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Significant shifts in inorganic carbon and ecosystem state in a temperate estuary (1985–2018)

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Abstract

Estuaries regulate carbon cycling along the land-ocean continuum and thus influence carbon export to the ocean, and global carbon budgets. The Elbe Estuary in Germany has been altered by large anthropogenic perturbations, such as widespread heavy metal pollution, minimally treated wastewater before the 1980s, establishment of wastewater treatment plants after the 1990s, and an overall nutrient and pollutant load reduction in the last three decades. 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 characterized by very high dissolved inorganic carbon (DIC) and ammonium concentrations, toxic heavy metal levels, dissolved oxygen 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. Large anthropogenic perturbations can therefore alter estuarine ecosystems (on the order of decades), as well as induce large and complex biogeochemical shifts and significant changes to carbon cycling.

Estuaries connect rivers to the coastal ocean and are critical zones for carbon cycling. They are generally considered net-heterotrophic, where the total ecosystem respiration outweighs gross primary production, resulting in net dissolved inorganic carbon (DIC) production (Gattuso et al. 1998). Globally, estuaries are estimated to release ~ 0.25 Pg C yr^{-1} into the atmosphere, which can counterbalance the shelf uptake of ~ 0.25 Pg C yr^{-1} (Cai 2011). In estuaries, DIC dynamics are influenced by strong gradients in environmental parameters, such as pH, salinity, nutrient concentrations and biogeochemical processes, including photosynthesis, organic matter (OM) decomposition, air-sea gas exchange, calcium carbonate ($CaCO_3$) dissolution and precipitation (Bauer et al. 2013; Oliveira et al. 2017; Ward et al. 2017).

River and estuary waters have been subjected to anthropogenic perturbations since their catchment areas often encompass residential and commercial development, that is, industrialized zones and agricultural land-use (Wolff et al. 2010). Globally, nutrient inputs from human activity, such as agriculture, wastewater treatment plants and industry, have led to eutrophication. The nutrient inputs can fuel algal blooms, often leading to hypoxia (Riemann et al. 2016; Hudon et al. 2017). The bacterial respiration of newly produced OM can also enhance the input of carbon dioxide (CO_2) (Howarth et al. 2011). Pollution from high levels of heavy metals on the other hand can limit phytoplankton productivity, for example, by disrupting their physiological state (Fisher et al. 1981; Le Faucheur et al. 2014). All these

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Additional Supporting Information may be found in the online version of this article.

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anthropogenic disturbances can alter DIC, dissolved oxygen (DO), and pH in estuarine and coastal waters.

Over time, political and socioeconomic developments have led to direct and indirect changes in environmental conditions. A change in human-induced pressures can lead to a shift in baseline conditions and the establishment of a new ecosystem state (Duarte et al. 2009; Rankinen et al. 2019). For example, since the first international conference on North Sea protection in 1984, measures were initiated to combat pollution including nutrient inputs (Ehlers 1990). Since then, phosphorus and nitrogen inputs from major rivers have decreased by more than half by the 2010s (van Beusekom et al. 2019). Reduced nutrient inputs led to lower green macroalgae blooms (van Beusekom et al. 2017, 2019), and in the less eutrophic northern Wadden Sea (located in the south eastern North Sea) intertidal seagrass returned (Dolch et al. 2013). Initiation of environmental protective policies for pollution abatement and subsequent water quality improvement in coastal ecosystems has been observed globally, like in the Pearl River Estuary in China (Zhao et al. 2020), Delaware Estuary in the United States (Sharp 2010) and Bilbao Estuary in Spain (García-Barcina et al. 2006). Determining anthropogenic influences on the carbon system in estuaries is therefore a prerequisite to disentangling long-term trends in carbon dynamics, environmental states, overall ecosystem health, and recovery time scales.

The present study describes the historical changes from 1985 to 2018 in DIC, and other key ecosystem parameters along the Elbe Estuary, which is one of the largest estuaries discharging into the North Sea. The analysis was used to identify three different ecosystem states of the Elbe Estuary, with distinct biological and biogeochemical characteristics. We focus on changes in seasonal and spatially differentiated data over time. The aim of the study is to demonstrate how an estuarine ecosystem function changes during and after periods with major (e.g., heavy metal) pollution and anthropogenic nutrient inputs. We argue that after a polluted state, an estuarine ecosystem can undergo a multiple-year transitional state before entering an ecosystem state with lower pollution levels, and this transition can take multiple decades.

Methods

Study site

The Elbe River is 1094 km long with a 142 km long tidal stretch. The Elbe Estuary comprises the tidal region, extending from the tidal border at Geesthacht weir (585.5 Elbe-km) to the mouth at Cuxhaven, Germany (727 Elbe-km) (Fig. 1). Elbe-km refers to the distance from the point where the Elbe passes the border between the Czech Republic and Germany. The estuary is a turbid, well-mixed, mesotidal coastal plain estuary, with the maximum turbidity zone (MTZ) extending from around 650 to 700 Elbe-km (Amann et al. 2015).

The Elbe Estuary water temperature increases from winter at $< 5^{\circ}C$ to $> 20^{\circ}C$ in summer (Schöl et al. 2014). The Elbe River basin is the driest compared to other German River basins, where the annual mean precipitation for the basin amounts to 628 mm yr^{-1} (Hesse 2018). The daily freshwater discharge, reported from the gauging station at Neu Darchau (536.4 Elbe-km), ranges between 200 and 3000 $m^3 s^{-1}$, with maxima in winter to early spring, and minima in September (Mudersbach et al. 2017; Hesse 2018). The long-term daily mean discharge is 710 $m^3 s^{-1}$ (1875–2013) (Mudersbach et al. 2017). With this range in river discharge, the water residence time of the estuary varies between 2 and 12 weeks (Bergemann et al. 1996).

The estuary was divided into seven zones (Fig. 1), based on the zonation proposed by the TIDE project (Geerts et al. 2012). It considered morphological, suspended sediment and salinity characteristics (refer to Supporting Information Table S1). In this study, the upper estuary includes zones 1–3 (z1–z3), the middle (mid) estuary zones 4–5 (z4–z5), the lower estuary zone 6 (z6), and the outer estuary zone 7 (z7) (Fig. 1; Supporting Information Table S1).

Data sources

The Elbe Estuary has been extensively studied and monitored over the past 35 yr by the "Flussgebietsgemeinschaft Elbe" (FGG Elbe). The FGG Elbe data portal (https://www.fgg-elbe.de) provides ecosystem data between 1985 and 2018. The FGG Elbe acquired estuary water samples every 5–10 km by helicopter, sampling altogether 36 stations, at a sample depth between the water surface and about 0.5 m (Fig. 1). The helicopter survey (duration of 3–4 h) permits the collection of water samples at all stations during the same tidal phase of the ebb tide, allowing the highest possible near-synoptic comparability between the samples with regard to the influence of the tides (Arge Elbe 2000). There were almost monthly transects from 1985 to 1993. From 1994 to 2018, sampling predominately took place in February, May, June, July, August, and November of each year.

Dissolved inorganic carbon

The DIC concentrations were derived at FGG Elbe laboratories during the analysis of total dissolved carbon, in order to determine DIC and dissolved organic carbon (DOC). At every station of the helicopter survey, a 5 L HDPE bottle was used for carbon samples (Arge Elbe 2000). After sampling in the field, the sample was filtered through a 0.45 μm membrane filter to remove particulate carbon at the "Wassergütestelle Elbe" (Elbe water quality agency). The DIC content of the samples was determined by liberating CO_2 from the filtered sample by acidification (HCl). The sparged CO_2 was then cooled, dehumidified and detected by nondispersive infrared sensor (NDIR). Total dissolved carbon on the filtered sample was determined using the 680°C combustion catalytic oxidation method with NDIR detection (U. Wiegel, pers. comm). DIC was subtracted from total dissolved carbon to determine the amount of DOC. DIC concentrations were reported as whole,

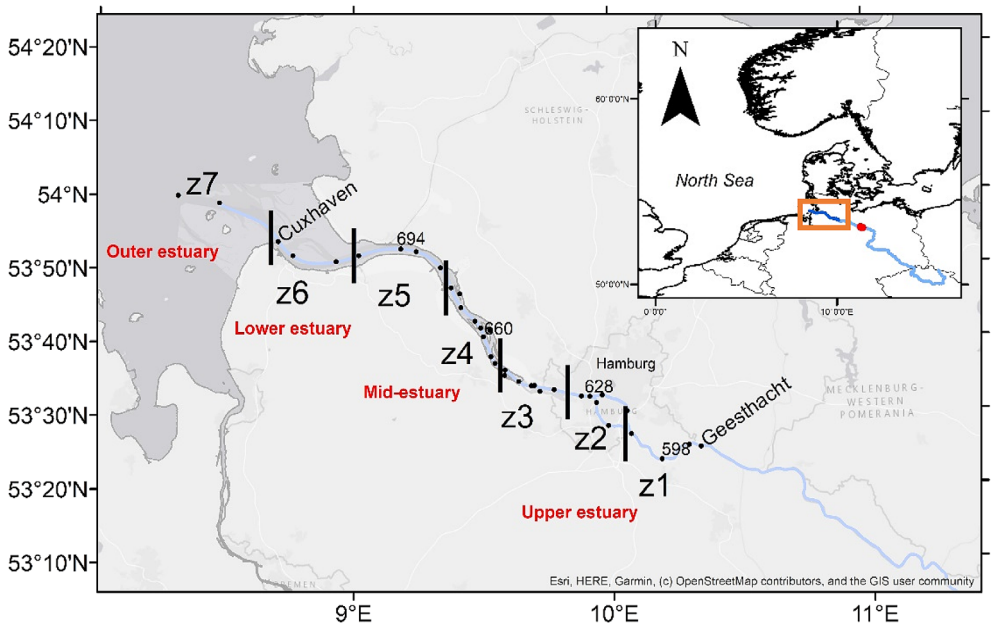

Fig. 1. Map of the Elbe River and the estuary separated into seven zones and four regions, with sampling stations (black points) along the main shipping channel (light blue). Insert map: Schnackenburg station (474.5 Elbe-km, red filled circle) is located in the Elbe River. The tidal region is in dark blue and highlighted with an orange box, and the nontidal Elbe River in light blue.

rounded numbers in units of mg L^{-1}, and we converted these into μmol L^{-1}. This rounding to mg L^{-1} subsequently smoothed out small potential differences between sampling stations, with some sampling stations showing matching DIC concentrations along the estuary from the same sampling day (U. Wiegel, pers. comm). To confirm the reliability of FGG Elbe DIC data, we compared FGG Elbe DIC concentrations to DIC data produced from current conventional analytical methods (Supporting Information Figs. S1–S5), with an estimated error of $\pm$ 100 μmol L^{-1}, corresponding to a 5% error in a 2000 μmol L^{-1} DIC sample. The estimated analytical error of 100 μmol L^{-1} of the monthly DIC concentrations would not mask the seasonal variation, since the difference between spring/summer and autumn/winter concentrations can be > 1000 μmol L^{-1}. In addition, the estimated error of 100 μmol L^{-1} is smaller than the standard deviation of the DIC mean for the recovery state (1997–2018) for all months (Supporting Information Figs. S2, S3, S6–S9). Therefore, FGG Elbe DIC data can be used for the historical analysis in this study, by assigning an estimated analytical error of 100 μmol L^{-1} to the DIC records.

Ecosystem and water quality parameters

Ecosystem parameters from the FGG Elbe data portal were analyzed following the German Institute for Standardization methods (Supporting Information Table S4), including DO, pH, nutrients, biological oxygen demand over 7 d (BOD_7), total organic carbon (TOC), DOC, and suspended particulate matter (SPM), in samples collected from every station of the helicopter survey. Ammonium (NH_4^+) was used in this study as a main water quality indicator of agricultural use and untreated wastewater (Adams et al. 2001; Mialet et al. 2011), as well as to trace historical nutrient changes in the estuary. Nitrate (NO_3^-) and phosphate (PO_4^{3-}) time series plots are available in the Supporting Information Fig. S10. In addition, weekly heavy metal water column concentrations (mercury [Hg], copper [Cu], and nickel [Ni]) were available from the continuous Schnackenburg monitoring station at 474 Elbe-km (Fig. 1).

Particulate organic carbon

Concentrations of particulate organic carbon (POC), as reported by FGG Elbe, were based on two different methods: (1) the difference between TOC and DOC, with an estimated uncertainty of 20% based on the Pythagorean Theorem (U. Wiegel, pers. comm), and (2) the analytical chromatographic method with an uncertainty of up to 50% (U. Wiegel, pers. comm). Since FGG Elbe measured POC directly only between 1991 and 2011, for the entire period discussed here, POC was calculated as the difference between TOC and DOC, expressed as concentration per volume of water (μmol L^{-1}) and in percentage (%) of SPM. POC in % of SPM represents the content of POC available for biological processing (Sullivan et al. 2001; Abril et al. 2002). In this study, POC in % of SPM was used to describe the mineralization and production of POC.

Data treatment and statistical analysis

To obtain an overview of the ecosystem dynamics between 1985 and 2018, the mean annual DIC, DO (in % saturation),

pH, BOD_7, NH_4^+, TOC, and heavy metals were calculated for each available sampling station and zone, with the respective standard deviation of the annual mean based on the monthly samples. Heavy metals were compared to the concentration limits for the protection of aquatic biota communities set by the International Commission for the Protection of the Elbe River (Internationale Kommission zum Schutz der Elbe [IKSE]; IKSE 2006). Based on changes in all parameters, three ecosystem states were distinguished as discussed below. Each parameter in every state was tested for normal distribution with a Shapiro–Wilk test ($p < 0.05$), with subsequent analysis using the Mann–Whitney *U* test to determine, if statistically significant differences in the median of each parameter existed between ecosystem states. The derivative of the mean annual DIC in each zone was used to quantify changes in DIC between consecutive ecosystem states. The Pearson correlation coefficient was applied to the mean annual DIC concentrations in the mid to outer estuary to quantify DIC changes over time.

Seasonal changes in estuarine biology and biogeochemistry were determined from monthly DIC, DO, nutrients, and pH records along the Elbe Estuary, with an example year for the polluted (1986), transitional (1993), and recovery (1997) state. An example year for each state was used as the seasonal variation in the Elbe Estuary during each state was consistent, however, with variability in each year as shown in Supporting Information Figs. S2, S3, S6–S9 (*see* details in Supporting Information Material, FGG Elbe data). In the upper (z1–z3), mid (z4–z5), and lower-to-outer (z6–z7) estuary, DIC (in each ecosystem state) was tested for a normal distribution with a Shapiro–Wilk test ($p < 0.05$). Subsequent analysis used the Mann–Whitney *U* test or independent *t*-test to determine statistical significant differences in respective median or mean between ecosystem states. For the polluted state, concentrations of NH_4^+, NO_3^-, and DO were used to estimate potential nitrification (Sanders et al. 2018), as NH_4^+ was highest in the estuary in this state (Fig. 4), with December 1986 as a winter example.

Results

Spatial and temporal variations of ecosystem parameters in the Elbe Estuary (1985–2018)

Three ecosystem states were identified (Figs. 2–4) corresponding to major biogeochemical shifts in estuarine water quality. A "polluted" state from 1985 to 1990, a "transitional" state from 1991 to 1996, and a more recent "recovery" state after 1997. The polluted state most likely started prior to 1985 (Kempe 1988; Netzband et al. 2002), but in this study we only examine records since 1985, when DIC measurements were first available by FGG Elbe. The three ecosystem states were distinct, and based on all comparisons (Table 1), there was a significant difference in 90% of ecosystem parameters (DIC, NH_4^+, BOD_7, TOC, pH, and DO) between ecosystem states in each zone of the Elbe Estuary ($p < 0.05$; Table 1), and in all heavy metals (Hg, Cu, and Ni) in the Elbe River ($p < 0.05$; Table 1). The exceptions (BOD_7, TOC, and DO) with no significant difference ($p > 0.05$ for 10% of all comparisons; Table 1), were not consistent in their location for the selected parameters. The three ecosystem states were distinct not only due to the change in mean annual concentrations over time (*see*, e.g., DIC records in Fig. 2), but also with regard to changes in the spatial variability, the along-estuary patterns, from the upper to outer estuary. The significant differences (Table 1) were not the same for each parameter (Figs. 3, 4), with nonlinear changes observed between ecosystem states, as described below.

Polluted state (1985–1990)

Between 1985 and 1990, DIC and ecosystem data characterize a heavily polluted state of the Elbe Estuary. The mean annual heavy metal concentrations at Schnackenburg (474.5

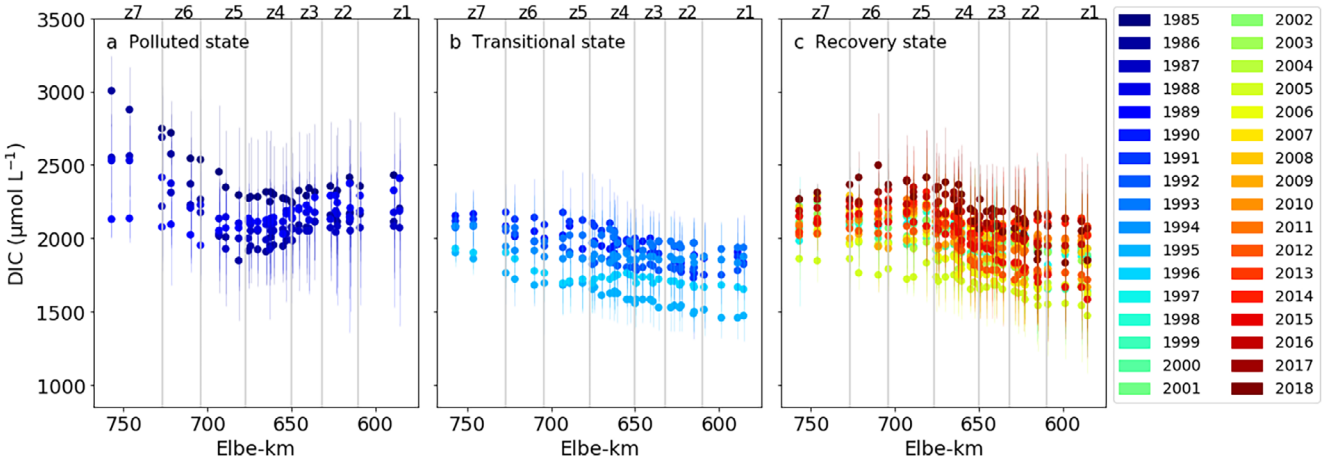

Fig. 2. Annual mean DIC for every helicopter sampling station along the Elbe Estuary for the proposed three ecosystem states: the polluted (1985–1990, **a**), transitional (1991–1996, **b**), and recovery (1997–2018, **c**) state. Vertical lines indicate the zonation of the Elbe Estuary from the TIDE project (Geerts et al. 2012). The error bars represent the standard deviations of the annual mean.

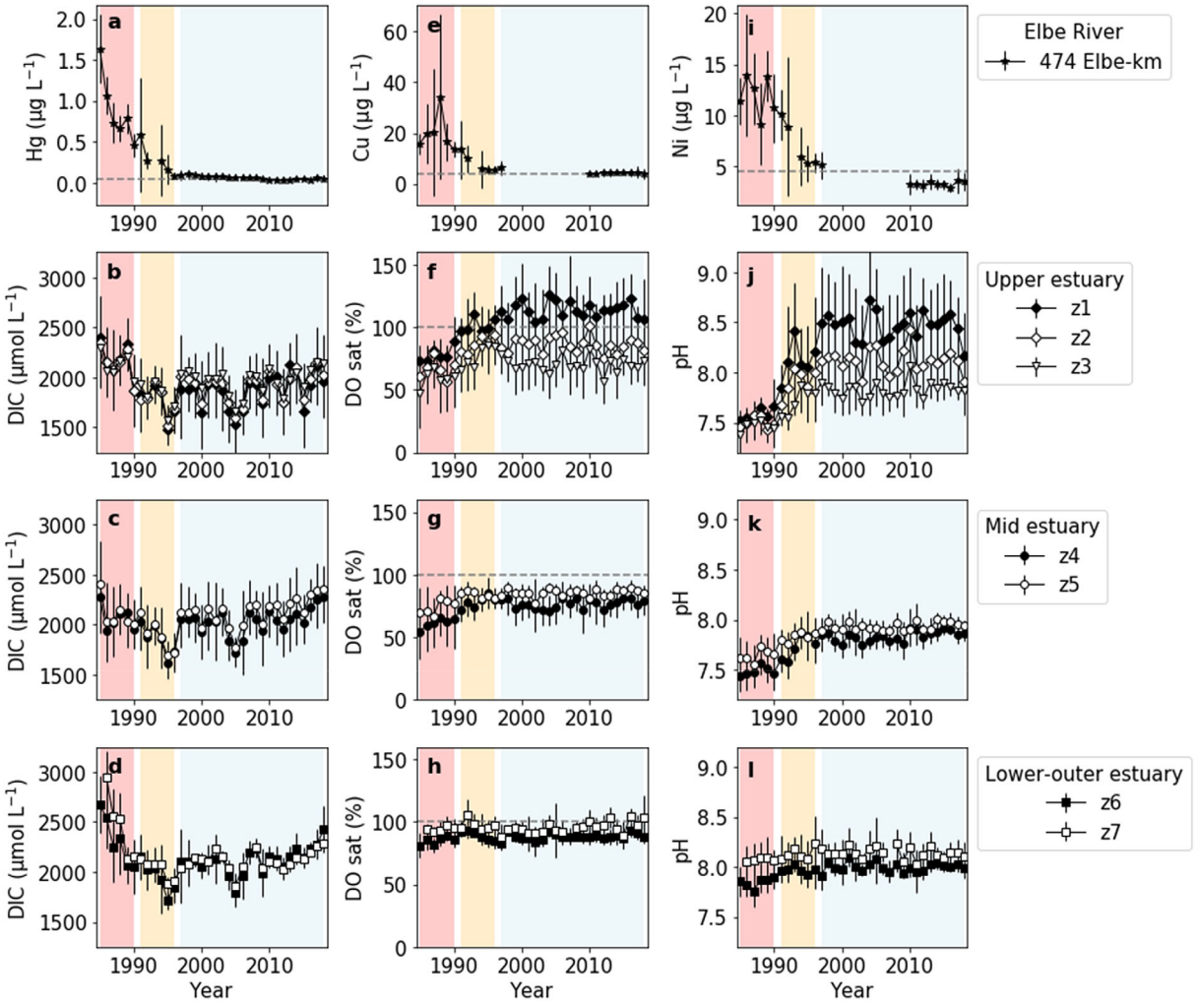

Fig. 3. Annual mean heavy metal concentration vs. time at Schnackenburg (474.5 Elbe-km), in the Elbe River (**a**, **e**, **i**), with IKSE targets for Cu, Ni, and Hg (IKSE 2006, dashes lines). Annual mean DIC (**b–d**), dissolved oxygen (% saturation, **f–h**) with 100% saturation (dashed line) and pH (**j–l**) for each zone vs. time, grouped into the upper (zones 1–3), mid (zones 4–5), and the lower and outer (zones 6–7) estuary. Error bars represent the standard deviations of the annual mean. Red shading marks the polluted state, yellow the transitional state and blue the recovery state.

Elbe-km) exceeded the IKSE targets by a factor of up to 2 for Ni, 9 for Cu, and 40 for Hg. While there was more than a threefold decrease in annual mean Hg from 1985 to 1990, Cu and Ni remained generally high and variable (Fig. 3a).

In the Elbe Estuary, annual mean DIC concentrations were highest on record from 1985 to 1990. Lowest values were found in the MTZ (z4–z5), increasing along the estuary by up to 58%, and reaching maximum concentrations at $> 2600\ \mu mol\ L^{-1}$ in the lower and outer estuary (zones 6–7) in 1985–1986 (Fig. 2a and Fig. 3c,d). Annual mean DO was undersaturated during this period in all regions (Fig. 3f,g), with higher levels (95% saturation) only in the outer estuary (Fig. 3h). Similarly, in the upper and mid estuary (z1–z5) pH was low (< 7.68; Fig. 3j,k), and increased to > 8 in the outer estuary (z7). In the estuary, annual mean BOD_7 and NH_4^+ were highest on record reaching $12 \pm 1.5\ mg\ L^{-1}$ and $219 \pm 80\ \mu mol\ L^{-1}$ during this period, but decreased by up to 70% from 1985 to 1990. TOC concentrations also decreased, by up to 66% in zone 5. The annual mean NO_3^- and PO_4^{3-} concentrations were highest during this polluted ecosystem state (Supporting Information Fig. S10).

Transitional state (1991–1996)

Dramatic changes in ecosystem parameters and heavy metals occurred between 1991 and 1996. Therefore, we consider this as transitional state following the highly polluted state. Throughout the transitional state, the mean annual DIC decreased by > 20% in the estuary, reaching the lowest annual mean concentrations on record in 1995–1996 (Fig. 2b). Along the estuary, the pattern also changed, with mean annual DIC continuously increasing from $< 1500\ \mu mol\ L^{-1}$ in the upper estuary (z1) to $1900\ \mu mol\ L^{-1}$ in the outer estuary in 1995, but

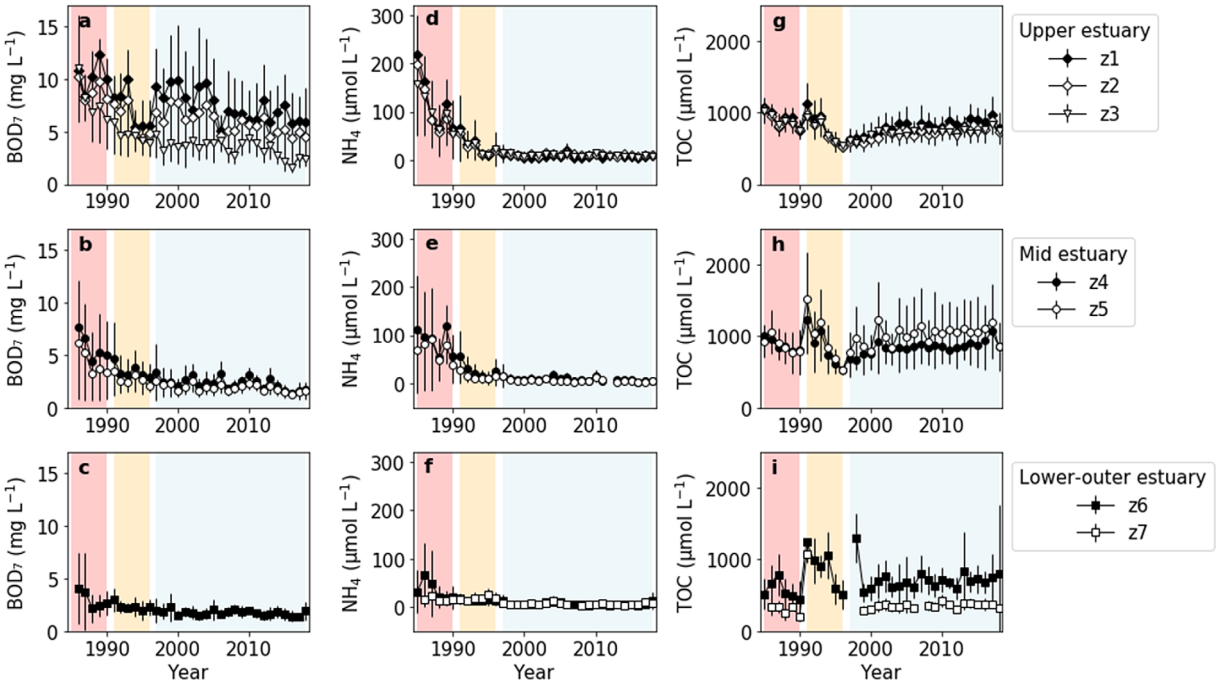

Fig. 4. Annual mean BOD_7 (**a–c**), NH_4^+ (**d–f**), and TOC (**g–i**) for each zone vs. time, grouped into the upper (zones 1–3), mid (zones 4–5), and the lower and outer (zones 6–7) estuary. Error bars represent the standard deviations of the annual mean. Red shading marks the polluted state, yellow the transitional state and blue the recovery state.

with a much lower along-estuary gradient than in the polluted period (Fig. 2b). Heavy metal concentrations also decreased at Schnackenburg (Fig. 1), and by 1996 Hg decreased by 86%, and Cu and Ni by ca. 50% (Fig. 3a,e,i, highlighted in yellow), while 39% of all samples reached IKSE targets.

In contrast to the low levels during the polluted period, both DO and pH increased in the upper estuary (z1–z3), with highest values in the upper most region (z1), where waters were supersaturated and pH was > 8 (Fig. 3f, j). In the upper region (z1–z3), mean annual BOD_7 decreased by 46–57% to < 4.0 mg L^{-1} (Fig. 4a), and NH_4^+ further decreased by > 60% (Fig. 4d,e) by 1996. TOC doubled to > 900 μmol L^{-1} in all zones in 1991 (Fig. 4g–i), reaching the highest annual mean over the entire record. After 1991, TOC decreased, and reached the lowest concentrations at < 550 μmol L^{-1} in the upper and mid estuary by 1996. NO_3^- and PO_4^{3-} (Supporting Information Fig. S10) were lower than during the polluted state, reflecting nutrient input reductions during the transitional state.

Recovery state (1997–2018)

We postulate that the Elbe Estuary entered an ecosystem recovery state, starting in 1997 following the transitional state. This period was characterized by significantly lower ($p < 0.05$; Table 1) heavy metal concentrations compared to the polluted and transitional states, below IKSE targets (Fig. 3a,e,i).

The year 1997 marked several significant changes in ecosystem parameters (Table 1). The annual mean DIC increase in zone 3 and 5 was largest during the transition from 1996 to 1997 (Supporting Information Fig. S11). In contrast to the observed DIC decrease throughout the transitional state, DIC increased in the mid, lower and outer estuary over time during the recovery state (Fig. 3c,d), and by 2018, reached levels close to those in the late 1980s. The observed DIC increase was significant ($p < 0.05$) in the mid to lower estuary (z5–z6) from 1997 to 2018 (Table 2). Significant positive increases in DIC over time were more pronounced in the last decade (2008–2018), reaching > 23 μmol L^{-1} yr^{-1} in the mid and lower estuary (z4–z6). From 1997, there was also a notable shift in the along-estuary DIC pattern (Fig. 2c), with an increase from the upper (< 2000 μmol L^{-1}) to mid estuary (> 2400 μmol L^{-1}), inverse to the polluted state pattern (Fig. 2a).

During this period, DO and pH were high in the upper and outer regions of the estuary (z1 and z7), at DO > 100% saturation and pH > 8.3 (Fig. 3h,l). Despite a slight decrease over time (1997–2018), BOD_7 was still highest in the upper estuary (z1), compared to the mid to outer estuary (Fig. 4a). Compared to the previous ecosystem states, mean annual NH_4^+ was lowest in the upper and mid estuary (z1–z5) during this period at < 21 μmol L^{-1} (Fig. 4d–f), and NO_3^- and PO_4^{3-} continued to decrease, by > 40% and > 20%, respectively. In contrast to the decreasing trend during the polluted and transitional states, TOC concentrations increased

Table 1. The median of DIC, BOD_7, NH4, TOC, DO saturation (%), and pH in each zone and for Hg, Cu, and Ni at Schnackenburg (474 Elbe-km) for the polluted (P), transitional (T), and recovery (R) state, without a statistical significant difference ($p > 0.05$) to the polluted (•), to the transitional ($^{\#}$) and to the recovery (*) state. If no symbol is present, the median is significantly ($p < 0.05$) different from the other two ecosystem states.

		Zone						
Parameter	**State**	**1**	**2**	**3**	**4**	**5**	**6**	**7**
DIC (μmol L^{-1})	P	2165	2165	2081	2081	2102*	2331	2331
	T	1748	1832	1832	1915	1915	1957	1957
	R	1915	1915	1998	1998	2081•	2165	2165
BOD_7 (mg L^{-1})	P	10	9	8	5	3	2$^{\#}$	
	T	8*	6	4	3	2	2•	
	R	8$^{\#}$	6	3	2	2	2	
NH_4 (μmol L^{-1})	P	129	107	93	57	23	11$^{\#}$	12
	T	13	15	14	11	9	12•	15
	R	5	9	8	5	4	5	6
TOC (μmol L^{-1})	P	916	916	916	833	916$^{\#}$	583	333
	T	745*	724	754	758*	874•,*	754	
	R	803$^{\#}$	683	683	766$^{\#}$	916$^{\#}$	633	341
DO saturation (%)	P	78	73	66	67	79	86	93*
	T	99	91*	80	78*	85	90	96
	R	109	92$^{\#}$	71	78$^{\#}$	86	89	95•
pH	P	7.60	7.50	7.50	7.50	7.70	7.90	8.00
	T	8.00	7.80	7.60	7.70	7.80	8.00	8.10*
	R	8.60	8.00	7.80	7.80	7.90	8.00	8.10$^{\#}$
Heavy metals (μg L^{-1}) @ 474 Elbe-km		Hg	Cu	Ni				
	P	0.8	15.5	11.4				
	T	0.2	5.9	6.1				
	R	0.0	4.0	3.2				

Table 2. Pearson correlation coefficient (r) of mean annual DIC in the mid to outer Elbe Estuary correlated with time (decimal year), during the recovery state (1997–2018) and in the most recent decade (2008–2018), with the respective rate of change in DIC (β). The Shapiro–Wilk test of normality was applied prior to statistical analysis and the Spearman rank correlation was applied to zone 7 data, as the dataset did not exhibit a normal distribution.

	1997–2018		2008–2018	
Zone	**Coefficient (r)**	**β (μmol L^{-1} yr^{-1})**	**Coefficient (r)**	**β (μmol L^{-1} yr^{-1})**
4	0.40	9	0.69*	24
5	0.54*	11	0.70*	24
6	0.50*	10	0.64*	23
7	0.33	5	0.55	14

*Correlation is significant at $p < 0.05$.

by 11–58% by 2017–2018 in the upper and mid estuary (z1–z5; Fig. 4g–i).

Seasonal and spatial variations

Polluted state (1985–1990)

In 1986, seasonal variation in DIC was on the order of 1000 μmol L^{-1} along the entire estuary, with highest levels in autumn and winter at > 3000 μmol L^{-1} (Fig. 5a). In all seasons, DIC concentrations were lowest in the mid estuary (z4–z5), followed by a marked increase by up to 2.9-fold along the salinity gradient to the outer estuary, matching the unique mean annual DIC pattern during the polluted state (Fig. 2a). The seasonal DIC increase in the mid to outer estuary was present every year in this state, with a decreasing slope over time (Supporting Information Fig. S12).

DO and pH minima varied seasonally in zones 2–5, in zones 4–5 in May–June, zone 2 in July–August and zones 3–4 in September–December (Fig. 5). The DO and pH minima location

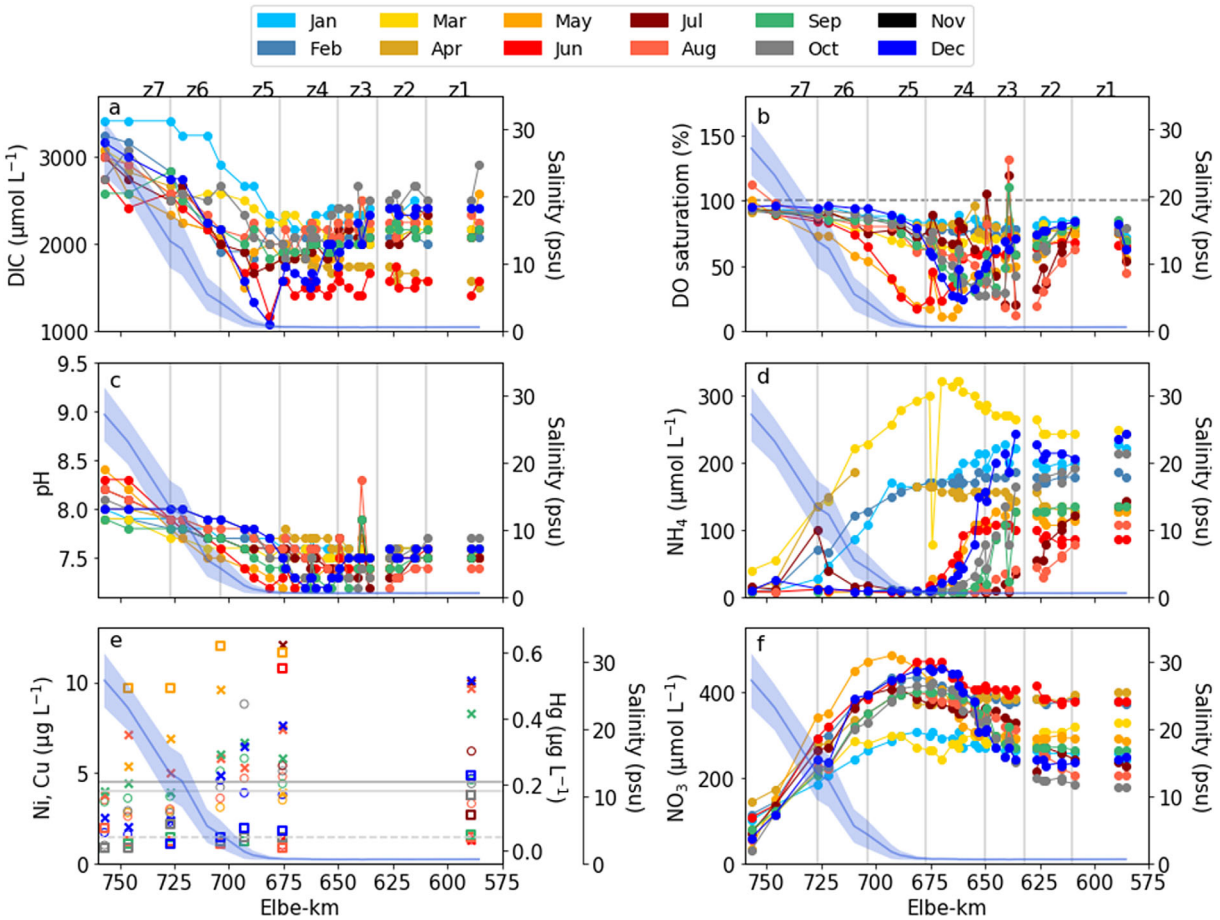

Fig. 5. Monthly DIC (**a**), dissolved oxygen (% saturation) with 100% saturation (dashed line, **b**), pH (**c**), NH_4^+ (**d**), heavy metal (**e**), and NO_3^- (**f**) along the Elbe Estuary in 1986. In (**e**), Cu (circle), Ni (cross), and Hg (square) with the corresponding IKSE targets in dark gray at 4.5 μg L^{-1} for Ni, gray at 4 μg L^{-1} for Cu, and dashed gray at 0.04 μg L^{-1} for Hg (IKSE 2006). The annual mean salinity gradient is shown with dark blue line with shaded blue areas representing one standard deviation.

coincided with major decreases in NH_4^+ and increases in NO_3^-. DIC decreases occurred in the same regions in July, September, October, and December. The mean NO_3^- and DO concentrations (O_2), in zones 3–4 in December 1986, were used to provide an estimate of estuarine nitrification. From 636 to 662.7 Elbe-km, O_2 decreased by 166 μmol L^{-1}, while NO_3^- increased by 200 μmol L^{-1}, and therefore the ratio of $\Delta O_2 : \Delta NO_3^-$ change was 0.83. For the other months in 1986 (May–October), the ratio of $\Delta O_2 : \Delta NO_3^-$ was between 1.0 (August) and 2.0 (June). Decreasing O_2 and NH_4^+, coupled with increasing NO_3^- (z2–z4; Fig.5), suggest that nitrification in the upper to mid estuary contributed significantly to the DO depletion.

During the polluted state, the only region with evidence of primary production exceeding respiration was zone 7 in the summer months, when pH increased to 8.4 (June) and DO became supersaturated at 112% (August) (Fig. 5b,c). Primary production in the outer estuary was established, because 78% of heavy metal samples were below the IKSE targets in the lower-outer estuary (Supporting Information Table S5), compared to only 24% in upper-mid estuary.

To investigate the potential sources of DIC in the lower-to-outer estuary shown in Fig. 5, DIC variability along the salinity gradient, with a conservative mixing line between two end members, river and North Sea, was compared to DOC and POC variability. A pronounced positive nonconservative behavior with deviations from the mixing line (Officer 1979), was observed in January and June, and less pronounced in May, July, September, October, and December (Fig. 6b–e). This suggests that there was an internal source of DIC in the estuary during all seasons, with positive excursions from a linear mixing line in 1987 and 1988 (Supporting Information Fig. S13). Concurrently, a negative deviation from linearity was observed in DOC in July, August, October, December, and less pronounced in May and April (Fig. 6g–j). The deviations from the conservative mixing line indicate DOC consumption and DIC production along the salinity gradient. In the outer

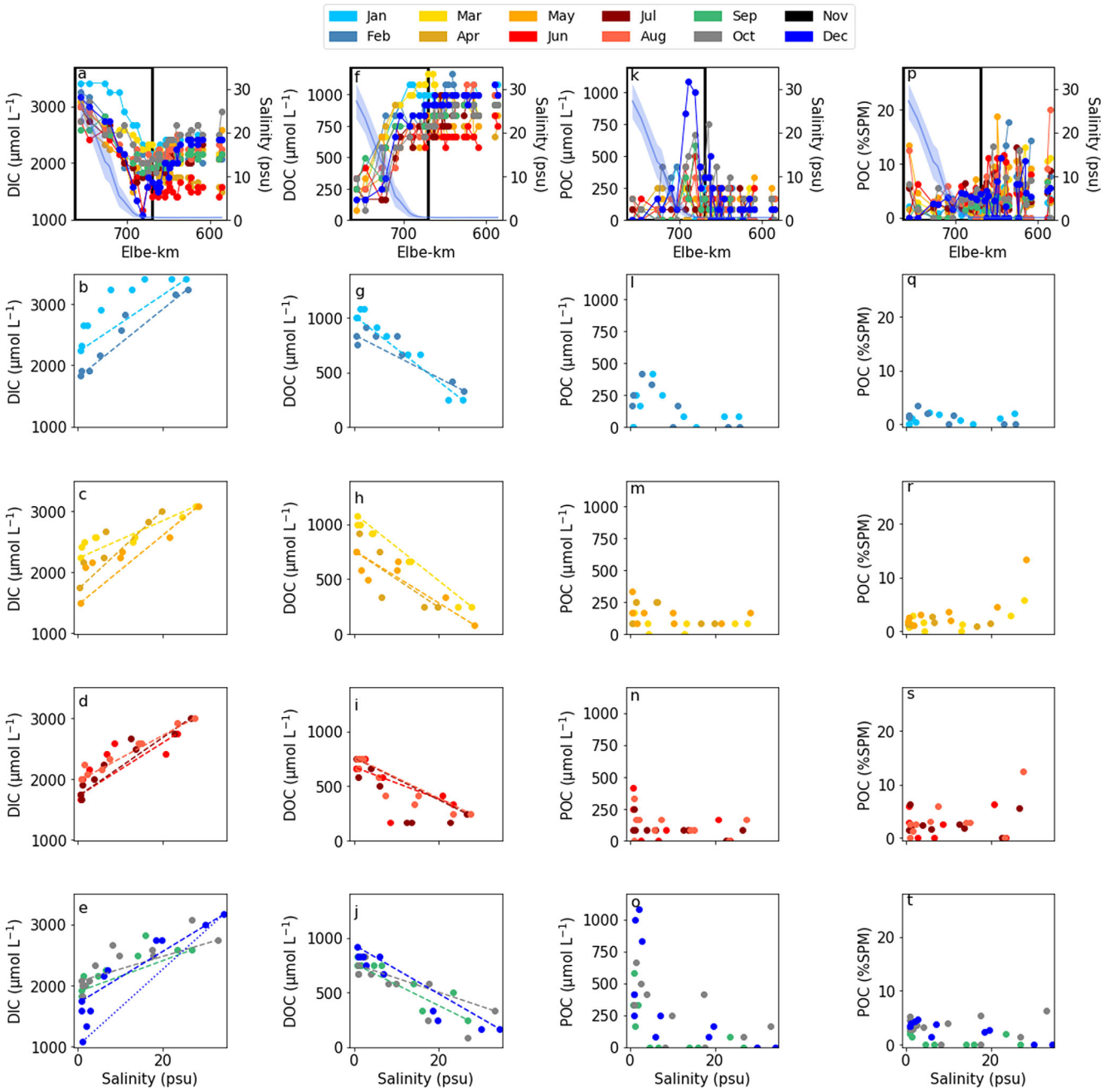

Fig. 6. Distribution of monthly carbon parameters along the Elbe Estuary in 1986: DIC (**a**), DOC (**f**), POC (**k**), and POC % of SPM (**p**), with the annual mean salinity gradient shown in dark blue line with shaded blue areas representing one standard deviation. The black box represents the location of the salinity gradient against which the carbon parameters are plotted: DIC (**b–e**), DOC (**g–j**), POC (μmol L^{-1}, **l–o**), and POC (% of SPM, **q–t**). Conservative mixing between the river and the North Sea end member is indicated by the dashed lines. In December, two mixing lines were identified for DIC from 675.5 and 681.3 Elbe-km, with the stronger positive excursion in the latter Elbe-km.

region, POC as % of SPM increased to > 10% in spring–summer (Fig. 6r,s).

Transitional state (1991–1996)

Compared to the polluted state with high DIC concentrations, a new seasonal pattern evolved in the estuary (Fig. 7a). Monthly DIC was significantly ($p < 0.05$) lower during the transitional state (1993) in the upper and lower-outer estuary, with exceptions in April and June (Supporting Information Table S6). DIC fluctuated little along the estuary and between seasons, with slightly higher concentrations in autumn and winter (Fig. 7a; Supporting Information Fig. S14). In contrast

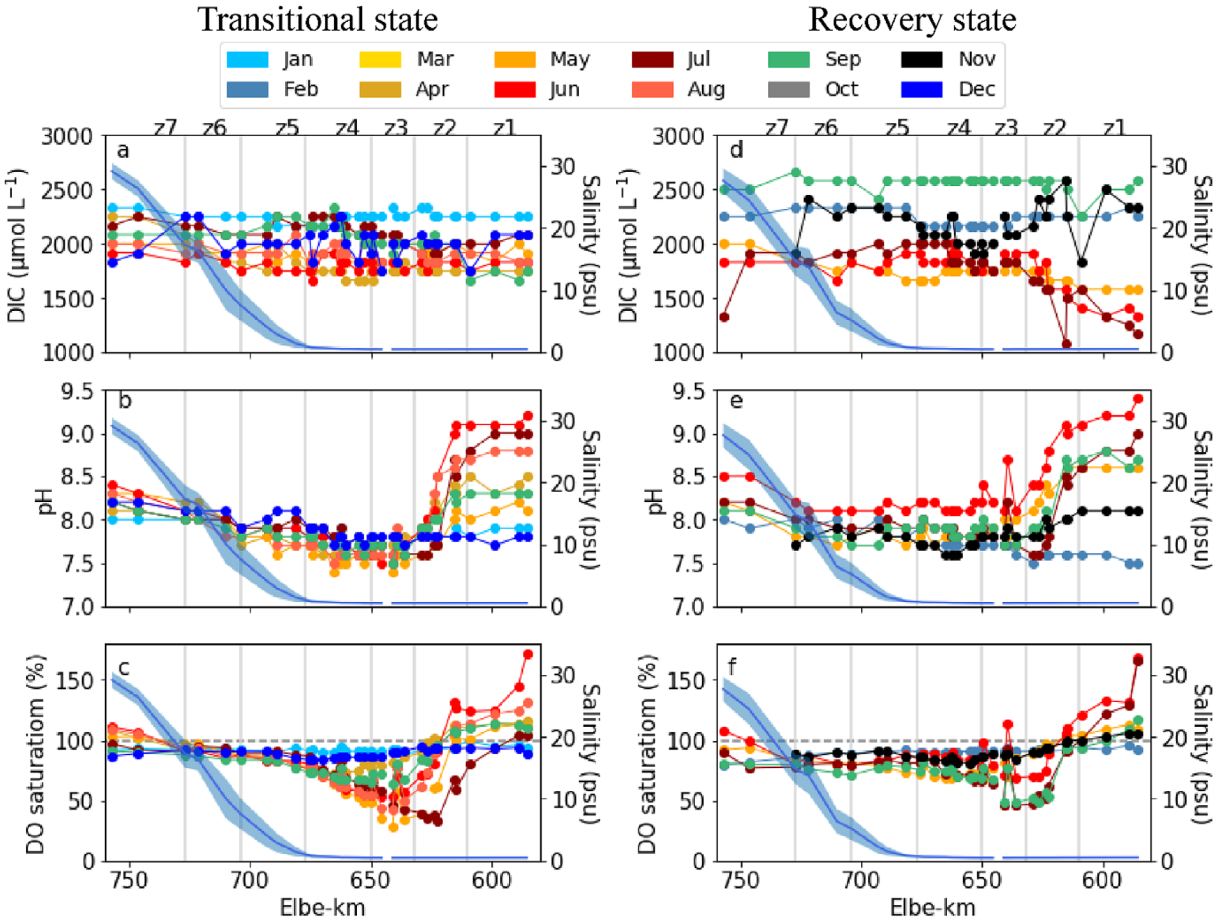

Fig. 7. DIC, pH, and dissolved oxygen (DO) saturation with 100% saturation (dashed line) (from top to bottom) along the Elbe Estuary in 1993 (**a–c**) and 1997 (**d–f**). Annual mean salinity in dark blue with shaded blue representing one standard deviation.

to the DO undersaturation and low pH in the polluted state, during the transitional state we observed high pH (> 9) and DO (> 100% saturation) in the upper estuary (z1) in May to August. In autumn and winter, pH (7.2–8.1) and DO (80–100%) remained constant along the estuary.

Recovery state (1997–2018)

During the recovery state, seasonal fluctuations in DIC, particularly in the upper estuary were pronounced (Fig. 7d). Supersaturated spring to summer DO and high pH during the recovery state coincided with a significant DIC drawdown to approximately 1000 μmol L^{-1} in the upper estuary (z1). The z1 DIC during the recovery state (1997) was significantly ($p < 0.05$) lower than during the transitional state (1993; Supporting Information Table S6). DIC increased from the upper estuary to the mid-estuary, coupled with a decrease in DO and pH (Fig. 7d). This seasonal DIC pattern can be observed in May to August throughout the recovery state (Supporting Information Figs. S6–S9). Similar to the previous ecosystem states, DIC concentrations were generally higher in autumn and winter at > 2000 μmol L^{-1} (Fig. 7d; Supporting Information Figs. S2, S3).

Discussion

Polluted state (1985–1990)

During the polluted state, high DIC, organic carbon, nutrients and heavy metals, and low oxygen and pH (Figs. 2–4) indicate that the Elbe Estuary was heavily polluted. This was likely due to the discharge of minimally treated industrial wastewater and urban sewage into the Elbe River in East Germany and Czechoslovakia (Netzband et al. 2002). During this period, Kempe (1988) also stated that the Elbe River was one of the most polluted river systems in the world. These polluted upstream waters had a significant effect on the biology and biogeochemistry in the Elbe Estuary, with release of large amounts of nutrients, heavy metals and OM into the Elbe River (Guhr et al. 2000). The high DIC, undersaturated oxygen and low pH, in the upper estuary (z1–z3) indicate net heterotrophy with minimal primary production. In this region, heavy metals exceeded the IKSE targets and therefore were

most likely toxic to phytoplankton (Fisher et al. 1981; Le Faucheur et al. 2014) and low tolerant bacteria (Babich and Stotzky 1985). Dark effluents and suspended solids from the pulp industry throughout the Elbe River catchment (Guhr et al. 1993; Netzband et al. 2002) may have also inhibited primary production due to light limitation (Pearson 1980; Amann et al. 2012). This was, however, not reflected in higher SPM values in the estuary (not shown). Excessive nutrient concentrations (220 μmol L^{-1} NH_4^+, 358 μmol L^{-1} NO_3^-, 10 μmol L^{-1} PO_4^{3-}) within the estuary indicate that primary production was not nutrient limited. Thus, it is likely that phytoplankton production in the upper estuary was reduced by high and potentially toxic levels of heavy metals and low light availability.

In the mid estuary, our findings indicate that nitrification was a key process controlling the biogeochemical patterns. The strong decrease in excessive NH_4^+ in the freshwater region (z2–z4), declining oxygen and pH to minimal values and increasing NO_3^- levels (Fig. 5), indicate that intense nitrification played a significant role in oxygen consumption even in the winter months during this ecosystem state. Kerner et al. (1995) determined that up to 50% of the DO were consumed by nitrification in the 1980s in the Elbe Estuary, while Kerner (2000) also reported oxygen deficiencies in the Elbe Estuary at low temperatures in winter months. We can assume that during nitrification (oxidation of ammonia via nitrite to nitrate), 0.5 mol of O_2 consumed produced 1 mol NO_3^- (e.g., in Fiencke et al. 2005). Since the molar ratio change for O_2 decrease and NO_3^- increase was roughly 0.83 (z2–z4 in December, 1986 in Fig. 5), this indicates that approximately 50% of the oxygen depletion could have been caused by nitrification. While oxidation of NH_4^+ to NO_3^- reduces pH (Soetaert et al. 2007) as seen in Fig. 5c, estimating the pH variations due to associated alkalinity changes (Middelburg et al. 2020) is beyond scope of this study. Nitrification occasionally coincided with a decrease in DIC (Fig. 5), likely because most of the nitrifiers were also chemolithoautotrophs, as they assimilate CO_2 (Denecke and Liebig 2003). This all confirms that nitrification was an important driver for oxygen consumption in the mid Elbe Estuary during the polluted state, and nitrifiers affected DIC concentrations.

The notable DIC increase in the mid to outer estuary is one striking feature of the polluted state (Fig. 5; Supporting Information Fig. S12). DIC dynamics from October 1981 (Kempe 1982) mirrored this, so most likely this pattern was already present earlier than 1985. The positive deviation from linearity for DIC along the salinity gradient (z5–z7), coupled with negative deviations in DOC (Fig. 6), indicates that remineralization of labile OM contributed to the increasing DIC in the mid to outer estuary, especially when heavy metals fell below critical (IKSE) targets. This is supported by the fact that DOC remained high and constant along the freshwater region of the estuary (z1–z4; Fig. 6), that is, no net remineralization of DOC occurred in this region. Thus, we can deduce that most of the labile OM in the estuary was processed by heterotrophic activity in the less toxic lower and outer estuary regions, subsequently considerably enriching DIC.

Furthermore, in the outer estuary, as heavy metals decreased to nontoxic levels, the POC increase as percentage of SPM during the warmer months (Figs. 5, 6) indicated the presence of labile OM. This is supported by Hesse et al. (1992), who found that chl-a concentrations in the outer estuary (z7) were high (> 30 μg L^{-1}) in spring and summer 1989. Labile OM from coastal phytoplankton production could have been carried into the estuary and made available for bacterial remineralization. While outer estuarine waters, as part of the Wadden Sea, have been described as net heterotrophic (van Beusekom et al. 2019), Kempe and Pegler (1991) showed strong drawdown of carbon from primary production in the coastal North Sea, German Bight and Wadden Sea (CO_2 = 100–300 ppmv) in the 1980s summer season. Therefore, we find that, during the polluted state, only in the estuarine regions with decreased toxicity, remineralization of both DOC and POC from industrial waste and from labile autochthonous (z7) and allochtonous (Elbe River watershed) OM contributed to the enrichment of DIC observed along the salinity gradient (Figs. 2, 5).

In the low-salinity (< 15 psu) mid to lower regions (z5–z6), the increase in DIC could also be due to $CaCO_3$ dissolution, as described by Kempe (1982). They observed a CO_2-rich Elbe Estuary with low pH of < 7.5 and undersaturated waters with respect to calcite. In that study, imported marine carbonates dissolved, forming excess alkalinity, and this could have increased the DIC content. In the upper to mid estuary (z1–z4), pH was also generally ≤ 7.5 and increased along the salinity gradient (z5–z7) (Fig. 5c). However, Kempe (1982) showed an alkalinity increase of < 300 μmol L^{-1} (reported as 0.3 meq L^{-1}). In the present study, the DIC increase along the salinity gradient amounted to approximately 2000 μmol L^{-1}. Therefore, the alkalinity increase found in Kempe (1982) was minor compared to the observed DIC increase.

Transitional state (1991–1996)

A pivotal moment in the history of the Elbe River catchment region was the German reunification in 1990, with ensuing closures in industrial and agricultural sectors in former East Germany and former Czechoslovakia (related to the regime change in 1989). We find that this influenced the Elbe, such that the 6 yr (1991–1996) after the polluted state were a period of intense biological and biogeochemical changes in the Elbe Estuary. Over time, the DIC decrease in the entire estuary (Fig. 3), with concomitant DO and pH increases (> 100% saturation and > 8 pH) in the upper and outer estuary, in spring and summer (Fig. 7), indicating that net primary production re-established in the estuary and in regions upstream of the Geesthacht weir (Amann et al. 2012). This occurred likely due to the reduction in Elbe River heavy metal

concentrations by 50% by 1996 (Fig. 3a,e,i), which no longer inhibited biological activity. In 1991, Guhr et al. (2000), reported intensified primary production, shown in highest oxygen production potential (20 mg L^{-1}) in the river Elbe (318 Elbe-km). That was, in part, also associated with pronounced summer maxima in TOC (Guhr et al. 2000). This suggests that as pollution decreased during this period, intense primary production took place in the upper estuary and upstream Elbe River regions, and this production significantly altered TOC concentrations in the estuary (Fig. 4g–i; Table 1).

From 1990 to 1999, 181 municipal wastewater treatment facilities were newly built or rebuilt in Germany and the Czech Republic (Netzband et al. 2002). As a result, the direct industrial discharge of NH_4–N decreased by 90.4% between 1989 and 1995 (IKSE 2000). This helped to reduce NH_4^+ and TOC levels in the Elbe Estuary (Fig. 4), and most likely decreased the rate of heterotrophic OM decomposition. This is reflected in the 31–69% decrease in BOD_7 and 20% decrease in DIC in the Elbe Estuary throughout this period. NH_4^+ is the initial substrate of nitrification and the lower NH_4^+ levels suggest that nitrification to NO_3^- no longer dominated oxygen consumption. A weaker along-estuary increase in NO_3^- corroborates this, since the observed NO_3^- increase in December 1993 (Supporting Information Fig. S15) was only about half of the December 1986 increase (Fig. 5, z2–z4). Kerner (2000) also reported that after 1989, there was a shift away from dominating nitrification, to bacterial mineralization of phytoplankton-produced OM in the Elbe Estuary.

In the upper to mid-estuary, late spring and summer DO and pH, respectively, reached > 150% and > 9 due to phytoplankton production (z1), but decreased along-estuary to < 50% and < 7.5 driven by bacterial mineralization (z2–z3) (Fig. 7). Despite the seasonality in DO and pH, DIC exhibited only small seasonal variations (Fig. 7). However, this is still not yet fully explained and is beyond scope of this study.

Recovery state (1997–2018)

After the period of high pollution and subsequent transitional state, the recovery state began in 1997. Unlike the previous ecosystem states, the upper region was characterized by strong DIC drawdown in spring and summer, coinciding with super-saturation in DO and high pH (> 8.5) (Fig. 7). Primary production in the upstream and upper estuary regions likely reduced DIC in the upper estuary (z1) in late spring and summer (Amann et al. 2015), and in the Elbe River (318–585 Elbe-km) as shown by Kamjunke et al. (2021). In the upper estuary (z1), primary production producing fresh labile OM could have contributed to the high BOD_7 in the upper estuary, which decreased with time and along the estuary. Therefore, the source of high BOD_7 most likely changed from industrial wastewater treatment plants, decomposition of such external OM, and from nitrification in the 1980s, to plankton-derived OM in the past 20–25 yr. For instance, in zone 2 close to Hamburg, Kerner (2007) identified a positive correlation between POC and BOD_7 during May to August (1992–2004), where labile OM was dominated by phytoplankton (Kerner 2000; Kerner 2007).

During the recovery ecosystem state, a new DIC pattern was established throughout late spring–summer months, with an increase from the upper estuary to a peak in the mid-estuary (Fig. 2c). It coincides with a decline in DO to undersaturated values and a pH < 8. The strongest increase in DIC and decrease in DO and pH occurred in zone 2–3, close to Hamburg harbor, an area with a threefold increase in water depth and increased light limitation (Gocke et al. 2011; Schöl et al. 2014). This indicates the establishment of a new pattern of carbon processing, with net heterotrophy along the estuary, and with strongest bacterial remineralization processing in the harbor region. Amann et al. (2015) also found decreasing POC, increasing CO_2 and evasion of CO_2 into the atmosphere mainly from the upper to mid Elbe Estuary in spring and summer, with more pronounced trends in zones 2–3.

Other main contributors to the along-estuary DIC enrichment could be lateral import of DIC from adjacent tidal marshes. Weiss (2013) estimated that DIC export from marshes could contribute nearly a third of the excess DIC in the Elbe Estuary, since tidal marshes contained sediments enriched in $CaCO_3$ originating from the Wadden Sea. While OM degradation generates CO_2 and decreases pH in the water column, the system is buffered by $CaCO_3$ dissolution. This causes a drop in pCO_2 and increases pH and DIC, mainly in the form of HCO_3^-. Therefore, adjacent marshes are generally important for maintaining high DIC in estuaries (Cai and Wang 1998; Raymond and Bauer 2000). However, Weiss (2013) sampled the tidal marshes adjacent to zones 4–6, showing lowest average DIC export in spring, summer and early autumn in zone 4, and highest export in zone 6 in early autumn. Tidal marsh DIC inputs were therefore likely not the main driver of the along-estuary DIC pattern, since the observed DIC peak in this study was located in the mid-estuary (z4–z5) in spring and summer.

A minimal addition to the along-estuary DIC increase could include microbially mediated aerobic oxidation of methane producing 1 mol of CO_2 per 1 mol of CH_4 oxidized (Matoušů et al. 2016). The authors found highest CH_4 concentrations with a median of 416 nmol L^{-1}, in the upper Elbe Estuary in the Hamburg harbor. The Hamburg harbor (z2) was characterized by highest CH_4 oxidation rates with a median of 161 nmol L^{-1} d^{-1}, or 4.83 μmol L^{-1} $month^{-1}$. In summer 1997, the along-estuary DIC increase was from < 1500 to > 1900 μmol L^{-1} in zone 2. Thus, the CH_4 oxidation rates are not in the same order of magnitude as the observed DIC changes, and methane as source of CO_2 can only explain a small part of the observed DIC production.

Additional sources of DIC include other freshwater contributions from tributaries and groundwater along the Elbe Estuary (Supporting Information Table S7). Amann et al. (2015) assumed that the influence of such water bodies was minimal

due to the much larger volume of the estuary. Assessment of the influence of adjacent water bodies is out of scope of the present study.

Seasonal maximum DIC concentrations in late autumn and winter (November–February) were up to double those of spring and summer (Fig.7d). This could be due to increased mobilization and export of DIC via rainfall and snowmelt in the Elbe catchment area comprised of carbonate-rich sediments (Amann et al. 2015). The low winter temperatures would have reduced bacterial activity. However, undersaturated DO along the estuary, specifically in February, indicates dominating heterotrophy (Fig. 7), which may have also contributed to the higher DIC concentrations in winter.

The significant temporal increase in DIC in the mid to lower estuary (Figs. 2, 3c,d; Table 2) indicates that changing rates of autochthonous biogeochemical processes, such as bacterial remineralization, or contributions from other allochtonous DIC sources, such as the North Sea and Wadden Sea (Reimer et al. 1999), may have influenced DIC concentration during the recovery state. Another interesting point is that upper estuary TOC concentration increased by 55% by 2017, and this could have reflected enhanced phytoplankton biomass. For example, Amann et al. (2012) demonstrated that POC increase was partly due to increased phytoplankton biomass in the upper Elbe Estuary (z1, comparing 1993–1998 and 2005–2008). The mid to lower Elbe Estuary could be receiving a higher amount of labile OM over time, which could be available for remineralisation, subsequently enriching DIC. The drivers for this increase are further assessed in a separate study (L. C. V. Rewrie et al., unpubl.). Another upcoming anthropogenic stress that could have influenced the estuary during the recovery state is climate change, with rising temperatures and intensification of the hydrological cycle (Christensen and Christensen 2003). These factors are investigated further (L. C. V. Rewrie et al., unpubl.), including changes in the carbonate system, but so far, our analyses indicate that the ecosystem of the Elbe Estuary continues to undergo a change in its inorganic and organic carbon cycle.

Conclusion

The inorganic carbon system in the Elbe Estuary, a temperate estuary affected by varying levels of anthropogenic pressures, including heavy pollution, has changed significantly several times since the 1980s. Over the following three decades, three distinct shifts in ecosystem state were identified, based on carbon (DIC) dynamics and other key ecosystem parameters. The polluted state (1985–1990), with high DIC in the entire estuary, was dominated by heavy metal pollution and inhibition of primary production, with undersaturated DO and low pH (< 7.7). The high organic carbon in the estuary can be attributed to Elbe River inputs from minimally treated industrial and sewage inputs. The upper and middle estuary was characterized by intense nitrification of excessive NH_4^+ concentrations, driving the mid-estuary DO minima. The coastal region outside the estuary mouth had extremely high DIC concentrations reaching 3000 μmol L^{-1}. We postulate that the OM degradation, from allochthonous estuarine sources and autochtonous coastal phytoplankton, caused the observed enrichment in DIC, mainly in the lower-outer estuary where heavy metal pollutants decreased below toxic levels (as defined by the IKSE targets).

The ensuing transitional state from 1991 to 1996, was characterized by intense biogeochemical changes in the ecosystem caused by the reduction in heavy metal concentrations and nutrients in the Elbe River. Biological productivity in the upstream region, and likely upstream of the Geesthacht weir, drove distinct seasonal patterns in DO and pH in the upper regions of the estuary, signifying the re-establishment of a healthier and more productive ecosystem. DIC concentrations did not exhibit the same seasonal variability, of reduced concentrations due to primary production, and this is not yet fully explained.

During the recovery state (1997–2018), a new pattern in DIC established, with seasonal fluctuations in DIC, DO, and pH. The dominant control of primary producers on DIC during spring to summer in the upper estuary was followed by a change to heterotrophy in the mid to lower estuary. Significant increases in DIC were observed in the mid to lower estuary during the entire recent state, by > 23 μmol L^{-1} yr^{-1} in the most recent decade (2008–2018). These changes signify that the carbonate system in the Elbe Estuary is still undergoing changes, potentially due to intensifying remineralization of OM.

This study has demonstrated how human activities can alter an ecosystem, with nonlinear effects observed decades after a period of heavy pollution, followed by geo-politically driven clean-up strategies and successes, and recent environmental management strategies. Consequently, determining how estuaries and coastal systems function and respond to changing anthropogenic activities is useful and necessary, for example, when estimating how carbon and nutrient budgets in such ecosystems could have changed over time. Our research on the Elbe Estuary will hopefully contribute to a better understanding of the functioning of other estuarine ecosystems that are subject to varying levels of pollution and anthropogenic stressors.

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Conflict of Interest

None declared.

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