes and HDPE containers for the second campaign (fall). Field blanks were not collected as the ultrapure water available on site was found to be compromised. See also our response to comment 1.1.
- CRM validation: Dissolved REE analyses were indeed validated against SLRS-6 (National Research Council Canada), a natural river water certified reference material whose dissolved REE concentrations were certified by an internal study (Yeghicheyan et al., 2019, Geostandards and Geoanalytical Research). This directly addresses the concern that solid-phase CRM validation does not confirm dissolved-phase matrix accuracy. Other elements were validated with SLRS-6 and TMDWS.3 (for Mn and Fe). A supplementary table reporting measured concentrations, certified values, and percent recoveries will be added to the revised manuscript.

2.7

Further analytical clarity is needed regarding instrumentation. The Methods section suggests both ICP-OES and ICP-MS were used for major and trace elements, but it is not fully clear which analytes were measured on which instrument and why. This ambiguity could imply duplication unless clarified. The isotopes monitored for REE quantification should be explicitly reported. The authors should also indicate whether any matrix separation or column chemistry was performed prior to ICP-MS analysis, particularly given salinity variability across sites.

ICP-OES was used exclusively for Fe and Mn in sediment digests, while ICP-QQQ-MS was used for all REE measurements and for dissolved Fe and Mn in porewater and overlying water samples. There is no duplication, the two instruments were applied to distinct sample types and analyte sets. This will be clarified in the Methods section of the revised manuscript. The dominant isotope was monitored for each REE; the specific isotope list will be provided in the revised Methods section. Matrix separation prior to ICP-MS analysis was not required given the low salinity of the Mackenzie River and delta waters, which are predominantly fresh to slightly brackish. Column chemistry is typically warranted for marine or estuarine matrices where high *dissolved solids can suppress or interfere with detection; this was not the case here. This will be stated explicitly in the revised manuscript.*

2.8

The statistical treatment would benefit from additional transparency. The approach to handling below-detection-limit data (half detection limit substitution) should be further justified, as PCA and ANOVA results can be sensitive to such treatments. The normalization procedure applied prior to PCA should be more clearly defined and supported with an appropriate methodological reference. The R packages used for PCA, MANOVA, and related analyses should be reported for reproducibility. It is also noteworthy that pH, salinity, REE anomalies (e.g., Ce/Ce*), and grouped LREE/HREE parameters were not included in the statistical analyses; inclusion or justification for exclusion of these variables would strengthen interpretation and potentially provide additional insight into seasonal fractionation processes.

See also our response to comment 1.4 regarding the LOD substitution approach. LOD substitution, PCA normalization, and R packages used will be fully specified in the revised Methods. Specifically, R v4.4.3 was used (R. Core Team, 2025) and spearman correlation, PCA, MANOVA and ANOVA were calculated using the base stats package from R. 95% confidence ellipses were calculated using ellipse v0.5.0 package

Regarding the exclusion of pH, salinity, Ce/Ce, and LREE/HREE from the statistical analyses: pH was not measured during this campaign and could therefore not be included. Salinity varied over a narrow range across our freshwater to slightly brackish sites and was not considered a primary driver of the observed seasonal patterns; its inclusion would not have altered the multivariate structure meaningfully. Ce anomalies (Ce/Ce*) are not discussed in the manuscript as our dataset provides no evidence for anomalous Ce behavior, and their inclusion in the PCA without a mechanistic basis would be difficult to interpret. Finally, LREE/HREE groupings were not included as this study reports total REE concentrations and treats the REE series as a group; REE fractionation patterns are identified as a direction for future work (see response to comment 1.9) rather than in the present analysis.*

2.9

In the Results section, Figure 2 requires clearer explanation regarding normalization procedures and the distinction between overlying water, porewater, and sediment data. The definition of "overlying water" should be explicitly stated (e.g., 1–2 cm above the sediment–water interface versus broader water column). Fe and Mn concentrations should be reported in the text alongside DOC and ∑REE values to maintain consistency in presentation. Figure 3 could potentially be examined across salinity or pH gradients to determine whether seasonality remains dominant when controlling for physicochemical gradients. Figures 4 and 5 would benefit from reconsideration. While Fe–Mn–REE correlations are well established, the rationale for selecting Ce and Nd as representative REEs should be explained. Alternatively, grouping by LREE, HREE, and ∑REE may better capture seasonal

fractionation trends. Currently, panels 5b–d most directly support the DOM control argument; some redundancy in earlier figures could potentially be moved to supplementary material to streamline the narrative.

- Figure 2: The caption states that values are normalized to the series maximum to display values between 0 and 1. A sentence will be added explicitly stating that this figure is intended to illustrate the dominance of seasonal over spatial variability, and that absolute concentrations are provided in the relevant tables and figures.

- Overlying water definition: The caption and legend will be clarified to distinguish sediment, porewater, and overlying water, the latter corresponding to the river water column above the sediment–water interface.

- Fe and Mn in text: Fe/Mn and REE/DOC are discussed in separate paragraphs to preserve the parallel structure of the manuscript, which we consider an asset for readability. We prefer to maintain this organization.

- Figure 3 across salinity/pH gradients: Salinity varied over a narrow range insufficient to define a meaningful gradient, and pH was not measured. These constraints are already noted in the manuscript and will be made more explicit in the revised text as justification for the statistical approach taken.

- Ce and Nd as representative REEs: Ce and Nd were selected because they are among the most abundant REEs in natural waters, are widely used as representative tracers in the literature, and their co-presentation allows detection of any Ce anomaly relative to the smooth lanthanide trend defined by Nd. The absence of a Ce anomaly in our dataset supports treating the REE series as a coherent group, consistent with our overall analytical approach. The rationale for this selection will be stated explicitly in the revised manuscript.

- Figure redundancy: We prefer to retain the current figure structure as it supports the stepwise narrative of the manuscript. Should the Associate Editor request consolidation, we are prepared to move panels to supplementary material.

2.10

In the Discussion, the covariance of Fe–Mn and REE should be more explicitly justified mechanistically rather than inferred from correlation patterns. The vertical structure of overlying water chemistry and its transition into porewater should be more clearly described to support interpretations of sediment–water exchange processes. The section on DOM quantity versus REE complexation quality should move beyond stating that multiple factors contribute and instead more directly interpret what the dataset reveals regarding ligand availability relative to binding strength. The brief reference to complexation models and binding site density could either be removed or expanded slightly to avoid appearing cursory. The conclusion should more clearly synthesize Fe, Mn, DOM seasonality, and REE mobility into a unified mechanistic summary that reinforces the manuscript's broader significance.

We believe the convergence of evidence supports our interpretive approach, and we have strengthened the discussion following the reviewers' suggestions in response to previous comments on DOM quantity vs REE complexation (comment 2.3 above) and on Fe-Mn vs REE (comment 2.4). We remain open to further guidance from the editor should additional clarification be desired.

2.11

> **In conclusion, this manuscript provides an important and well-supported contribution to Arctic trace element biogeochemistry. The seasonal contrast in dissolved REE is convincingly demonstrated, and the dataset is robust. The revisions suggested above are primarily clarifications and structural improvements intended to enhance methodological transparency, mechanistic depth, and reproducibility. No additional sampling, new experiments, or major reanalysis are required. I therefore recommend acceptance following minor revision.**

We thank the reviewer for the positive assessment and the recommendation for acceptance following minor revision. We trust that the revisions outlined in our responses above address all points raised.

REFERENCES CITED

- Davranche, M., Gruau, G., Dia, A., Marsac, R., Pédrot, M., Pourret, O., **2015**. *Biogeochemical Factors Affecting Rare Earth Element Distribution in Shallow Wetland Groundwater*. **Aquat Geochem** 21(2-4).
- Davranche, M., Pourret, O., Gruau, G., Dia, A., **2004**. *Impact of humate complexation on the adsorption of REE onto Fe oxyhydroxide*. **Journal of Colloid and Interface Science** 277(2).
- Mueller, K.K., Couture, R.-M., Fortin, C., Campbell, P.G.C., **2023**. *Nickel and copper complexation by natural dissolved organic matter – titration of two contrasting lake waters and comparison of measured and modelled free metal ion concentrations*. **Environmental Chemistry** 21(1).
- R. Core Team, **2025**. R: A Language and Environment for Statistical Computing (Version 4.4.3). R Foundation for Statistical Computing.
- Sonke, J.E., **2006**. *Lanthanide−Humic Substances Complexation. II. Calibration of Humic Ion-Binding Model V*. **Environmental Science & Technology** 40(24).
- Tadayon, Y., Vantelon, D., Gigault, J., Dia, A., Pattier, M., Dutruch, L., Davranche, M., **2024**. *Rare earth elements interaction with iron-organic matter colloids as a control of the REE environmental dissemination*. **Journal of Colloid and Interface Science** 655.