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.

Rewrie et al. (2023) investigated the variations in biogeochemical parameters, including DIC, POC, DO, and pH, in the Elbe Estuary over a long time period of 23 years. They discovered a significant long-term increase in DIC in the Elbe Estuary, which might be primarily influenced by a rise in POC content in the upper estuary. The researchers suggest that the increased internal load of DIC during the drought period can be attributed to an extended residence time in the estuary, allowing for a longer period of POC remineralization. The manuscript highlights the correlation between POC in the upper estuary and DIC in the mid and lower estuary, which may provide valuable insights for understanding DIC variations driven by climate change and human-induced disturbances. However, I have several concerns regarding the manuscript, and I hope the authors will carefully consider them.

Main comments

1.The authors have solely examined the correlation between POC data in the upper estuary and DIC concentrations in the mid and lower estuary. Including POC data from the mid and lower estuary in the manuscript would offer a clearer understanding of the relationship between POC and DIC. Additionally, while the authors have provided a preliminary estimate of inorganic carbon export, they have not thoroughly discussed

other potential factors influencing inorganic carbon export. I am curious about the relationship between dissolved organic carbon (DOC) and DIC in the Elbe Estuary. Since labile DOC can also be consumed by microbes, it may contribute to the DIC pool. I recommend the authors add some discussions on the correlations between DOC and DIC.

We thank the reviewer for this suggestion to include DOC.

We will include a reference in the introduction describing the respiration of organic carbon in the Elbe Estuary. For example after 'During the current recovery state, the annual mean DIC in the mid to lower Elbe Estuary has increased significantly by up to 11 µmol L^{-1} yr^{-1} from 1997 to 2018 (Rewrie et al., in press), but the source of this increase remains unclear.' We will include '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.'

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.

2. The authors utilized the CO2SYS program to calculate TA and pCO2 using DIC and pH as input parameters. However, it should be noted that the TA model in the CO2SYS program does not account for the contribution of organic alkalinity. Previous studies have reported significant concentrations of organic alkalinity (ranging from 10 to 70 umol kg^{-1}) in rivers and estuaries. Ignoring the presence of organic alkalinity in the calculated TA values may introduce substantial uncertainties. Therefore, I recommend that the authors include discussions addressing the uncertainties associated with the calculated TA values.

Thank you for this recommendation. We will include a discussion to compare the calculated TA and the available DOC measurements (from FGG Elbe data portal) with previous studies that describe organic alkalinity. The discussion example is; 'The CO2SYS program does not account for contribution of organic alkalinity in the calculated TA. Organic alkalinity can constitute a smaller fraction to TA compared to that provided by the inorganic compounds however, it could be a significant component of TA in systems influenced by dissolved organic matter inputs (Voynova et al., 2019). Mean DOC and TA in the Elbe Estuary (z1-z7) were respectively 498 ± 92 µmol kg^{-1} and 1985 ± 309 µmol kg^{-1} for the entire record (1997-2020, not shown). Similar TA concentrations (< 2200 µmol kg^{-1}), but slightly lower DOC (< 450 µmol kg^{-1}), were observed in an intertidal saltmarsh in the northeast USA. Song et al. (2020) reported the organic TA fraction contributed 0.9-4.3% of the TA, and thus only a minimal amount. In contrast, Hunt et al. (2011) reported a 21-100% contribution of organic alkalinity to TA, with much lower TA (116 µM to 956 µM) and extremely high DOC, up to 1480 µmol L^{-1}, in 15 rivers of northern New England (USA) and New Brunswick (Canada). Kuliński et al. (2014) reported the much lower TA in the river could explain the larger organic alkalinity contribution. Thus, it is likely organic alkalinity constituted a small fraction of the TA in the Elbe Estuary. There were changes in DOC along the upper to mid-estuary, with OC changes in percentage ranging between -124% and 21% in zones 2 to 5 between 1997 and 2020 (reference to OC removal figures and DOC concentration along the estuary). This indicates the potential contribution of DOC to organic alkalinity along the upper to mid Elbe Estuary. In the lower to outer estuary, there were positive non-conservative mixing of DOC along the salinity gradient and this may

have influenced production of organic alkalinity. However, in order to determine the amount of organic TA contributing to overall TA, the difference between calculated and measured TA or direct measurements organic alkalinity are required. In future studies, where both measured and calculated TA are available, we suggest the organic alkalinity influence on TA in the Elbe Estuary should be assessed.'

Hunt, C. W., Salisbury, J. E., & Vandemark, D. (2011). Contribution of non-carbonate anions to total alkalinity and overestimation of pCO 2 in New England and New Brunswick rivers. Biogeosciences, 8(10), 3069-3076.

Kuliński, K., Schneider, B., Hammer, K., Machulik, U., & Schulz-Bull, D. (2014). The influence of dissolved organic matter on the acid–base system of the Baltic Sea. Journal of Marine Systems, 132, 106-115.

Song, S., Wang, Z. A., Gonneea, M. E., Kroeger, K. D., Chu, S. N., Li, D., & Liang, H. (2020). An important biogeochemical link between organic and inorganic carbon cycling: Effects of organic alkalinity on carbonate chemistry in coastal waters influenced by intertidal salt marshes. Geochimica et Cosmochimica Acta, 275, 123-139.

Voynova, Y. G., Petersen, W., Gehrung, M., Aßmann, S., & King, A. L. (2019). Intertidal regions changing coastal alkalinity: The Wadden Sea-North Sea tidally coupled bioreactor. Limnology and Oceanography, 64(3), 1135-1149.

3.This manuscript extensively references a paper (Rewrie et al., in review) that is currently under review. It is generally not considered appropriate to rely heavily on the findings of a paper that is still undergoing the review process. Additionally, it seems there is a high correlation between that paper and the current manuscript. It would be helpful if the authors could provide an introduction outlining the differences and commonalities between this manuscript and the paper they have cited (Rewrie et al., in review) in the response to reviewers.

We have explained the Rewrie et al. (2023) manuscript above.

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., in review), 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., in press), 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).'

We will change the second aim to be specific '(2) investigate how the onset of the recent drought has modulated the carbon cycling within the estuary.'

4.The authors have utilized potentiometric pH and DIC measurements to calculate pCO2. However, it is important to note that potentiometric pH measurements may introduce significant uncertainties when measuring pH in saline waters. What is the salinity of the samples collected in the outer estuary? The authors should take into consideration this potential source of uncertainty in their analysis and discussion.

On line 160, we applied the recommended total standard uncertainty for pH of 0.01 units. This error was also suggested in Dickson (1993). We will include this reference as well.

Dickson, A. G. (1993). The measurement of sea water pH. Marine chemistry, 44(2-4), 131-142.

Minor comments

Abstract:

L.25 Is it possible that a portion of the gained DIC can be attributed to the degradation of DOC?

We believe DIC gained by respiration of DOC is negligible compared to POC remineralization as answered above.

Introduction:

L.55 “source”?

Thank you for highlighting this. We will change this to ‘source’.

L.45-60 Why do the authors use "OM" and "POC" interchangeably in this paragraph? Does "OM" include DOC?

Our aim was not to use OM and POC interchangeably. We wanted to highlight that organic carbon was a form of organic material as highlighted on lines 52-53 ‘This phytoplankton generated organic matter (OM) input’

To clarify we are referring to organic carbon in the paragraph and upon feedback from the Referee_1, we will change the sentence 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’.

We will change the sentence on line 57 to ‘This reduces labile OM export to the adjacent coastal waters (Abril et al. 2002; Crump et al., 2017; Sanders et al., 2018)’.

L.55 I suggest that the authors include an introduction discussing the contribution of DOC degradation to DIC.

We will include a reference in the introduction describing the respiration of organic carbon in the Elbe Estuary as answered above.

Method:

L.150 Please add a reference for the CO2SYS program.

We will include the reference (Lewis and Wallace, 1998) after ‘Using the CO2SYS program version 2.5 in Excel’.

L.130 what is the precision of pH, DOC, and DIC measurements?

We will provide the significant digits/indication of results in Table S1.

L.190 “from May to August”?

The correction factor was related to the monthly river discharge. To clarify, we will change the sentence to ‘A correction factor to the monthly river discharge was applied to each estuarine zone (zones 1 to 6) to account for tributary inputs along the estuary (Amann et al., 2015).’

L 220 In the study of an estuary, why did the authors use a Schmidt number (Sc) in freshwater? The gas transfer velocity parameter (k) described by Wanninkhof (2014) is generally applicable to the open ocean.

The flux of CO_2 between water and atmosphere was calculated for zones 1 to 6. For the entire record (1997-2020) the mean salinity in zone 6 was 11 ± 5 psu and for zones 1 to 6 was 2 ± 4 psu. In Wanninkhof (2014) the coefficients for the Schmidt number for seawater is for 35 psu. Therefore, due to the relatively lower salinity range in the Elbe Estuary we applied the freshwater Schmidt number. We decided to use a Schmidt number (Sc) in freshwater to also allow for comparisons of the calculated flux of CO_2 between water and atmosphere with published studies on the Elbe Estuary (Norbisrath et al. (2022) and Amann et al. (2015)).

We did not compare different approaches to calculate k as the aim was to provide a tentative evaluation of the overall inorganic carbon export as stated on lines 380. To clarify this in the methods on line 201 we will include (italic) ‘*To tentatively estimate the inorganic carbon export dynamics*, the flux of CO_2 between water and atmosphere in mol m^{-2} d^{-1} was estimated for each sampled station, in the upper to lower region (*z1-z6*, Fig. 1a), between 1997 and 2020 with the equation.’

Even though we have not used a correction factor for the k calculation (such as in Volta et al. 2016), the mean air-water CO_2 flux (21 ± 6 mol C m^{-2} yr^{-1}, 1997-2020) places the Elbe Estuary within flux estimates for North Sea tidal estuaries and specifically the Elbe Estuary of 27.4 mol C m^{-2} yr^{-1} (Volta et al. 2016). As requested by the other reviewer we will include the air-water CO_2 flux in both mol C m^{-2} yr^{-1} and Gmol yr^{-1}.

Result:

L.285 How does the physical mixing between freshwater and seawater influence DIC in the outer estuary?

In May to August, we found positive and negative non-conservative mixing in DIC along the salinity gradient in 43% and 23% of the assessed months between 1997 and 2020. This was not included in the manuscript however, we acknowledge that the non-conservative mixing plots would support our findings that DIC production can occur in the lower to outer estuary. We will include the DIC along the salinity gradient in May to August from 1997 to 2020 in the supplementary material to show that we do observe DIC production and consumption and include this in our results and discussion. As written in the submitted article on line 630 we believe a site-specific study would better explain the DIC consumption and production in this region.

Fig.2a is difficult to read. Add the legend into the plot may be better.

We will include the legend in the plot to make it clearer for the reader.

L. 345 Why "*Such dominating heterotrophy in recent years (2018–2020) and DIC generation in the upper region (z1), would subsequently reduce the internal DIC load in the mid to lower estuary*"?

We wanted to identify the difference between DIC in the upper and mid estuary would be lower because DIC was produced in the upper estuary and therefore higher concentrations in the upper region. A smaller difference between DIC concentration in the upper and mid-estuary indicates a smaller difference between DIC loads. Therefore, a lower internal DIC load in the mid to lower estuary.

To clarify we will revise this sentence to 'The dominating heterotrophy in recent years (2018–2020) and subsequent DIC generation in the upper region (z1) could reduce the difference between the DIC load in the upper and mid estuary. In turn, reducing the internal DIC load in the mid to lower estuary (Fig. 4).'

Discussion:

L.420 According to this sentence, the author has identified a correlation between POC and DIC in another manuscript that is currently under review. I am curious about the differences between this manuscript and the one mentioned. The main focus of this manuscript appears to be the role of POC in the upper estuary in driving DIC increase in the mid and lower estuary. If this point has already been addressed in the author's other manuscript, it may not be appropriate to emphasize it again in this manuscript.

Thank you for highlighting this. To clarify Rewrie et al. had only identified a significant increase in the annual mean DIC in the mid-lower estuary. Therefore, we will remove 'identified by Rewrie et al. (in review).'

L.425 Please revise this sentence. It is not complete.

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).'

L.430 I don't believe that the statement "*there are no other major sources of carbon along the estuary (Abril et al., 2002)*" can directly suggest that POC was efficiently remineralized and converted to DIC by the mid-estuary. The role of DOC in this process should also be considered. It is important to investigate the potential contribution of DOC to DIC through remineralization processes in the mid-estuary.

As requested by both reviewers we would discuss the potential contribution of DOC by calculating the removal of OC for both DOC and POC (please find a further elaborated answer in the beginning of this response).