Supplementary

This file contains:
Supplemental methods
M1
M2

Supplementary figures S1 to S5
Supplementary table S1 reference to the csv file

1 CO_2 efflux calculation

1.1 pCO_2 calculation

The historical pCO_2 in the Elbe River has been calculated by the CO2SYS (Lewis and Wallace, 1998), due to the availability of major ions data. The reliability of CO2SYS was demonstrated in the research of Ran et al. (2021), by the comparation with in situ measurement pCO_2 data. Previous research in the Elbe estuary highlights differences between Phreeqc (Parkhurst and Appelo, 1999) and CO2SYS (Amann et al., 2014). Consequently, a comparative analysis of these two methods was conducted. The results show good agreement, while the CO2SYS could slight overestimate compare to those derived from Phreeqc.

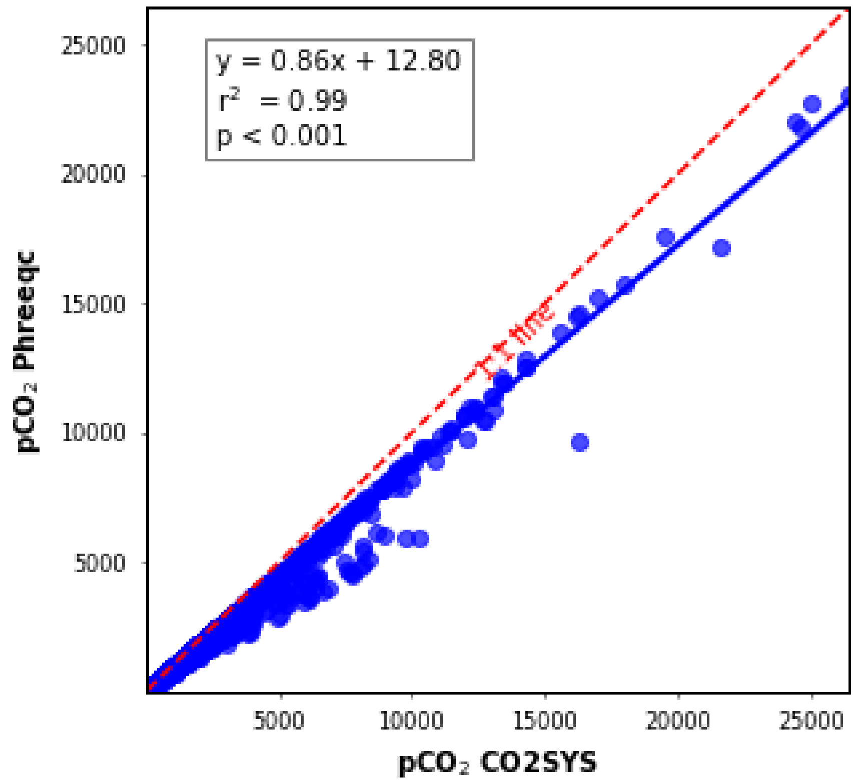

Figure S4, Comparison of calculated pCO_2 by CO2SYS and Phreeqc. The red dashed line is 1:1 line and the blue line is the regression including 95% confidence interval (95%CI)

1.2 Data quality of MERIT-HYDRO

For the quality of flow discharge data from MERIT-Hydro (Lin et al., 2019; Yamazaki et al., 2019), we compare it with the daily observation from 10 hydrological stations in the Elbe River. The results show an overestimation of around 27.5 % between the GRADES and observation flow discharge especially in monthly and annual scales (r^2 = 0.80, p <0.001).

Our method for scale gas transfer velocity was from Raymond et al. (2013). The slope for modeling each equation of this research were from NHDplus dataset developed by USGS. Liu et al. (2022) manually identify ~ 500 locations and compared with the dataset of NHDplus slope and GRADES dataset, found the consistent of two datasets. Therefore, we also applied the slope results of GRADES for our estimation CO_2 emissions in higher stream orders while the 1^{st} order estimated from EU-Hydro-River Network Database Version 1.3, and the EU-DEM v1.0 dataset (EEA, 2022).

1.3 water surface area calculation

Water surface area of the Elbe River was scaled through river length and river width reference to three products of the river network of EU-Hydro, HydroRIVERS (Lehner and Grill, 2013), and MERIT-Basins . By the comparation of three different rivers network maps, we found that the MERIT-Basins and HydroSHEDS have a similar river network structure and Strahler orders. Previous studies showed that the HydroSHEDS usually underestimates the 1^{st} Strahler order (Raymond et al., 2013) while the EU-Hydro-River dataset could be more representative of the observed river network.

Therefore, the length of the Elbe River within different Strahler orders was calculated by MERIT-Hydro in higher Strahler orders while the 1^{st} order was by the EU-Hydro-River. Totally, 3250 river reaches with 41,548,000 discharge data was extracted from GRADES for the scale of the annual water surface area of the Elbe River. Besides, we estimate the width of the 1^{st} order from the Log relationship between stream order and river width from higher orders.

The river width was calculated by the equation from Raymond et al. 2012 (Ln width= 0.423 × Ln Q + 2.56). The annual flow discharge was also resampled from the daily GRADES discharge, in combination with the river length from the MERIT-Basins dataset. Finally, we calculated an annual average total surface area of the Elbe River was 735±57 km^2 from 1984 to 2018, accounting for about 0.5 % of the basin area (Table S1).

1.4 $F_{CO2total}$ estimation

Rivers with a low Strahler order often contribute more to CO_2 emissions than high order rivers. This is because they have a larger water surface area, are closer connection to the soil, and have more turbulence due to a steeper slope (Butman and Raymond, 2011; Marx et al., 2017; Ran et al., 2021). Therefore, significant underestimations of the emissions could result from the use of only points in the high order rivers to calculate CO_2 emission for the entire basin.

To estimate emissions from high order rivers (Strahler orders 6, 7, and 8), the annual water surface area and average annual F_{CO2} from 1990 to 2018 were used. It was calculated that the highest order rivers released 0.31±0.27 Tg C yr^{-1} between 1984 and 2018.

To estimate CO_2 emissions from medium order rivers (Strahler orders 4,5), the percentages from Butman and Raymond (2011) and Ran et al. (2021) were applied, which showed that these rivers constituted 13% and 29% of the total river network, respectively. The CO_2 efflux data from the high order rivers were then used to estimate the emissions from the medium order rivers.

For the small rivers (Strahler orders 1,2,3), it was assumed that CO_2 emissions have not changed since the 1990s due to the relatively low impact of human activities on these rivers. During the estimation, the CO_2 emissions from 2018 was identified as the year with the lowest human impact. The CO_2 emission of 0.7 Tg C yr^{-1} was applied for the reference value of small rivers of the Elbe River. Finally, the estimation shows that CO_2 emissions from the Elbe rivers were 1.3 ± 1.3 Tg C in 2018. This is much lower than before 1990 (3.6 ± 1.5 Tg C), but it's still 3.5 times the DIC loads to the Elbe estuary (Figure 3a).

2. Loads estimation

The fluxes of dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), and particulate organic carbon (POC) were scaled from the 1990s to 2018 in the Elbe River at Geesthacht station to serve as a basis for comparison with CO_2 efflux. The carbon loads to the Elbe estuary were calculated using two curve-fitting methods.

The first method was based on the segmented log-log relationship between concentration (C) and instant flow discharge (Q) (Bakhmeteff, 1912). The datasets were divided into two segments using the median Q value, denoted as b50inf (when $Q < Q_{median}$), and b_{50sup} (when $Q > Q_{median}$) (Meybeck and Moatar, 2012). The second estimation was conducted using LOADEST, which incorporates nine different models, including the log-log relationship (Runkel et al., 2004). The software automatically selected the best model based on residual values.

In the comparison of these two methods, our analysis revealed that both approaches showed promising linear relationships (Figures S4). Therefore, we determined the average value as the final result for estimating the annual load to the coastal region.

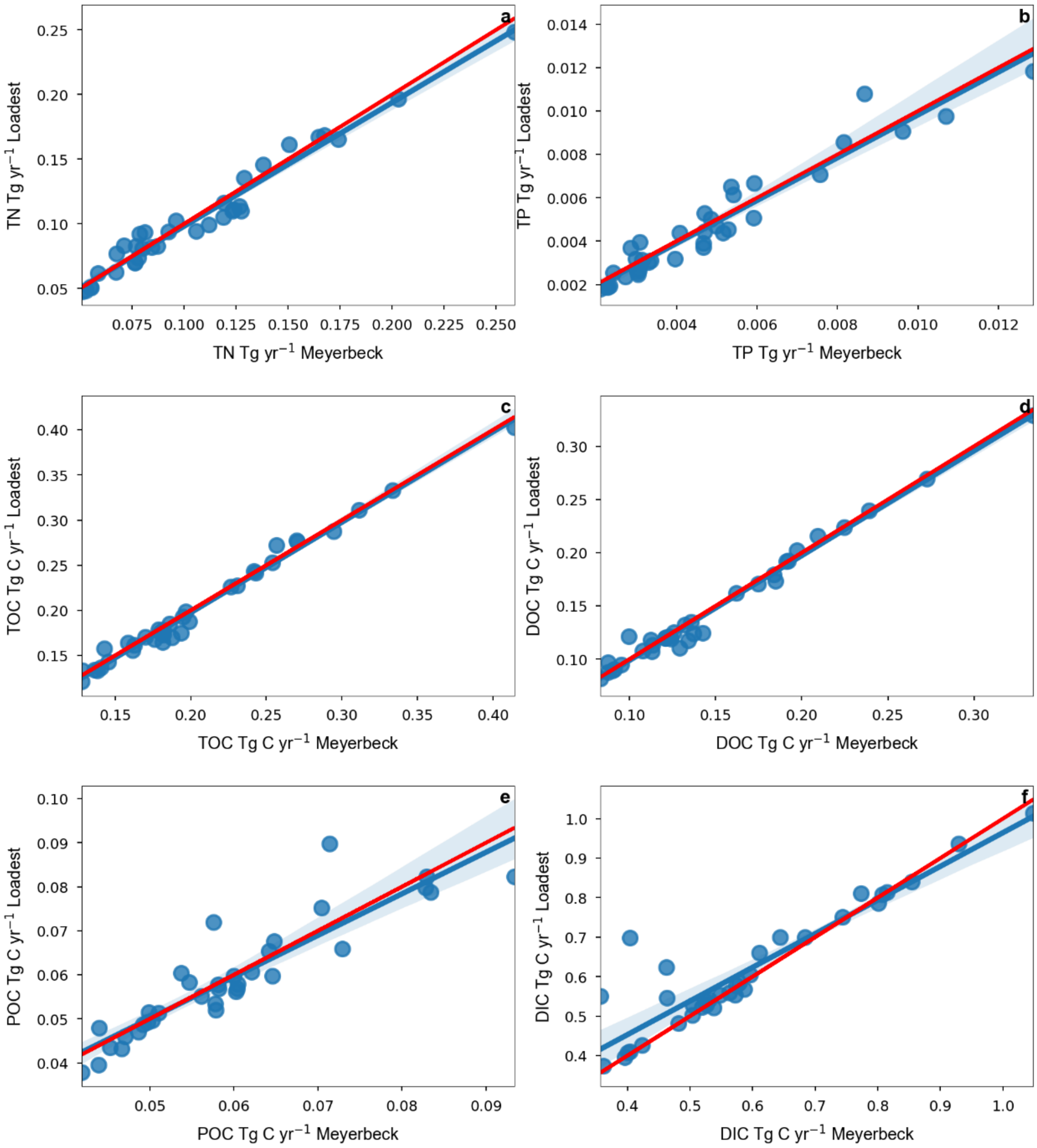

Figure S5 Comparation of different load calculation methods (x: Meybeck and Moatar; y: Loadest)

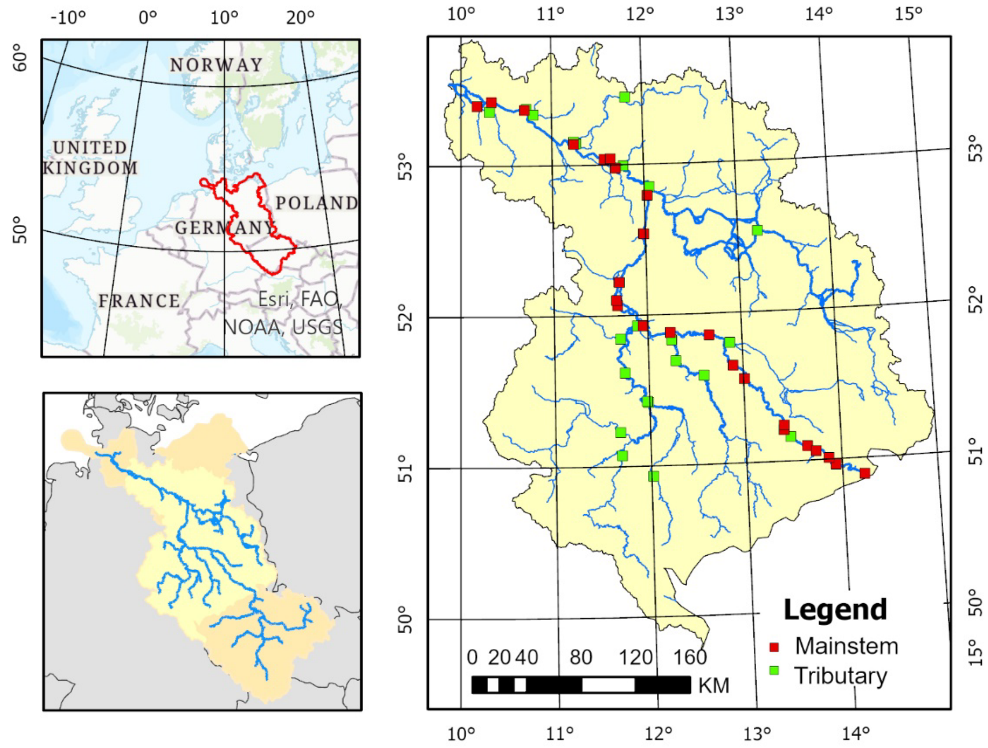

Figure S1 locations of the sample stations in the Elbe River

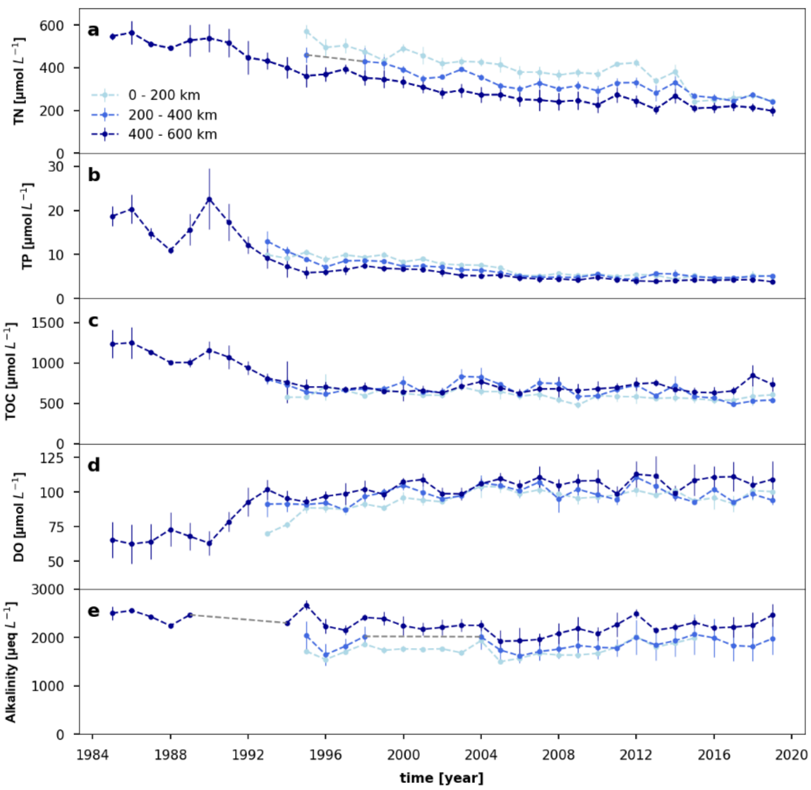

Figure S2 Long term trends in water quality in the Elbe from the 1990s to 2018: (a) TN, (b) TP, (c) TOC, (d) DO%, (e) Alkalinity. Values are annual mean with standard deviation indicating spatial variations within mainstem. The red/green/blue dots represent the distance of 0-200/200-400/400-600 km to Germany/Czech boundary.

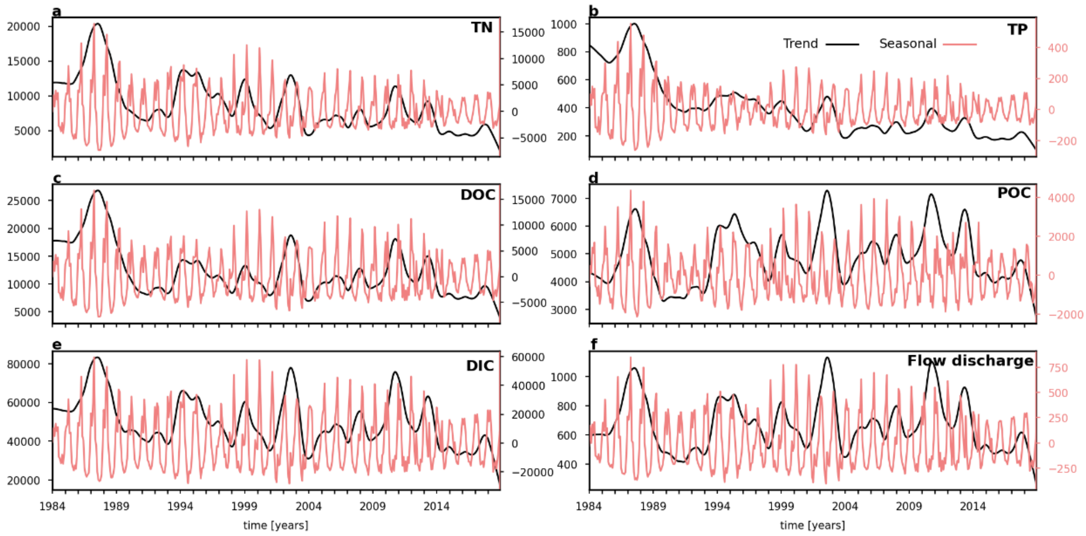

Figure S3, Seasonal decomposition of monthly sum loads of: (a)TN (10^4-ton month^{-1}); (b)TP (10^4-ton month^{-1}); (c)DOC (10^4-ton month^{-1}); (d) POC (10^4-ton month^{-1}), (e) DIC (10^4-ton month^{-1}), and (f) Flow discharge (m^3 s^{-1}); where the black line represents the trends after seasonal decomposition, the coral line represents the seasonal components after seasonal decomposition

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