Supplement of

Recent inorganic carbon increase in a temperate estuary driven by water quality improvement and enhanced by droughts

Ecosystem parameters

The analytical measurement methods for the ecosystem parameters with the respective German Institute for Standardisation methods are listed in Table S1. Since 1997, specifications were reported and available (since 2004) on the International Commission for the Protection of the Elbe River website (IKSE, www.iksemkol.org). The FGG Elbe acquired surface water samples from 36 stations in the estuary by helicopter at ebb current (ARGE Elbe, 2000), and sampling was generally completed in February, May, June, July, August and November (see Rewrie et al. (in review) for a detailed description on the FGG Elbe sample collection program and methods). However, in some years there were exceptions. Instead of February, January 2020 and March 2009-2011 were sampled. Instead of November, December 1998-2019 were sampled. In 2010, samples were collected on 01.06.2010 and 30.06.2010, and the latter was used to represent July 2010.

DIC concentrations were derived during the analysis of dissolved organic carbon (DOC). Rewrie et al. (in review) provides an extensive overview on the FGG Elbe DIC measurements used in this study, and comparisons to other conventional DIC methods of analysis. To determine particulate organic carbon (POC), the difference between TOC and DOC was calculated, with an estimated uncertainty of 20% (Wiegel, pers. comm). See description of the organic carbon method in Table S1, along with methods for DIC, TOC, DOC, dissolved oxygen (DO), pH, BOD_7.

Table S1. Methods for determination of ecosystem parameters included in the present study. Analyses were conducted according to the German industry standards (DIN).

Parameter	Description	Units	DIN
Conductivity	Platinum probe	$mS\ m^{-1}$	DIN EN 27888-C8
Temperature	Resistance thermometer	°C	DIN 38404-C4-2
DO	Oxygen membrane probe	$mg\ L^{-1}$	DIN EN 25814-G22
pH	Potentiometrically with glass electrode		DIN 38404-C5
TOC, DOC, DIC	Catalytic high-temperature oxidation, CO_2 detection via IR detector	$mg\ L^{-1}$	DIN 38409-H3-1, DIN EN 1484-H3
BOD_7	Oxygen probe	$mg\ O2\ L^{-1}$	DIN EN 1899-2 (H52)
SPM	Vacuum Filtration on Glass fiber filter (Whatman GF/F, 0.45µm)	$mg\ L^{-1}$	DIN 38409-H2-3

The apparent oxygen utilisation (AOU) was calculated;

$$AOU = [O_{2eq}] - [O_2] \ , (S1)$$

Where $[O_2]$ is the DO concentration observed and $[O_{2eq}]$ is the DO concentration expected at equilibrium with air at an Absolute Pressure of 101325 Pa (sea pressure of 0 dbar) including saturated water vapour. The function uses the solubility coefficients derived from Benson and Krause (1984), and as fitted by Garcia and Gorden (1992, 1993) in Matlab.

Calculations of carbon loads in the Elbe Estuary

Loads (L) of POC in Gmol C month^{-1} in zone 1 and DIC in each zone were calculated by:

$$L = Q \times [Param] \ , (S2)$$

where Q was the respective mean monthly river discharge ($m^3\ s^{-1}$) and [Param] is the concentration of DIC or POC. The Q was based on Neu Darchau discharge, with an applied correction factor for each zone in the estuary (Amann et al., 2015) to account for additions from tributaries along the estuary. Error bars indicate the standard deviation (σ) of the product:

$$\sigma_{(L)} = \sqrt{\left(\frac{\sigma_{[DIC]}}{[DIC]}\right)^2 \times \left(\frac{\sigma_Q}{Q}\right)^2} \ \times L \ , (S3)$$

The difference in DIC loads ($\Delta DIC_{(L)}$) between the upper region (z1) and the mid and lower region (z4-z6, represented by zi) were calculated for each month to represent the internal DIC load:

$$\Delta DIC_{(L)} = L_{(zi)} - L_{(z1)} \text{, (S4)}$$

Negative values indicate DIC loss within the estuary, while positive values indicate DIC gain. Error bars indicate the standard deviations (σ) of the difference.

$$\sigma_{\Delta DIC(L)} = \sqrt{\sigma^2_{L(zi)} + \sigma^2_{L(z1)}} \text{, (S5)}$$

Uncertainty for $pCO2$ and TA

The median of the calculated uncertainty output from the CO2SYS program for pCO_2 was 209 µatm (18% uncertainty relative to the mean pCO_2) and for TA was 100 µmol kg^{-1} (5% uncertainty relative to the mean TA) in the Elbe Estuary (z1-z7) between 1997 and 2020 (Table S2).

Table S2. The mean (± standard deviation, σ) and median of the combined standard uncertainty (u_c) for pCO_2 in µatm and TA in µmol kg^{-1} in zones 1-7

Parameter	u_c mean (± σ)	u_c median
pCO_2	268 ± 205	209
TA	109 ± 28	100

Comparing calculated TA and pCO_2 with respective uncertainty output and measured TA and calculated pCO_2 by Amann et al. (2015) between 2009 and 2011 we find a good fit between the datasets, with an example of August 2010 shown in Fig. S1 for the Elbe Estuary.
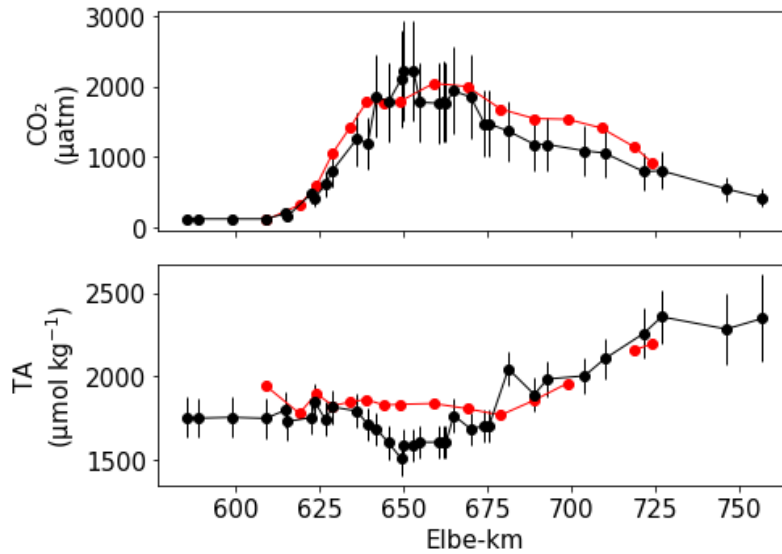
Fig. S1. Calculated pCO_2 and TA (black) with the uncertainty as error bars in August 2010. Calculated pCO2 and measured TA (red) from Amann et al. (2015) in August 2010.

To compare calculated TA and pCO_2 with measured TA and calculated pCO_2 in Norbisrath et al. (2022), the mean of TA and pCO2 in the Elbe Estuary was calculated in regions assigned by Norbisrath et al. (2022) for June 2019 (Table S3). To account for the respective uncertainty for each calculated TA and pCO_2 measurement the pooled uncertainty (Pu) was calculated, assuming equal sample size between each calculated measurement:

$$P_u = \sqrt{\frac{u_1^2 + u_2^2 + \dots + u_k^2}{k}} \text{, (S6)}$$

Where u is the uncertainty given for each calculated measurement and k is the number of samples in each group.

Table S3. The mean (± standard deviation (σ)) for measured TA in µmol kg⁻¹ and calculated pCO_2 in µatm from Norbisrath et al. (2022) in June 2019. The mean and the pooled uncertainty (Pu) for calculated TA in µmol kg⁻¹ and pCO_2 in µatm from the present study (Rewrie et al.) in June 2019.

Box (Elbe km)	Norbisrath et al. (2022)		Rewrie et al.			
	TA (µmol kg⁻¹)	pCO_2 (µatm)	TA (µmol kg⁻¹)		pCO_2 (µatm)	
			Mean	Pu	Mean	Pu
1 (586-620)	1289 ± 8	465 ± 341	1667	103	575	207
2 (621-640)	1512 ± 40	2074 ± 488	1587	99	2178	704
3 (641-665)	1630 ± 42	1833 ± 120	1668	99	1811	558
4 (666–695)	1733 ± 35	1554 ± 210	1817	101	1130	313
5 (696 – 712)	1879 ± 21	713 ± 208	1897	114	830	249
6 (713 – outer region (approx. 757))	Max 2449		2222	189		

Air-water CO_2 exchange

To compare calculated air-water CO_2 flux estimates with previously calculated air-water CO_2 flux estimates in Norbisrath et al. (2022), the mean air-water CO_2 flux in the Elbe Estuary was calculated in regions assigned by Norbisrath et al. (2022) for June 2019. We find a good fit with air-water CO_2 flux estimates to those calculated in Norbisrath et al. (2022) shown in Table S4.

Table S4. Mean (± standard deviation) air-water CO_2 flux estimates in mmol m⁻² d⁻¹ for June 2019 in the Elbe Estuary calculated by Norbisrath et al. (2022) and in this study (Rewrie et al.). The regions (Box 1-5) were defined in Norbisrath et al. (2022).

Box (Elbe km)	Norbisrath et al. (2022) air-water CO_2 flux estimates (mmol C m⁻² d⁻¹)	Rewrie et al. air-water CO_2 flux estimates (mmol C m⁻² d⁻¹)
1 (586-620)	2 ± 14	7 ± 12
2 (621-640)	68 ± 22	79 ± 13
3 (641-665)	59 ± 5	67 ± 13
4 (666–695)	38 ± 11	40 ± 8
5 (696–712)	9 ± 6	28 ± 12

Biological oxygen demand over 7 days (BOD$_7$) in the Elbe Estuary

To obtain an overview of the ecosystem the biological oxygen demand over 7 days (BOD$_7$) was plotted for each zone (Fig. S2).
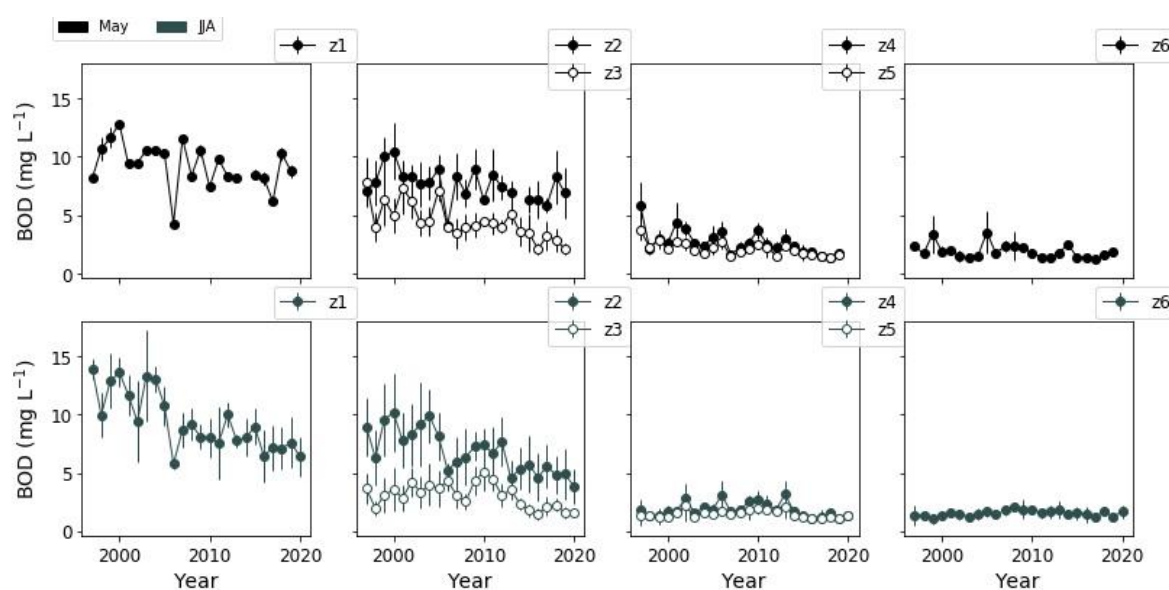
Fig. S2. Mean biological oxygen demand over 7 days (BOD_7) in late spring (May) and summer (June-August (JJA)) for each zone in the upper (z1-z3), mid (z4-z5) and lower (z6) estuary. Errors bars represent the standard deviation of the mean. In zone 1, the Pearson Correlation Coefficient was applied to BOD_7 over time, with a significant decrease in May (r=-0.39, p < 0.10) and summer JJA (r=-0.79, p<0.05).

Along-estuary DIC gain in mid-lower estuary and POC in upper estuary

The statistical difference between the POC concentrations in z1 and the along-estuary DIC gain in zones 4-7 was assessed. The Shapiro-Wilk test was used to determine normality of the dataset and the Bartlett's test was applied to test for equality of variances between the groups that were compared. All datasets (excl. z4 in May) presented a normal distribution and homogeneity of variance between the comparative groups (excl. JJA z4-z7), and therefore the independent t-test was applied to test the statistical difference between the means (Table S5-S6). In summer (JJA) in zones 4 to 7, the variances between along-estuary DIC gain in zones 4-7 and POC concentration in z1 were unequal and therefore the Welch's t-test was applied, which does not assume equal population variance. The Mann-Whitney U Test was applied to the datasets that presented non-normal distribution (z4 in May), and compared the medians of the data (Table S5 & S7).

Table S5. Tabulated p values for the independent t-test and Welch's t-test comparing the means (Table S6) and Mann-Whitney U test (#) comparing the medians (Table S7) for the POC concentration in zone 1 (z1) with the along-estuary DIC gain (ΔDIC) in the mid-outer estuary in late spring (May) and summer (June-August, JJA) between 1997 and 2020. Data for May from 1997-2019.

		ΔDIC			
	Month	z4	z5	z6	z7
POC in z1	May	(#) 0.00	0.16	0.07	0.21
	JJA	0.02	0.74	0.07	0.01

Table S6. The mean (± standard deviation of the average for each zone between 1997 and 2020) for the POC concentration in zone 1 (z1) and the along-estuary DIC gain (ΔDIC) for late spring (May) and summer (June-August, JJA) between 1997 and 2020. Data for May from 1997-2019.

	POC (μmol kg^{-1})	ΔDIC (μmol kg^{-1})			
	z1	z4	z5	z6	z7
May	377 ± 165	158 ± 207	286 ± 247	272 ± 209	296 ± 208
JJA	347 ± 94	247 ± 171	359 ± 155	425 ± 180	475 ± 205

Table S7. The median for the POC concentration in zone 1 (z1) and the along-estuary DIC gain (ΔDIC) for late spring (May) and summer (June-August, JJA) between 1997 and 2020. Data for May from 1997-2019.

	POC (μmol kg^{-1})	ΔDIC (μmol kg^{-1})			
	z1	z4	z5	z6	z7
May	359	106	251	236	309
JJA	351	257	371	411	496

River discharge as a driver of DIC changes in the Elbe Estuary

The statistical difference between river discharge in 1960-2020 and in 2014-2020 was assessed using the Mann-Whitney U Test (Table S8), as both datasets presented a non-normal distribution from the Shapiro-Wilk test (p < 0.05).

Table S8. The median for the long-term river discharge period (1960-2020) and the recent low river discharge period (2014-2020), compared using the Mann-Whitney-U-test with the p value.

River discharge (m^3 s^{-1})		Mann–Whitney U
1960-2020	2014-2020	test (p value)
555.0	406.0	0.00

The statistical difference between the internal DIC load in the non-drought (1997-2013) and drought (2014-2020) period was assessed. The Shapiro-Wilk test was used to determine normality of the dataset and the Bartlett's test was applied to test for equality of variances between the groups that were compared. All datasets (excl. May z5 1997-2013 and Jun z4 2014-2020) presented a normal distribution and homogeneity of variance of the comparative

groups, and therefore the independent t-test was applied to test the statistical difference between the means (Table S9-S10). The Mann-Whitney U Test was applied to the datasets that presented non-normal distribution (Table S9 & S11).

Table S9. Tabulated p values for the independent t-test comparing the means (Table S10) and the Mann-Whitney U Test (#) comparing the medians (Table S11) for the internal DIC load in monthly, May-August and summer (June-August, JJA), comparing the normal river discharge period (1997-2013) and the recent low river discharge period (2014-2020). August 2002, August 2010 and June-July 2013 were excluded as flood months. Data for May from 1997-2019.

Internal DIC load	May	Jun	Jul	Aug	May-Aug	JJA
z4	0.00	0.02 (#)	0.17	0.44	0.55	0.03
z5	0.00 (#)	0.12	0.03	0.30	0.23	0.01
z6	0.03	0.38	0.04	0.13	0.12	0.01
z4-z6	0.00	0.03	0.00	0.06	0.07	0.00

Table S10. Mean (± standard deviation of the average for each zone between 1997 and 2020) internal DIC load in the mid to lower (z4-z6) estuary in monthly, May-August and summer (June-August, JJA) during the normal river discharge period (1997-2013) and the recent low river discharge period (2014-2020) in Gmol C month^{-1}. August 2002, August 2010 and June-July 2013 were excluded as flood months. Data for May from 1997-2019.

Year range	Internal DIC load	May	Jun	Jul	Aug	May-Aug	JJA
1997-2013	z4	0.3 ± 0.17	0.5 ± 0.27	0.4 ± 0.31	0.3 ± 0.22	0.4 ± 0.26	0.4 ± 0.28
	z5	0.6 ± 0.21	0.7 ± 0.32	0.7 ± 0.29	0.4 ± 0.21	0.6 ± 0.28	0.6 ± 0.31
	z6	0.7 ± 0.24	0.8 ± 0.33	0.7 ± 0.32	0.5 ± 0.19	0.7 ± 0.29	0.7 ± 0.31
	z4-z6	0.5 ± 0.27	0.7 ± 0.32	0.6 ± 0.33	0.4 ± 0.23	0.6 ± 0.31	0.6 ± 0.32
2014-2020	z4	0.7 ± 0.16	0.3 ± 0.18	0.2 ± 0.24	0.2 ± 0.30	0.3 ± 0.28	0.3 ± 0.24
	z5	1.0 ± 0.21	0.5 ± 0.21	0.4 ± 0.24	0.3 ± 0.32	0.5 ± 0.34	0.4 ± 0.26
	z6	1.0 ± 0.18	0.7 ± 0.19	0.4 ± 0.22	0.4 ± 0.34	0.6 ± 0.33	0.5 ± 0.29
	z4-z6	0.9 ± 0.22	0.5 ± 0.24	0.4 ± 0.24	0.3 ± 0.31	0.5 ± 0.33	0.4 ± 0.28

Table S11. The monthly median (in Gmol C month^{-1}) internal DIC load in monthly, May-August and summer (June-August, JJA) during the normal river discharge period (1997-2013) and the recent low river discharge period (2014-2020). August 2002, August 2010 and June-July 2013 were excluded as flood months. Data for May from 1997-2019.

Year range	Internal DIC load	May	Jun	Jul	Aug	May-Aug	JJA
1997-2013	z4	0.2	0.6	0.5	0.2	0.4	0.5
	z5	0.6	0.7	0.6	0.3	0.6	0.6
	z6	0.7	0.8	0.7	0.5	0.7	0.7
	z4-z6	0.5	0.7	0.6	0.4	0.6	0.6
2014-2020	z4	0.7	0.3	0.3	0.2	0.3	0.3
	z5	1.1	0.5	0.4	0.4	0.5	0.4
	z6	1.0	0.7	0.5	0.5	0.6	0.5
	z4-z6	0.9	0.5	0.4	0.3	0.5	0.4

The statistical difference between the POC load in z1 and the internal DIC load in zones 4-6 in 1997-2020 was assessed. The Shapiro-Wilk test was used to determine normality of the dataset and the Bartlett's test was applied to test for equality of variances between the groups that were compared. The internal DIC load and the POC load in z1 in June and July z4, and August z4-z5, presented a normal distribution and homogeneity of variance between comparative datasets, and therefore the independent t-test was applied to test the statistical difference between the means (Table S12-S13). June and July z5-z6, and August z6, presented a normal distribution but the variances

between comparative datasets were unequal and therefore the Welch's t-test was applied. The Mann-Whitney U Test was applied to comparative datasets in May as datasets presented non-normal distribution (POC z1 in May), which compared the medians of the data (Table S13 & S14).

Table S12. Mean (± standard deviation of the average for each zone between 1997 and 2020) POC load in zone 1 (z1) and internal DIC load in the mid to lower (z4-z6) estuary from 1997 to 2020 in Gmol C month^{-1}. August 2002, August 2010 and June-July 2013 were excluded as flood months. Data for May from 1997-2019.

		May	Jun	Jul	Aug
	POC z1	0.6 ± 0.29	0.4 ± 0.17	0.4 ± 0.19	0.3 ± 0.16
Internal DIC load	z4	0.4 ± 0.24	0.5 ± 0.26	0.4 ± 0.30	0.3 ± 0.25
	z5	0.7 ± 0.28	0.7 ± 0.30	0.6 ± 0.30	0.4 ± 0.25
	z6	0.8 ± 0.25	0.8 ± 0.30	0.7 ± 0.32	0.5 ± 0.26
	Sum (z4-z6)	$\mathbf{1.78 \pm 0.25}$	$\mathbf{1.92 \pm 0.28}$	$\mathbf{1.60 \pm 0.30}$	$\mathbf{1.10 \pm 0.25}$

Table S13. Tabulated p values for the independent t-test and Welch's t-test comparing the means (Table S11) and the Mann-Whitney U Test (#) comparing the medians (Table S13) for the internal DIC load in the mid-lower estuary with the POC load in zone 1, in May-August between 1997 and 2020 (in May to 2019).

	Month	Internal DIC load		
		z4	z5	z6
POC load (z1)	May	0.00 (#)	0.14 (#)	0.00 (#)
	June	0.26	0.00	0.00
	July	0.61	0.02	0.00
	August	0.26	0.55	0.03

Table S14. Median POC load in zone 1 (z1) and internal DIC load in the mid to lower (z4-z6) estuary in Gmol C month^{-1} between 1997 and 2020 (in May to 2019). August 2002, August 2010 and June-July 2013 were excluded as flood months.

		May	Jun	Jul	Aug
	POC z1	0.6	0.4	0.4	0.3
Internal DIC load	z4	0.3	0.6	0.4	0.2
	z5	0.6	0.6	0.6	0.3
	z6	0.8	0.8	0.7	0.5

Recent DIC in Elbe Estuary

An example showing higher DIC concentrations in the upper estuary compared to mid estuary (July-August 2017, Fig. S3), potentially indicating DIC production in the upper estuary.
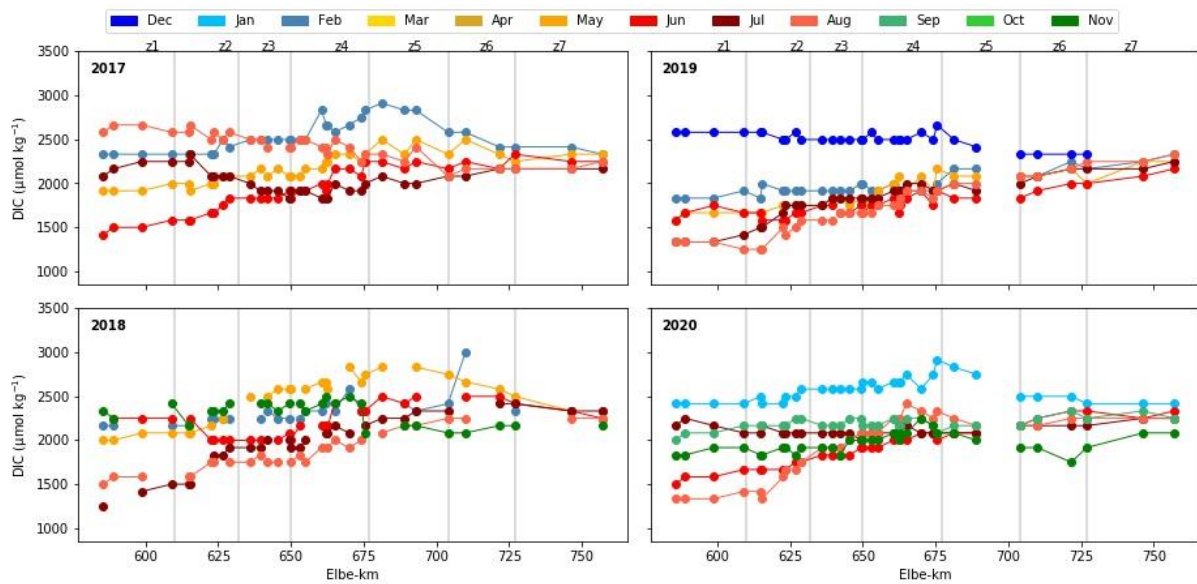
Fig. S3. DIC along the Elbe Estuary in 2017-2020. Vertical lines indicate the zonation of the Elbe Estuary from the TIDE project shown in Fig. 1a (Geerts et al., 2012).

Annual inorganic carbon export estimates

Table S15. Mean (± standard deviation, std) and median for the air-water CO_2 flux estimate and the DIC export in the Elbe Estuary in the non-drought (1997-2013) and the drought (2014-2020) period in Gmol C yr^{-1}. Tabulated p values for the independent t-test comparing the means (*) and the Mann-Whitney U Test ([#]) comparing the medians for air-water CO_2 flux estimate and DIC export in the non-drought (1997-2013) and the drought (2014-2020) period. Flood years of 2002, 2010 and 2013 were included (incl.) and excluded (excl.) from statisitcal tests.

	Non-drought (1997-2013)		Drought (2014-2020)		*p* value
	Mean (± std)	Median	Mean (± std)	Median	
DIC export (incl. flood years)	55 ± 14.0	50	38 ± 5.4	39	0.00[#]
DIC export (excl. flood years)	50 ± 6.4	49	38 ± 5.4	39	0.00*
Air-water CO_2 flux (incl. flood years)	6 ± 1.5	6	6 ± 1.9	5	0.22[#]
Air-water CO_2 flux (excl. flood years)	6 ± 1.6	6	6 ± 1.9	5	0.22[#]

POC as percent of SPM

POC in % of SPM represents the content of POC available for biological processing (Sullivan et al. 2001; Abril et al. 2002), and therefore the parameter can describe the mineralisation and production of POC (Fig. S4).
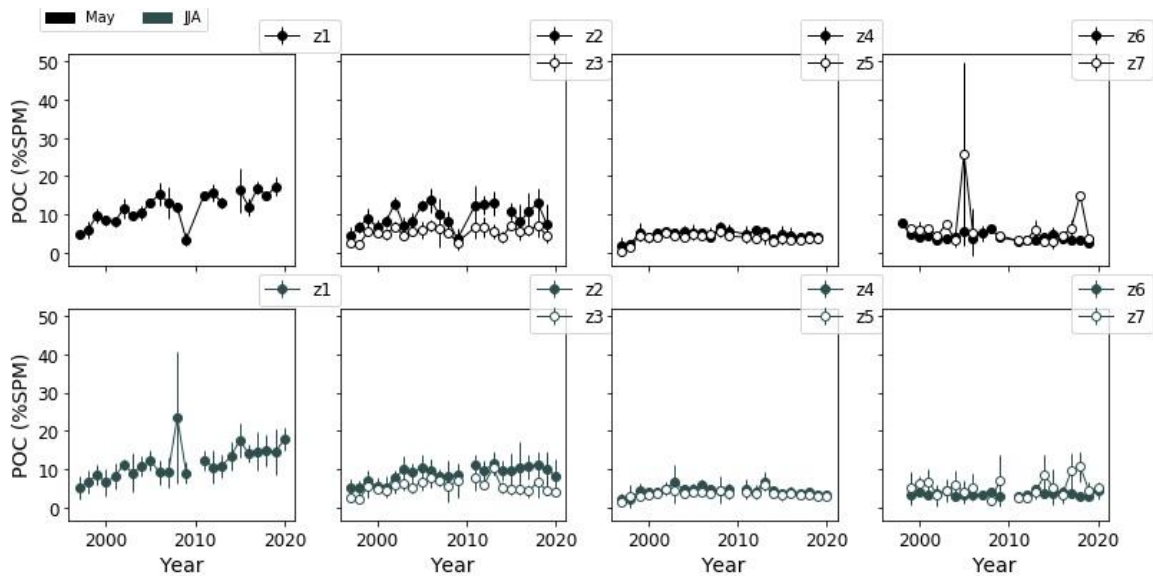
Fig. S4. Mean POC as percent (%) of suspended particulate matter (SPM) in late spring (May) and summer (June-August (JJA)) for each zone in the upper (z1-z3), mid (z4-z5) and lower-outer (z6-z7) estuary. Errors bars represent the standard deviation of the mean. POC as % of SPM calculations based on POC and SPM samples collected on the FGG Elbe helicopter campaign (Table S1).

Water residence time in Elbe Estuary as a function of river discharge

Table S16. Typical water residence time in the six zones in the inner Elbe estuary as a function of three different river discharge amounts (Q) (Bergemann et al., 1996).

Region	Zone	Elbe-km	Residence time		
			$Q = 250$ m^3 s^{-1}	$Q = 700$ m^3 s^{-1}	$Q = 1200$ m^3 s^{-1}
Upper estuary	1	586 – 610	< 2	< 1	< 1
	2	610 – 632	3-4	2	1
	3	632 – 650	7	2-3	1-2
Mid- estuary	4	650 – 677	17	5-6	3-4
	5	677 – 704	24	9	6
Lower estuary	6	704 – 727	30	11	6

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