Response to reviewers:

We thank both reviewers for their constructive and helpful review of our paper.

From both reviewers there were queries concerning the reference 'Rewrie et al. (in review)'. This manuscript was accepted by Limnology and Oceanography with the Article DOI: http://doi.org/10.1002/lno.12395 and is now published. We are happy to provide a brief explanation on the differences between the two papers.

Rewrie et al. (2023) assessed changes in DIC and ecosystem parameters from 1985 to 2018. From the abstract: 'Based on an extensive evaluation of key ecosystem variables, and an analysis of the available inorganic and organic carbon records, this study has identified three ecosystem states in recent history: the polluted (1985-1990), transitional (1991-1996) and recovery (1997-2018) states. The polluted state was characterised by very high dissolved inorganic carbon (DIC) and ammonium concentrations, toxic heavy metal levels, dissolved oxygen (DO) undersaturation and low pH. During the transitional state, heavy metal pollution decreased by > 50%, and primary production re-established in spring to summer, with weak seasonality in DIC. Since 1997, during the recovery state, DIC seasonality was driven by primary production, and DIC significantly increased by 11 µmol L^{-1} yr^{-1}, and > 23 µmol L^{-1} yr^{-1} in the recent decade (2008-2018), in the mid to lower estuary, indicating that, along with the improvement in water quality the ecosystem state is still changing'

In the present manuscript, we focus on the changes in DIC in the recent recovery state (1997-2018) and extend the dataset by two years to 2020 due to more recent data availability. This study investigates the reason for the DIC increase over time by utilizing changes in organic carbon in the upper estuary. This study also evaluates the impact of the recent drought on the carbon cycling in the Elbe Estuary. We believe that publishing the manuscript described above, which precedes this one will answer most questions raised by the reviewers. However, we have attempted to carefully address the reviewer's comments in the sections below.

Comments to Authors

This is an interesting dataset describing longitudinal gradients and long-term trends in POC and DIC for the Elbe Estuary. The findings from an analysis of these data would be of interest to estuarine ecologists and to the broader community studying the global C cycle. My main concern with the paper is that there are many aspects that are either not well explained, or insufficiently explained. This issue pervades key components of the paper including conceptualization of the study, description of methods and inferences made from the data.

Methods: the level of detail in explaining methods is highly uneven among the various components of the study. For example, the means for calculating air-water CO2 fluxes is highly detailed, whereas other equally important elements (e.g., POC loads and DIC mineralization) are hardly described at all in the main body of the paper. These fluxes, and how they are derived should be explained more fully and at an early stage. For example, in the Abstract there is reference to the "spring internal DIC load" (line 30), but at this stage, the leader is not likely to understand what this is (remineralization of organic C) or how it was determined. Also, I did not see an explanation of how POC was measured (perhaps I missed this).

To ensure the methods are clearly provided we will move equations S2 to S5 from the supplementary materials into the methods section.

We had referenced Rewrie et al. (2023) which extensively describes the inorganic and organic carbon measurement methods to reduce repetition. However, to increase clarity in this manuscript, we will include a sentence on line 134 to describe that POC was calculated as the difference between TOC and DOC (Table S1), with an estimated uncertainty of 20% based on the Pythagorean Theorem (U. Wiegel, pers. comm).

Introduction: the first paragraph focuses on C cycling in estuaries, with a mention of eutrophication. The second paragraph focuses of climate change, and specifically, the occurrence of drought. The third (final) paragraph does not link the ideas presented in the first and second paragraphs in such a way as to provide a clear direction for the paper. There should be some consideration (prediction) of how estuarine C cycles may be affected by drought. My initial reaction was that drought would reduce external (watershed) inputs of POC and DOC to the estuary. I was surprised that there was no consideration here, or elsewhere, of the importance of allochthonous organic matter inputs, particularly as this is the driving mechanism accounting for the excess of C mineralization relative to autotrophic fixation in estuaries (see e.g., Hoellein et al. 2013). The third paragraph should provide some clear expectations of the direction of the paper from a conceptual point of view, which the stated objectives fail to do. Also, there should be some consideration of allochthonous C inputs and how these may have changed over time (and in response to drought).

Thank you for this suggestion and reference. We do in fact argue in the later sections of the manuscript that allochtonous POC sources are key to the DIC processing in the estuary. To highlight the importance of allochthonous C in the introduction, we will edit the first paragraph on line 50-53. E.g. 'River-borne and in situ primary production supplies allochthonous and autochthonous organic carbon to and within estuaries (Abril et al. 2002; Hoellein et al. 2013), subsequently providing labile forms of carbon'.

In the second paragraph, we described the influences of extreme floods and droughts on OM and nutrient cycling within estuaries on lines 71-76. To link the first and second paragraph we will change the sentence on lines 74-76: 'This in turn can extend the retention of carbon and nutrients during droughts, permitting more extensive remineralization of allochthonous and autochthonous organic material within an estuary (Hitchcock and Mitrovic, 2015), and subsequently altering carbon and nutrient cycling'.

To clarify the reasons behind assessing the period between 1997 and 2020 we will change the third paragraph on lines 87-88 to 'To assess the impact of the drought on the carbon cycling in the estuarine ecosystem, we assess a longer period between 1997 and 2020, to allow comparisons between a non-drought and drought period.'

The reliance on Rewrie et al. in review, here, and at many points throughout the paper, is not helpful, particularly as these are vague references to "ecosystem recovery", "major shifts in ecosystem state" and "amelioration of water quality". It is not clear to the readers of this paper what these changes are, and what implications they may have for C cycling in the Elbe. There is a subsequent statement that these changes include a reduction in BOD and an increase in NPP. The former implies that the changes may have to do with improved wastewater treatment resulting in reduced organic matter inputs to the estuary. But if that is the case, should these fluxes not be accounted for in this paper describing trends in POC and DIC? Also, if wastewater treatment practices have been improved, this should bring about a reduction in nutrient inputs, and potentially diminish, not enhance NPP. I short, I found it difficult to understand the long-term trends presented in this paper while not understanding what are the changes occurring in this system that seem to be the focus of a different paper.

To clarify the key findings of Rewrie et al. (2023) we will change the introduction from line 88 and will remove 'It has been described as the ecosystem recovery state of the estuary (Rewrie et al., 2023), following major shifts in the ecosystem state after the 1980s heavy pollution.' And then include 'Since 1997, the ecosystem of the Elbe Estuary was designated in a recovery state (Rewrie et al., 2023), characterised by non-toxic levels of heavy metals permitting autotrophy and heterotrophy within the estuary, which followed a heavily polluted state in the 1980s and the ensuing transitional state (1991-1996).'

To clarify the changes in the water quality in the Elbe Estuary we will specify the BOD changes observed in the upper estuary. Since the decrease was not directly inverse to the POC increase, we will remove 'opposite of the observed POC increase' and include on line 410 'The summer mean BOD_7 decreased from 12±1.7 mg L^{-1} in 1997–2005 to 8±1.1 mg L^{-1} in 2006–2020'. After this sentence we will also include 'While there was a continuous decrease in nutrients from the late 1990s (Wachholz et al. 2022), the nutrient supply was sufficient to support phytoplankton production (Kamjunke et al., 2021; Dähnke et al 2022).' This highlights that despite the overall decrease in nutrients the concentrations were predominately sufficient for primary production in the Elbe River and Estuary, as has been found by other researchers (e.g. Dähnke et al 2022), who will also be referenced.

Dähnke, K., Sanders, T., Voynova, Y., & Wankel, S. D. (2022). Nitrogen isotopes reveal a particulate-matter-driven biogeochemical reactor in a temperate estuary. Biogeosciences, 19(24), 5879-5891.

Wachholz, A., Jawitz, J. W., Büttner, O., Jomaa, S., Merz, R., Yang, S., & Borchardt, D. (2022). Drivers of multi-decadal nitrate regime shifts in a large European catchment. Environmental Research Letters, 17(6), 064039.

We would like to highlight that in the submitted manuscript we had indeed identified a potential reduction in nutrient inputs in 2018 to 2019 on lines 508-510, which was associated with the drought.

Results: throughout the paper, loads are presented as mass per unit of time (e.g., the total mass of CO2 leaving the estuary), which is not very helpful to facilitating cross-system comparisons (vs. presenting these as values per unit area of the estuary). By analogy, river loads (watershed export) are more commonly normalized to watershed area (i.e., as a yield per square meter) to allow comparisons among watersheds of different size. Readers could take the values provided in this paper and divide by the specified area of the estuary to obtain estimates for comparisons to other estuaries. But the potential for making inter-system comparisons would be enhanced if the authors were to present their data as per unit area of the estuary.

Thank you for this suggestion. The reason why we used the mass per unit of time was to allow us to calculate a ratio of the export and compare to other estuaries on

lines 582-587. To allow the reader to see our results in both forms of units we will combine Gmol yr^{-1} to one axis with a log scale and will also present on the twin axis the export plot per unit area.

Other Comments:

The Abstract lacks a 'big picture' perspective. The overall findings of the study are difficult to discern among the details of the results.

To put our results in perspective to other studies we will include (italic) and change to the following:

'We have identified that seasonal changes in DIC processing in an estuary require consideration in order to understand *and accurately estimate* the long-term and future changes in air-water CO_2 flux *and* DIC export to coastal waters. ~~, as well as the impacts of prolonged droughts on the land-ocean carbonate system.'~~ *Regional and global carbon budgets should take into account carbon cycling in estuaries, in relation to impacts of water quality changes and extreme hydrological events'*

The aim here was to describe that the changes in DIC flux from estuaries will change due to what DIC is added in the estuary, which itself is influenced by changes in availability of labile POC (water quality) and the influence of external forces, in this study hydrological event (drought) influences both inside DIC addition and external flux.

Site Description: it would be helpful if this included an indication of salinity levels along the length of the estuary (perhaps add data to Figure 1, or at least delineate polyhaline, mesohaline, etc.).

Thank you for this suggestion. To address this we will include an average with standard deviation salinity gradient on Figure 1b.

DOC: I was surprised that in a paper on estuarine C dynamics there was virtually no mention of DOC. Is it the case that internal production of POC and subsequent remineralization of POC are the dominant C fluxes in this system? At a minimum, it would be useful to report the proportions of total C represented by DIC, POC and DOC in river inputs to the estuary vs. relative contributions in export to the sea (and for drought vs. non-drought conditions).

Yes, we suggest that the production of allochtonous POC (in the river and in the coastal regions adjacent to the estuary) and its subsequent remineralization of POC are controlling the C fluxes in this system, and are responsible for the recent observed increase in DIC. We will include a reference in the introduction describing the respiration of organic carbon in the Elbe Estuary, for example, 'The organic carbon cycling in the Elbe Estuary was evaluated before (Amann et al., 2012), identifying that from the late 1990s, POC fuelled heterotrophic respiration whereas respiration of DOC in the estuary was negligible. However, the last decade was not included.'

In response to both reviewers, we will include information on DOC to show the concurrent DOC changes as well, to support our findings that the remineralization of POC, rather than DOC fuels the DIC production. To address the reviewer's

concern we will estimate the removal of DOC and POC in the estuary, defined as filtering capacity in Amann et al. (2012) in the Elbe Estuary.

To assess the importance of the upper estuary DOC and POC respiration and subsequent DIC production in the Hamburg Harbour and the mid-estuary the organic carbon removal as shown in Amann et al. (2012) expressed in percent was calculated:

$$C_{FC}\% = \frac{(C_{z1} - C_{zi})}{C_{z1} \times 100}$$

Where C is the POC or DOC concentration in the respective zone with zi representing zones 2-3 for POC and zones 2-5 for DOC. The OC removal for POC was calculated for zone 2 and 3 due to the influence of the maximum turbidity zone in zone 4 and 5 (Amann et al. 2012). The negative values indicate OC addition.

We found that the POC removal was up to ~ 4 times greater (80%) compared to the DOC removal (21%). In the regions when DOC and POC were removed between 1997 and 2020, the mean removal was 7 ± 5% and 41 ± 18%, corresponding to a mean concentration loss of 39 ± 30 μmol kg^{-1} and 160 ± 104 μmol kg^{-1}, respectively. This indicates respiration of upper estuary POC dominates DIC production in the Hamburg Harbour to mid Elbe Estuary.

To further support upper estuary POC dominates DIC production in the mid-estuary, we would like to highlight that in the submitted article we discussed (on lines 429-430) 'The magnitude of along-estuary DIC gain in the mid-estuary and POC input into the estuary show no significant difference in late spring and summer (Table S5).' We would also like to highlight in the submitted article we discussed POC in % of SPM was used to describe the mineralisation of POC in the mid-estuary. On line 434 'We find that POC drops to < 4% of SPM in May to August (1997–2020) in the mid estuary (z4–z5, Fig. S5), indicating widespread OM remineralization in the estuary.'

The story that the remineralisation of upper estuary POC dominates DIC production in the Hamburg Harbour to the mid-estuary does not change. We will include figures for the OC removal in percent and the concentrations of DOC and POC along the estuary for late spring (May) and summer (June-August) in the results and supplementary material and integrate the findings into the discussion.

In the lower to outer estuary, we have identified that other sources of OM likely support DIC production as described in the submitted article on lines 525 to 542. To assess DOC production in this region, we assessed the mixing of DOC along salinity for May to August between 1997 and 2020. We found positive non-conservative mixing of DOC along the salinity gradient in 42% of the assessed months. This corroborates our suggestion of OC production in the outer estuary can fuel DIC production therein. We will include additional DOC mixing along the salinity gradient figures in the supplementary material to support our findings in the discussion.

Amann, T., Weiss, A., & Hartmann, J. (2012). Carbon dynamics in the freshwater part of the Elbe estuary, Germany: Implications of improving water quality. Estuarine, Coastal and Shelf Science, 107, 112-121.

Results (line 240): there is frequent use of indirect metrics (AOU, pH) to make inferences about autotrophic activity. Are there no primary data that can be used to support these inferences (e.g., CHLa measurements)?

To support primary production in spring and summer we plotted a seasonal plot of the monthly mean chl-a at 585.5 Elbe-km calculated from 1997 to 2020. We will place this plot in the supplementary material, since it is only supporting the findings of AOU and pH in the upper estuary, without altering the manuscript findings. AOU we find is a more powerful measurement of production/respiration balance. A time-series of chl-a does not provide more evidence than POC, which was chosen to represent the labile carbon produced during primary production and available for remineralisation, and for which we found a strong and significant correlation with DIC, in the same order of magnitude, and already in units of carbon. We will include (in italics) on line 242 following 'This suggests that dominating autotrophy depletes DIC in the upper estuary, and most likely the upstream river regions, *which is supported by highest chlorophyll a concentrations in May to August at 585.5 Elbe-km, reaching 166 ± 74 µg L^{-1}.'*

Results (line 260): the statement "significant POC increases occurred..." is followed by some specified values, but it is unclear what these numbers represent (the mean concentration? the increase in concentration? If the latter, increase relative to what?).

To clarify this sentence we would change to 'Significant mean POC increases occurred in late spring (May, 14 µmol C kg-1 yr-1) and summer (June–August, 8 µmol C kg-1 yr-1) in the upper estuary (Fig. 3, Table 1) from 1997 to 2020'.

Results (line 278): I did not understand why the TA:DIC ratio should be of interest, or what is the significance of this ratio being <1.

To clarify the importance of using the TA: DIC ratio we will include the following reference on line 276: The ratio of TA to DIC can serve as a broad indicator of the sources of carbon, for example, when < 1 this can reflect DIC input in the form of CO_2 (Joesoef et al., 2017).

Joesoef, A., Kirchman, D. L., Sommerfield, C. K., & Cai, W. J. (2017). Seasonal variability of the inorganic carbon system in a large coastal plain estuary. Biogeosciences, 14(21), 4949-4963.

Discussion (line 425): do you mean to say that mineralization rates increase linearly with POC concentrations, or that mineralization efficiency increases (i.e., that the proportion of POC that is remineralized increases)?

Upon feedback from both reviewers, to clarify we will change this section from line 423 to 427 to 'The upper estuary POC in late spring and summer tripled since the onset of the recovery state in 1997, which we suggest is driven largely by allochtonous POC produced in the Elbe River and autochthonous POC produced in the upper estuary. Abril et al. (2002) reported that POC mineralisation efficiency (i.e., the percentage of POC mineralized) is a linear function of POC concentration, and considering the increased POC concentration, we can expect a higher turnover of POC in the estuary in recent years. That is, from 1997 to 2020, the increase in POC in the upper estuary enhanced the availability of POC for remineralisation, and subsequently increased DIC production, as was observed in the increase in DIC concentration in the Elbe Estuary (Fig 3).'

Table 3.2: it would be helpful to include the standard error of the slope.

We will include the standard error of the slope for DIC and TA in Table 1.

Figure 4: it is somewhat confusing to use the designation “m-1” as this is much more commonly used to indicate per meter. Perhaps “mon-1” would be the better abbreviation for monthly values?

Thank you for highlighting this. We will change the unit to mon^{-1} in the figure and month^{-1} in text.