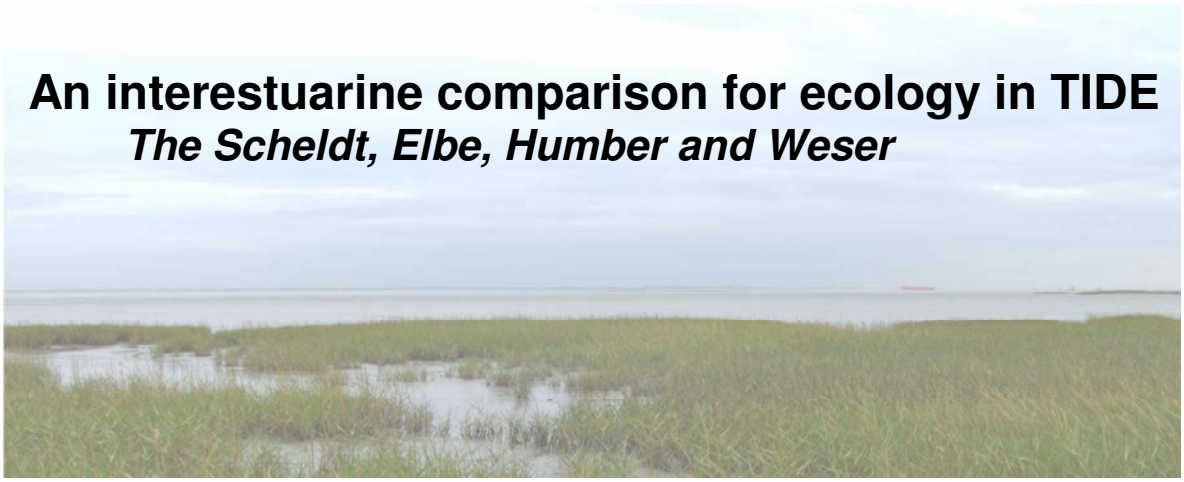
An interestuarine comparison for ecology in TIDE

The Scheldt, Elbe, Humber and Weser



Geerts L, Maris T, Meire P

With contributions of Beauchard O, Schöl A, Vandenbruwaene W., Van Damme S, Wolfstein K, Manson S, Saathoff S, Soetaert K, Cox T, Meire A, (February 2013)

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1 Introduction

1.1 Biogeochemical processing for N, P and Si in Northern temperate estuaries

Estuaries are the last barrier to the coastal zone and can be considered as a large biogeochemical reactor. With the tide intruding, while freshwater discharging from the rivers upstream, very dynamic environments are created, marked by a strong salinity gradient. Changes in ionic strength, dissolved organic matter content, pH and in the carbonate system between fresh and saltwater end members are induced, resulting in changed speciation of nutrient species and thus, reactivity of the estuarine system. Estuaries always have had a great appeal to humanity. About 40% of the global population lives within 100 km of the shoreline. However, this implies a large demographic and economical pressure upon estuarine ecology (Statham et al. 2011). Land use change and increasing population have caused increased nutrient inputs for total dissolved inorganic nitrogen and phosphate. Increasing efforts for water treatment since the 80ies, have reduced these nutrient inputs again. However, since phosphate is point source related, while nitrogen is rather diffuse source related, phosphate loads have been controlled more efficiently and nutrient ratios within the estuary and nutrient ratios of loads arriving in the coastal zone have changed disproportionally, changing phytoplankton communities and overall ecological functioning (Statham et al. 2011). This has often been associated with negative effects, such as nuisance algal blooms (e.g. *Phaeocystis*; Rousseaux et al. 2002), immediately fuelling the microbial loop instead of transferring energy to the higher, often economically valuable, trophic levels and promoting oxygen deficiencies (Rousseaux et al. 2006, Carbonnel et al. 2009).

Within the TIDE report main focus will be on water quality patterns and sink-source functions for oxygen and macronutrients and primary production in the water column. Data for intertidal exchange were not available. Nevertheless, importance of the intertidal is discussed when ought to be an important explanatory variable in the research question to be addressed.

Riverine inputs are recognized as the world's major source of macronutrients to the global oceans. However, macronutrients passing through estuaries are subjected to several biogeochemical transformations, both in the water column and by exchange with the sediment of the subtidal and intertidal area. Furthermore, there may be additional atmospheric or coastal inputs and overall strong physical control by hydro-morphology (residence time, light climate, suspended matter dynamics, freshwater discharge…) (Desmit et al. 2005, Statham et al. 2011). Groundwater input might be another, at present underestimated, source of input (Statham et al. 2011). Overall interactions within estuaries and the environment are presented in fig. 1.

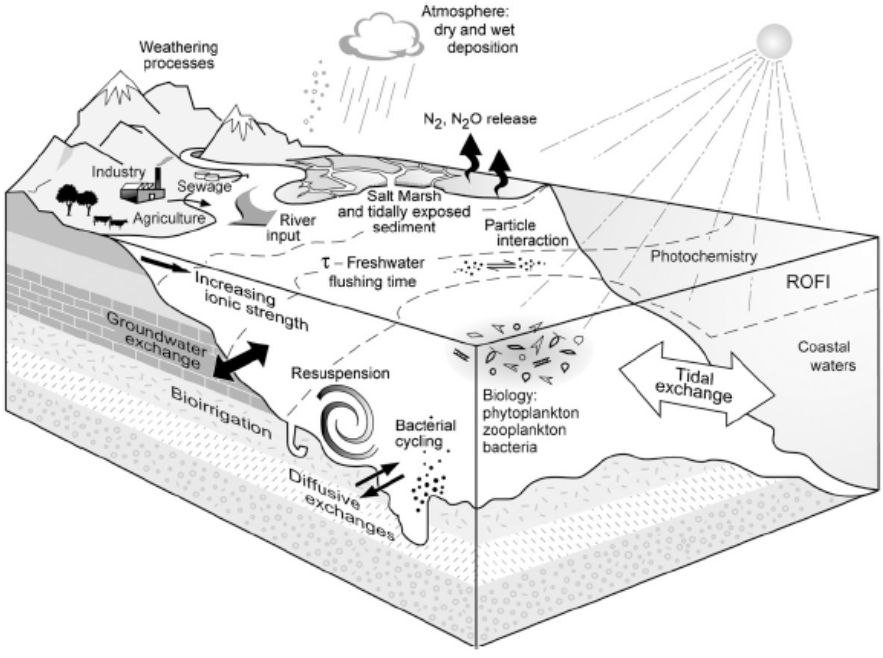


Fig. 1 Estuarine processes and exchanges for nitrogen, phosphorus and dissolved silica according to Statham et al. 2011 (ROFI = Region of Freshwater Influence).

Most northern temperate estuaries are net heterotrophic experiencing more respiration than production (van der Zee et al. 2007). In the following subsections some general background information per TIDE estuary is given. All estuaries share similar challenges for economy (all TIDE estuaries have at least one port) and ecology (protection of several Special Protected Areas along their estuarine gradient according to the European Habitat and Bird Directives).

1.1.1 Elbe

The Elbe estuary stretches from the tidal weir at Geesthacht up to mouth in the North Sea, beyond Cuxhaven (171 TIDE km). The Elbe river catchment is about 148 268 km² large. An average freshwater discharge of 730 m³/s is observed (Schlarbaum et al. 2010). The main tributaries flow into the upstream riverine part of the Elbe river (Quiel et al. 2011). The freshwater discharge from upstream entering the estuary is so large; that further input of tributaries within the estuary was considered of minor importance in TIDE. The Elbe is considered the largest source for total dissolved inorganic nitrogen and phosphate to the German Bight, a region often experiencing extensive *Phaeocystis* blooms. A large part of the Elbe is continuously dredged and most is channelled, to ensure navigability of large container ships up to Hamburg, one of the world's largest ports (Schlarbaum et al. 2010). The Elbe is recently (spring 1999) been further deepened about 1 m in the freshwater zone, near the Hamburg port area. An increase in tidal range, currently 4 m at spring tide, has placed the estuary at the border of a meso- and macro-tidal estuary (Kerner 2007). However, the Elbe was classified as partially mixed based on its salinity profiles. According to literature residence times varies from 10 days in winter, up to 72 days in summer. The salinity front is observed near Glückstadter, coinciding with the estuarine turbidity maximum zone (TIDE km 84 -114) (Schlarbaum et al. 2010). There are about 170 inhabitants per square kilometre. Agricultural land use dominates the catchment (Quiel et al. 2011 and refs herein). The water quality has improved since the 80ies, with phosphorus being banned from detergents in 1987. In the beginning of the 90ies a tremendous change concerning the load of the Elbe river has happened due to the breakdown of important industrial companies of the formerly German Democratic Republic. Improvements in wastewater treatment plants and in industrial inputs strongly influenced the water quality of the Elbe river and its estuary. Loads for nitrogen and phosphorus decreased significantly, but disproportional, leading to increased nitrogen phosphorus ratios (Schlarbaum et al. 2010).

1.1.2 Scheldt

The Scheldt estuary reaches from the tidal weir in Gent (Belgium) to the mouth in the North Sea at Vlissingen (the Netherlands) (160 TIDE km). The Scheldt river catchment is about 21 580 km³ large. The Scheldt estuary comprises two main tributaries, the Rupel and the Dender. Taking discharges into account, the Rupel can be considered the most important tributary. Freshwater coming from the upstream boundary, the Bovenschelde, is in part deflected to canals (e.g. Gent-Terneuzen). Within the Rupel, also inputs from sub-tributaries the Zenne, Dijle and Nete are gathered. The catchment is mostly urban, comprising about 400 inhabitants per square kilometre, and also experiences intense industrial activity near the port of Antwerp, Gent and Vlissingen (Arndt et al. 2011, van der Zee et al. 2007). Water quality decreased with increasing population, but has improved considerably since the 90ies due to enhanced water treatment effort. Since 1996 the water treatment of household effluents changed, significantly reducing phosphorus loads (Van Damme et al. 2005, Soetaert et al. 2006). However, it was not until 2007, water from the Zenne, entering the Scheldt estuary via the Rupel, was treated (corresponding to 1 million inhabitants) (Aquiris 2010). The average channel depth is about 15 to 20 m. The estuary can be classified as a well-mixed, macro-tidal estuary. The dominant tidal influences, cause residence times of 50 to 70 days in the Westerschelde (Soetaert et al. 1995). The Scheldt is relatively turbid, with maximum values of 400 mg/l suspended particulate matter. The salinity intrusion is observed near the Rupel mouth (salinities usually lower than one). Most intense algal blooms are observed in summer in the upper reaches of the freshwater part of the estuary (Arndt et al. 2011).

1.1.3 Humber

The Humber is the largest river catchment of England, covering about 20 % of its surface area (24 240 km²). Also in terms of freshwater flow, the Humber estuary is largest in the UK (250 m³/s) (Sanders et al. 1997). It can be classified as a large well-mixed, macro-tidal estuary. Tidal range

goes up to 6 m. Turbidity can increase up to 3000 mg/l near Brough and effectively inhibits any primary production in the water column. However, a phytoplankton bloom can be observed in the estuarine plume around Spurn point (Jickels et al. 2000). Despite high suspended matter concentrations, only $0.1 \cdot 10^6$ ton is carried to the sea. Most sediment is imported from the sea into the estuary. Most is coming from the erosion of the Holderness cliffs near Spurn Point (Mortimer et al. 1998). The estuary is fed by two main tidal freshwater rivers, the Ouse and Trent. The river catchment encompasses a mix of industrialized areas, agriculture and urban area. The estuarine turbidity maximum can be found in the lower salinity reaches. Both the salinity intrusion front and the turbidity maximum zone shift seasonally up- and downstream by differences in discharge. However, the fresh-saltwater interface is more susceptible for differences in seasonal discharge (Uncles et al. 2001, Uncles et al. 2006). The estuarine turbidity maximum zone is located 20 to 50 km downstream the tidal weir at Naburn. The TIDE estuary boundaries are set at the tidal limit of the Ouse, flowing to the Humber, and finally to Spurn point (TIDE km 122). The Trent is, like the Rupel for the Scheldt estuary, considered, as the most important tributary for the Humber. The origin of the suspended particulate matter is essentially mineral and falls within the clay size class. Residence times for suspended particulate matter have been calculated as large as 18 years, due to non-conservative mixing (repeatedly settling and re-suspension) (Statham et al. 2011). Residence time for dissolved substances increases up to 2 months in summer, less in winter (Jickels et al. 2000).

1.1.4 Weser

The Weser estuary reaches from the tidal weir in South Bremen up to the mouth in the North Sea (119 TIDE km). The river catchment is 46 000 km^2 large. The tidal range is about 4 m at Bremen, and 3.6 m at Bremerhaven, implying the Weser estuary, like the Elbe estuary, is placed at the border between a meso-tidal and a macro-tidal estuary. The Weser is considered a well-mixed estuary. The bottom sediments are fine-grained except for the area between 53 and 66 TIDE km, where muddy sediments dominate. Due to salt mining in the catchment, the freshwater part of the estuary can reach values up to 2 PSU, depending on the freshwater run-off (Grabemann & Krause 2001, Villars & Delvigne 2001). Residence time varies from 2 to 20 days depending on freshwater discharge. Only limited research has been performed upon water quality and nutrient fluxes in the Weser estuary (Grabemann et al. 1990, Schuchardt et al. 1993). Most studies focus upon the estuarine turbidity zone and sediment dynamics in general (e.g. Müller et al. 1990, Grabemann & Krause 2001). Suspended matter concentration can reach up to 1500 mg/l (Villars & Delvigne 2001). The estuarine turbidity maximum zone is found in the low salinity reaches (TIDE km 60 to 70) of the Weser estuary and its formation can be associated with tidal asymmetry effects. The exact position depends highly on freshwater discharge (Grabemann & Krause 2001 and refs herein). Much of the land use around the Weser is for agriculture and livestock. Like for the Elbe, also in the Weser nitrogen and phosphate from river inputs have reduced significantly. Nitrogen reduced since the 80ies, and phosphate since the 90ies. Also in the Weser estuary this has lead to disproportional nutrient ratios. Even though both nitrogen and phosphorus inputs markedly decreased, the river input to the Weser estuary can still be considered net positive for both nitrogen and phosphorus (RBC Weser 2009).

1.2 Nutrient fluxes

Nutrient fluxes are considered for **dissolved inorganic nitrogen, phosphate and dissolved silicate**. These macronutrients are essential and key elements in limiting primary production in estuaries (if light is not limiting, see further '*1.2.1 Hydro-morphology*') (Underwood & Kromkamp 1999, Carbonnel et al. 2009). Nutrient fluxes with respect to estuaries can be measured for (1) estuarine input, (2) transformation processes within the estuary and for (3) estuarine output to the coastal waters (Statham et al. 2011).

Estuarine **input** of macronutrients that can be considered in estuaries (see earlier, fig. 1):

- Exchange at the atmosphere – water boundary;
- Coastal input;
- Input from the main tributaries and the upper boundary of the estuary;
- Ground water input.

Point sources and diffusive sources can be discriminated. They can either be natural or anthropogenic, direct or indirect. Natural sources can include rock weathering. Anthropogenic sources often considered in estuaries are related to sewage effluents (households), industrial effluents (industry) and agricultural run-off (agriculture). Diffusive sources are most difficult to manage. Direct sources include direct disposal of e.g. nitrate, while indirect sources could be input of organic matter (pool for mineralisation etc.).

Transformation processes are described in further detail in the following section, '*1.2.2 Sink and source function regulation*', for each macronutrient separately, together with their potential input sources.

Output to the coastal waters is the cumulative **result of estuarine input and estuarine processing**, defining whether the estuary is a source or sink as a whole for the coastal zone. This defines the so-called filter capacity of an estuary (Soetaert et al. 2006, Quiel et al. 2011). The latter states which nutrient ratios are eventually held in the coastal zone, and consequently which phytoplankton communities will follow. This will define further flow through to the linear food chain and/or microbial loop; hence, very important for overall ecological functioning and provisioning of several ecosystem services. Excess of nutrients can cause eutrophication problems, often found to be detrimental for system functioning (Rousseaux et al. 2006; see also earlier, '*1.1 Biogeochemical processing for N, P and Si in Northern temperate estuaries*'). Once nutrient loads arrive in the sea they are no longer to be managed. Hence, estuarine management has a crucial role in ensuring the filter capacity for nutrients.

1.2.1 Hydro-morphology

Nutrient fluxes are highly seasonal (reflected in hydrodynamics) and vary spatially (reflected in salinity and morphology) (Sanders et al. 1997, Statham et al. 2011).

1.2.1.1 Salinity gradient

Due to tidal mixing and freshwater input, estuaries demonstrate a strong salinity gradient. Changes in ionic strength, dissolved organic matter content, pH and in the carbonate system between fresh and saltwater end members are induced, resulting in changed speciation of nutrient species and overall reactivity of the estuarine system (Statham et al. 2011).

1.2.1.2 Residence time and freshwater discharge

Residence times may vary from several weeks to several months for various estuaries. Residence time also varies seasonally in function of freshwater discharge. Usually freshwater discharge is lower in summer, generating more extended residence times. A long residence time implies more opportunity for sediment-water exchange and water column biogeochemistry to occur (Statham et al. 2011). Furthermore, it allows algae to grow, rather than being flushed out of the estuary (Underwood & Kromkamp 1999).

1.2.1.3 Suspended matter dynamics and light climate

Usually, high suspended particulate matter concentrations with a typical turbidity maximum zone near the oligohaline zone are observed in estuaries. This is due to river input, continuous re-suspension of the fine fraction of the sediment inventory and import from coastal waters. Non-conservative mixing makes that the suspended matter residence times are much longer than those observed for water and dissolved substances. For the Humber a suspended particulate matter residence time of 18 years was calculated (Turner 1990 in Statham et al. 2011). Suspended particulate matter increases the surface area for adsorption and desorption processes to occur and provides a hotspot for microbial and algal activity. However, suspended matter concentrations may also modify the light climate and hence, by consequence rather inhibit primary production by algae, than stimulate it (Statham et al. 2011).

1.2.1.4 Intertidal and subtidal area

Intertidal and subtidal area provides a large sediment surface at which exchange with the water column can take place. The larger this area, the more nutrients can be exchanged (Statham et al. 2011; for more details, see further, '*1.2.2 Sink and source function regulation*' per macronutrient).

1.2.2 Sink and source function regulation

1.2.2.1 Nitrogen

Inter-conversions (fig. 2) occur over a large range of redox states (-3 to +5). However, reactive nitrogen is the most important to consider, since this is most involved in biological activity. Therefore, most studies indeed focussed upon dissolved and mostly inorganic nitrogen species, more specifically upon nitrate. Most present estuaries are well oxygenated, and nitrate is thus most abundant. Also nitrate is mostly related to eutrophication issues. Gaseous forms (NO_x, N_2O) are much less studied. Nonetheless, these could give us more valuable information on nitrification and denitrification rates (Statham et al. 2011).

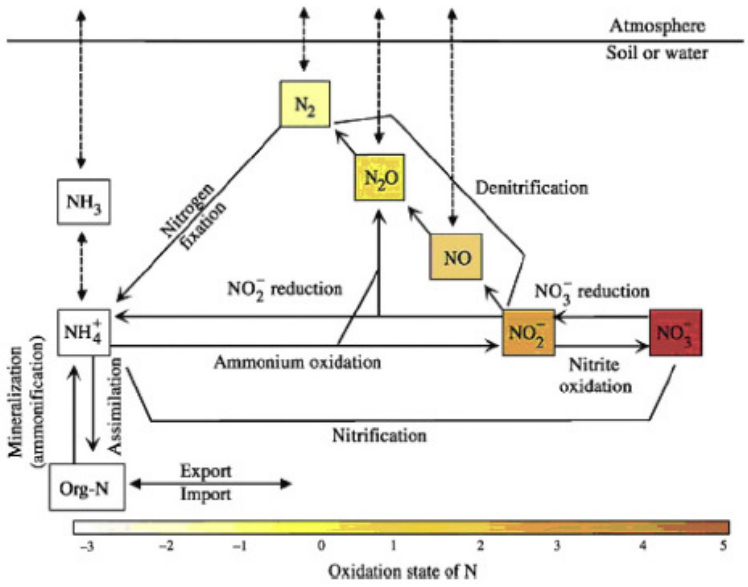


Fig. 2 Main inter-conversion routes for nitrogen (Statham et al. 2011)

Following processes (Sanders et al. 1997, Statham et al. 2011) occur in both the water column and sediments:

- export to adjacent coastal oceans;
- biological uptake, might be in resistant forms within the sediment;
- losses to the atmosphere by nitrification and denitrification processes;
- organic matter mineralisation.

Although most is transported to the adjacent coastal zone, in some cases removal by production of gaseous forms can be significant. Benthic denitrification has been shown to remove 44 % of nitrate in estuaries. Biological uptake depends on primary production and has been show to have significant effect on dissolved inorganic nitrogen concentrations in spring (Arndt et al. 2011). Nitrification and denitrifcation are influenced by high organic matter loads, nitrate concentrations and the presence of an oxic or sub-oxic zone (Statham et al. 2011). In the Elbe the turbidity maximum zone is observed together with a peak in nitrification. The ammonium source for nitrification rather came from particulate organic nitrogen degradation, than it came from dissolved organic nitrogen degradation in the turbidity maximum zone. Schlarbaum et al. showed that adsorption and desorption processes could play an important role in the distribution of dissolved organic nitrogen and ammonium concentrations (Schlarbaum et al. 2010 and refs herein). Although, nitrogen is thought to be not very particulate reactive opposed to phosphorus (Statham et al. 2011). The rate of denitrification reaches a maximum at concentrations of 500 µM nitrate (7 mg/l) (Jickels et al. 2000). Denitrification and consequent nitrogen removal is generally promoted by low oxygen concentrations (Soetaert et al. 2006). Although, nitrogen is less likely to be removed in deeper channels (Alexander et al. 2000). The larger the sediment surface, the larger the potential oxic-anoxic boundary zone for denitrification (Dähnke et al. 2008). Both intertidal marshes and mudflats also have been demonstrated to be important in nitrogen retention (Mortimer et al. 1998, Van Damme et al. 2009). Higher influx of nitrate was observed on intertidal mudflats in the freshwater part of the estuary (Mortimer et al. 1998). Fluxes by the sediment-water exchange can

be enhanced by macro-faunal activity through bio-irrigation (Mortimer et al. 1998, Braeckman et al. 2010).

Inputs for inorganic nitrogen species are associated with atmospheric exchange (N-deposition), surface water run-off, rivers and ground water input. Input by rivers is of primary importance. Either source can be direct, or indirect (through organic matter input). The importance of groundwater input is largely unknown.

Dissolved organic compounds are not considered, but are possibly of more importance than assumed at present (Statham et al. 2011).

1.2.2.2 Phosphorus

Phosphorus is regulated by inorganic and biological interactions. Hence, phosphorus dynamics are dependent on the presence of different particulate and dissolved phosphorus species and biological activity. Phosphorus is required for photosynthesis, general metabolism, cell wall synthesis and energy transfer (e.g. ATP) (Statham et al. 2011). Phosphate and particulate inorganic phosphorus bound to suspended matter both seem to be the most abundant phosphorus species involved in phosphorus dynamics (van der Zee et al. 2007).

Phosphate is very particle reactive. In estuaries a buffering mechanism exists at the suspended particulate matter-water and sediment-water interface.

In turbid estuaries (SPM > 50 mg/l), phosphate is strongly adsorbed to iron-oxyhydroxides (fig 3). As particulate phosphorus arrives in the high salinity zone, competition for adsorption sites by stronger anions (OH^-, F^-, SO_4^{2-}, …), causes suspended matter to release phosphate to the water column again (van Beusekom & Brockmann 1998, Deborde et al. 2007, Statham et al. 2011).

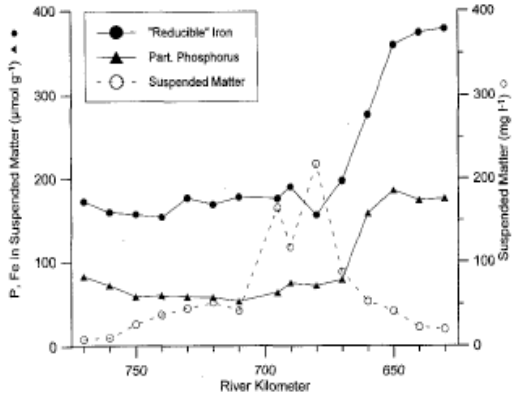


Fig. 3 Relationship of particulate phosphorus and Fe-oxyhydroxides, together with the salinity profile for the Elbe during a March sampling in 1995 (van Beusekom & Brockmann 1998)

An equilibrium would be reached for concentrations of 5 µM (0,015 mg P/l), and desorption is promoted at higher concentrations (Soetaert et al. 2006 and refs herein). Deborde et al. (2007) found adsorption and desorption processes of phosphate to be independent of phosphate concentrations. However, in the Gironde concentrations never exceeded 5 µM (Deborde et al. 2007). Paradoxically, large removal by suspended matter relative to sediment burial implies less storage of phosphorus within the estuary, since phosphate is easily released again in the high salinity zones (Jickels et al. 2000, van der Zee et al. 2007). This mechanism of phosphate release is observed in the conservative mixing diagram of many temperate estuaries, as so-called bell-shaped profiles (fig. 4). For very high suspended particulate matter concentrations as those observed in the Gironde (9000 mg/l), some phosphorus did not desorb towards the sea. This delayed desorption could be attributed to increased primary production in the high salinity reaches, were light became more available again. Most desorption was observed in the 0 to 12 PSU salinity range (Deborde et al. 2007). Also in the Scheldt and Elbe, most desorption was observed within this range, and from this point on (sal > 10 PSU) decreasing linearly towards the sea because of dilution (conservative behaviour) (van Beusekom & Brockmann 1998, van der Zee et al. 2007).

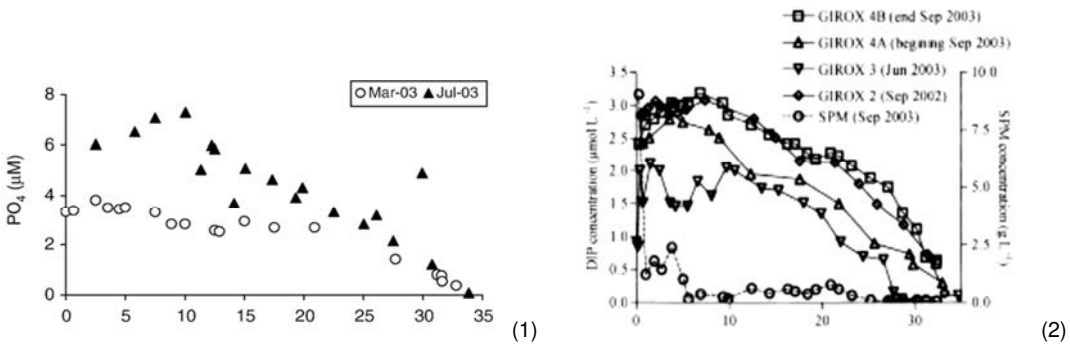


Fig. 4 Left: (1) Bell-shaped profiles for phosphate release near PSU salinity 10 range for the Scheldt in March and July 2003 (van der Zee et al. 2007); Right: (2) Bell-shaped profiles for phosphate release in the 0 to 12 PSU salinity range for the Gironde during the several GIROX cruises in January and September 2002-2003 (Deborde et al. 2007).

Organic matter mineralisation for dissolved inorganic phosphate is a rather slow process, and its importance is largely dependent on residence times (69 days for the Gironde). Nevertheless, for the Gironde example less than 10 % is mineralized in the sediment while about 50 % is mineralised in the estuarine turbidity maximum zone (Deborde et al. 2007). Most organic matter mineralisation appears to occur within the turbidity maximum zone, usually to be found in the lower salinity reaches (Abril et al. 1999). The higher mineralisation rate can be attributed to the larger reactive surface area of the suspended particulate matter and the availability of more degradable organic matter opposed to higher salinity reaches (van Beusekom & Brockmann 1998). Furthermore the residence time (and thus time for biogeochemical transformation processes) of non-conservative behaving suspended matter is significantly longer than for conservative behaving dissolved substances (Statham et al. 2011).

The suspended particulate matter might also settle before it arrives in the high salinity zone and form a pool of phosphate buried in the sediment. The phosphate burial in the sediment is very dependent on the redox state. When the iron-oxyhydroxides in the sediments are reduced, phosphate is again released to the water column. Also, when sediments are exported more downstream, iron-sulfate complexes are formed preferential upon iron-phosphate complexes, and phosphate is released (Statham et al. 2011). Combined with re-suspension phosphate release can be further enhanced (van der Zee et al. 2007). However, some phosphate may be more permanently buried when precipitated as authigenic minerals like apatites (van Beusekom & Brockmann 1998).

In general, phosphorus retention is promoted by high oxygen concentrations, opposite to the requirements for nitrogen retention (Soetaert et al. 2006). Tidal mudflats studied in the Humber, showed very small and variable phosphate fluxes comparable to fluxes in other temperate estuaries (Mortimer et al. 1998 and refs herein). Fluxes by the sediment-water exchange can be enhanced by macro-faunal activity through bio-irrigation (Mortimer et al. 1998, Braeckman et al. 2010).

Rivers are the most principal pathways for phosphorus input. Atmospheric inputs can be considered negligible compared to atmospheric deposition for nitrogen. Groundwater inputs are largely unknown and can be function of bottom geo-morphology (e.g. if a so-called 'iron curtain' is present, groundwater input can be inhibited). Phosphate dynamics are difficult to generalize and are very dependent on the physico-chemical properties of the environment (Statham et al. 2011).

Phosphate and particulate inorganic phosphorus (adsorbed to SPM) often are the main phosphorus species involved in phosphate dynamics (van der Zee et al. 2007). However, also dissolved organic phosphorous appears to become of more interest in phosphorus dynamics, but remains largely unstudied up to now (Statham et al. 2011).

1.2.2.3 Silica

Dissolved silica is mainly regulated by biology along the estuarine gradient. Thus fluxes are highly seasonal dependent. It is a critical component for diatoms to build up their cell walls (frustules). Hence, in summer lowest dissolved silica concentrations and corresponding highest biogenic silica (opal) concentrations are observed. The residence time has to be sufficiently long for the diatoms

to take up the dissolved silica. Highest concentrations are observed in winter and behave conservatively along the mixing gradient. Diatoms have been shown to take up 50 to 70 % of the total silica load during the productive period (Carbonnel et al. 2009). When algal growth is inhibited, or stopped (dissolved silica limitation < 0.01 mM ~ 0.3 mg DSi/l, light, grazing), diatom frustules might sink and be buried in the sediment. Biogenic silica dissolution increases with salinity and some bacterial communities have been shown to increase dissolution too. Furthermore, phytoliths within macrophytes (e.g. Reed) can be added by topsoil erosion or directly from vegetation of riverbanks or tidal marshes to the biogenic silica pool. Tidal marshes are most likely very important silica recyclers to the estuary. Retention of biogenic silica in tidal marshes, originating from imported biogenic silica of diatoms via suspended matter sedimentation and phytoliths in Reed, combined with increased residence times and increased sediment-water interactions, intensifies biogenic silica dissolution processes. Tidal marshes have been demonstrated to be a source for dissolved silica when freshwater discharge and dissolved silica concentrations within the estuary are low (Struyf et al. 2006, 2007). Recycling capacity has been shown to be higher for young marshes than for older, more elevated marshes. This can be related to different sedimentation rates (Struyf et al. 2007). In intertidal mudflats silica fluxes were found very small within the Humber estuary. However, this might not be as representative, since primary production within this estuary is very low. However, low dissolution patterns could also be linked to rather low overlying dissolved silica concentrations (Mortimer et al. 1998). Fluxes by the sediment-water exchange are in general enhanced by macro-faunal activity through bio-irrigation (Mortimer et al. 1998, Braeckman et al. 2010). However, most dissolved silica originates from rock weathering and can be associated with riverine input (Carbonnel et al. 2009, Statham et al. 2011). In rivers dissolved silica concentrations usually remained high all year round and biogenic silica low (Carbonnel et al. 2009), except sometimes in larger rivers (e.g. Elbe, personal communication Andreas Schöl 2013). In the tidal river dissolved silica concentrations are almost completely consumed, while biogenic silica concentrations rise. Contribution of phytoliths in the Scheldt to detrimental biogenic silica was found non-significant. Hence, delivery of silica from Reed phytoliths could not account for the increase in biogenic silica during the productive period. In summer dissolved silica concentrations can be consumed up to limitation levels (Van Damme et al. 2005, Soetaert et al. 2006). Within the estuary biogenic silica is mainly delivered by diatoms, especially in summer. In winter, most is imported as dissolved silica (Carbonnel et al. 2009). When silica export is inhibited, nuisance algal blooms can appear downstream in the coastal zone (Rousseaux et al. 2006). Opposed to the summer bloom, the spring bloom had no significant effect upon silica dynamics (Carbonnel et al. 2009). To understand regulating mechanisms, it is important to also consider biogenic silica fluxes (Carbonnel et al. 2009). Dynamics in the freshwater zone drive the dynamics in the coastal zone (Rousseaux et al. 2006).

1.2.3 Nutrient ratios

The ideal nutrient ratio for diatom growth is defined by Redfield as 106/16/1/16 corresponding to C/N/P/Si respectively (Billen & Garnier 2007). When light climate and residence time are suitable, primary production will increase with nutrient concentrations rising. However, within most estuaries light is limiting (SPM > 10 mg/l, mixing depth) and change in nutrient ratios will only affect algal growth there where a better light climate is reached, e.g. in the estuarine plume of the Humber estuary, beyond Spurn point (Nedwell et al. 2002, Soetaert et al. 2006). Last decades, nutrient loads have increased, because of population increase and land use change. Combined with unequal water treatment efficiency, this has lead to disproportional nutrient ratios in many estuaries (Statham et al. 2011). Nutrient ratios define phytoplankton species composition and succession along the estuarine gradient; hence define ecological functioning (Carbonnel et al. 2009). Phosphorus is typically limiting in freshwater, while nitrogen is limiting in estuarine and coastal systems. However, large riverine nitrogen input and more efficient phosphorus removal have shifted the limitation in many northern temperate estuaries to a limitation for phosphorus (Sanders et al. 1997, Soetaert et al. 2006). Nitrogen is mostly related to diffuse input sources and therefore much more difficult to manage. Although to a lesser extent, also silica loads have been altered by human activities. Hydrological measures such as embankments have reduced the contact with the riparian vegetation and consequently lowered silica input in the estuary. Furthermore, deforestation has lowered the baseflow delivery of silica twice to threefold in

temperate European watersheds (Struyf et al. 2010). Hence, lowered silica input and increasing nitrogen and phosphorus loads have increased overall silica limitation in estuaries.

1.3 Primary production

Primary production can be defined as the assimilation of inorganic carbon and nutrients in organic matter by autotrophs. Thus, primary production implies a rate. Usually only phytoplankton primary production is measured. Chlorophyll *a* is used as a proxy for algal biomass. However, primary production does not necessarily represent biomass, since for primary production measurements grazing and sedimentation are not taken into consideration. Gross primary production includes respiration processes (Underwood & Kromkamp 1999). In the estuaries considered in TIDE we can distinguish phytoplankton in the water column and microphytobenthos at the sediment upon intertidal mudflats. Microphytobenthos can contribute up to 50 % of primary production (Underwood & Kromkamp 1999 and refs herein). However, upscaling is found to be difficult, because of spatio-temporal variability.

Phytoplankton in estuaries largely depends on light availability (the so-called euphotic depth, the depth at which primary production equals respiration). The ideal mixing depth to euphotic depth ratio for production to exceed respiration, should be smaller than 6 (Cole & Cloern 1984 in Underwood & Kromkamp 1999). Microphytobenthos is more temporal and spatial variable because of flooding dynamics (and co-occurring different light regimes) and also depends upon the cohesiveness of the sediments. However, while light can penetrate deeper in sandy sediments, sandy sediments do not retain nutrients and within these loose sediments microphytobenthos can become nutrient limited (Underwood & Kromkamp 1999).

Hence, also nutrients might play a crucial role in affecting both biomass and primary production of phytoplankton and microphytobenthos. This can be examined by nutrient ratios. Often a correlation between chlorophyll *a* and dissolved inorganic nitrogen can be found. A nutrient gradient can modify exchange at the different tidal marshes and mudflats along the estuary (Underwood & Kromkamp 1999).

Furthermore, a species succession is defined by the salinity gradient in estuaries. Estuaries can be further subdivided in well-mixed and more stratified estuaries. This is largely function of tidal range. When tidal range exceeds 4 m, estuaries are considered macro-tidal. These estuaries are usually well-mixed. A tidal range between 2 and 4 m is called meso-tidal and this type of estuaries can be partially stratified, like is observed in the Elbe estuary (see earlier). Differences in mixing patterns are ought to be the reason why estimates for primary production are so different between estuaries (Underwood & Kromkamp 1999).

Other influencing factors are grazing, cell lysis, viruses and sedimentation. For grazing, abundance and grazer community composition are most important (personal communication Andreas Schöl 2013), next size selective grazing (Underwood & Kromkamp 1999), as it defines whether algae are directly processed to the microbial loop or whether algae first pass through the linear food chain.

Hydrology appears to be a very important factor. In the Elbe phytoplankton peaks are mainly regulated by the freshwater discharge and resulting residence time in the freshwater section of the estuary. When discharge is high, phytoplankton peaks are shifted more downstream. When discharge is low and residence time in the river itself is large, phytoplankton peaks are mainly observed in the upstream part of the river, and decay of algae is shifted downstream, most likely related to oxygen deficiencies (Quiel et al. 2011). Phosphorus limitation was demonstrated to have only limited effect. Most likely diatoms in the Elbe are capable for phosphorus storage. Arndt et al. (2011) demonstrated that temporal and spatial patterns in primary production in the Scheldt estuary during a summer diatom bloom are in fact mainly regulated by the physical environment. Higher river discharges placed the first controlling factor for primary production within the Scheldt estuary, next followed by light climate and silica limitation (Arndt et al. 2011).

1.4 Differences and similarities between Elbe, Scheldt, Humber and Weser

Estuaries are globally considered among the most productive biomes and are known for the delivery of several ecosystem services (Costanza et al 1997). TIDE focuses on estuaries of the Elbe (Germany), Weser (Germany), Humber (United Kingdom) and Scheldt (Belgium-the Netherlands). All these northern temperate estuaries are faced with similar challenges for economy and ecology. On the one hand large ports need to be further developed, while on the other hand European Natura 2000 Directives have to be implemented. TIDE aims to develop a framework for an integrated management and planning in these estuaries. Ecosystem services can only be optimised when ecological and hydro-geomorphological functioning are well understood. In this report we focus upon **ecological functioning**. Based upon specific management issues and research questions given by the several TIDE partners (Maris et al. 2011) and taking into account data availability for the estuaries examined, the following four questions concerning ecological functioning were decided at the Antwerp TIDE meeting (July 2012):

a) What are the important factors controlling ecosystem functioning within the TIDE estuaries?

Each estuary has it specific abiotic and biotic characteristics defining the framework in which ecosystem services can be delivered. In TIDE we focus upon ecological functioning in the water column (pelagic), because of data availability. Nonetheless, intertidal area constitutes a large part of the ecological functioning, providing habitat for plants and animals. When specific patterns per estuary are revealed, monitoring per estuary can be used more efficiently to further increase knowledge for estuarine specific ecosystem services.

b) How can we avoid oxygen deficiency situations in the TIDE estuaries?

Massive bacterial breakdown of organic matter can lead to wide spread oxygen deficiencies. This can be attributed to boundary input and/or estuarine processing. In TIDE mineralization, nitrification, denitrification and primary production are carefully studied. A dissolved oxygen concentration of 5mg/l is the minimum amount of dissolved oxygen required to sustain a healthy ecological functioning system (Holzhauer et al. 2011). Oxygen deficiencies (<5mg/l) appear to be a specific management issue for the Elbe and Scheldt estuary.

c) How do TIDE estuaries function as a filter for nutrients?

Estuaries can be a very important sink for nutrients. They reduce the loads significantly towards more downstream parts of the estuary and finally the coastal sea. This sink function is based on biogeochemical processing and assimilation by primary production in both the pelagic and benthic compartment. In TIDE we focused upon major dissolved nutrients for nitrogen, phosphorus and silica and examined the (expected) effect upon Redfield ratios and hence, primary production.

d) Which variables limit primary production in the TIDE estuaries?

Primary production and allochthonous organic matter is the basis of the estuarine food chain. Understanding the variables limiting primary production are essential to device management measures. If production is too low, the food chain can be hampered. Excessive production can cause oxygen problems impacting the higher trophic levels. Under nutrient limitation, e.g. silica, harmful algal blooms can cause major problems even for human health. However, high levels of primary production are not necessarily bad, since it might compensate for elevated biological oxygen demand (Maris et al. 2011). For the TIDE estuaries primary production was mainly studied for the Elbe, Scheldt and Weser estuaries. In the Humber no significant primary production in the water column could be detected.

Lessons learnt from differences and similarities can help to ensure further ecological functioning and hence, to optimize ecosystem services delivered.

2 Material and methods

2.1 Study area & period

The Elbe estuary is characterized by the largest river drainage basin (148 286 km^2), followed by the Weser (49 000 km^2), Humber (24 240 km^2) and Scheldt (20 863 km^2) (Sanders et al. 1997, Grabemann & Krause 2001, Arndt et al. 2011, Dähnke et al. 2008). These four northern temperate estuaries were selected based on their similar challenge to ensure both economic development and estuarine functioning. Water quality data are examined for the time period of 2004 up to 2009 and compared between the TIDE estuaries. Furthermore a coupling to hydro-morphology is made. In table 1 here below, the number of sampling stations for regular sampling campaigns, for continuous samplings, major tributaries, important locations and upper boundaries are given per estuary and zone. The estuarine zonation as decided in TIDE (Geerts et al. 2012) is used in all further data comparisons, unless specified otherwise.

Table 1 Overview of the number (#) of sampling stations for the regular and continuous sampling campaigns, tributaries, some major locations and the upper boundary/tributary per estuary and zone.

Estuary	Zone	TIDE-km	Regular (#)	Continuous (#)	Tributaries	Important locations	Upper boundary/ tributary
Elbe	***FW 1***	0-24	4	1 *(Bunthaus)*	Ilmenau	Geesthacht, Zollenspieker, Bunthaus	Schnackenburg *(-111 tide-km)*
	FW 2	24-46	4	1 *(Seemannshöft)*		St. Pauli, Seemannshöft	
	FW3	46-91	11	1 *(Blankenese)*	Este, Lühe, Schwinge, Pinnau	Blankenese, Lühesand Nort, Grauerort,Pagensander Nebenelbe, Glückstadt	
	OLIGO	91-118	4		Stör	Brunsbüttel	
	MESO	118-141	3		Oste	Cuxhaven	
	POLY	141-171	2			Scharhörn	
Scheldt	***FW 1***	0-31	4			Merelbeke	Bovenschelde
	FW 2	31-58	5		Dender, Durme	Appels, Dendermonde, St. Amands	
	OLIGO	58-89	7	1 *(Kruibeke)*	**Rupel**	Temse, Antwerpen	
	MESO	89-116	8			Zandvliet, Doel, Dutch-Flemish border, Bath, Waarde	
	POLY	116-160	6			Hansweert, Breskens, Vlissingen	
Ouse-Humber	***FW***	0-34	4	2 *(Cawood bridge, Selby bridge)*	Wharfe, Derwent	Naburn Lock	Ouse *(0 tide-km)*
	OLIGO	34-60	2	2 *(Boothferry bridge, Blacktoft Jetty)*	Aire, Don, **Trent**	Boothferry bridge	
	MESO	60-93	3	1 *(Corporation pier)*	Hull	Brough haven, New Holland, Albert dock, Goxhill	
	POLY	93-123	4			Grimsby, Spurnpoint	
Weser	***FW 1***	0-31	1		Hunte, Lesum, Ochtum	Bremen	Bremen Hemelingen *(-1,5 tide-km)*
	FW 2	31-44	1	2 *(Gütestation Brake,Gütestation Nordenham)*	Lune	Brake, Nordenham	
	OLIGO	44-69	1		Geeste	Bremerhaven	
	MESO	69-84					
	POLY	84-119	1				

2.2 Physics

Hydrodynamics and morphology are both important physical controlling aspects in primary production and biogeochemical processing.

2.2.1 Hydrodynamics

The exchange of water masses between adjacent open sea and freshwater, driven by tide, wind and precipitation processes, creates salinity gradients and induces transport of organic and inorganic matter (suspended solids, nutrients, silt…) (Duarte et al. 2009). Hydrodynamics are represented by freshwater discharge and residence times.

2.2.1.1 Freshwater discharge

The different TIDE partners for all four estuaries in TIDE collected freshwater discharge data. Monthly discharge data for the Elbe, Weser and Scheldt were available for the time period studied within the ecology report. For the Humber only yearly discharges were available. For the Scheldt and Humber not only freshwater discharges from the most upstream boundaries, but also those from the main tributaries are considered.

2.2.1.2 Residence time

Residence times are well descriptors of time and scale of physical transport processes. This allows comparison with time and scale of biological and chemical processes. E.g. when residence time is smaller than algal cell doubling time, algal blooms will be inhibited (Duarte et al 2009). Residence times were calculated according to the freshwater fractal method as described in (Vandenbruwaene et al. 2012).

2.2.2 Morphology

Morphology is described by intertidal areas, tidal amplitude, channel width, wet cross section, averaged depth (calculated as cross section divided by channel width) and bathymetrical depth.

2.2.2.1 Intertidal and subtidal areas

Intertidal and subtidal areas define the scale at which different processes can occur and can serve as an explanatory factor for water quality and ecology. To allow a minimum comparison between estuaries, intertidal and subtidal areas were calculated based on high and low water levels according to the method described in (Vandenbruwaene et al. 2012).

2.2.2.2 Geometry

Tidal amplitude, channel width, wet cross-section, averaged depth and bathymetrical depth can be additional explanatory factors for water quality and ecological processes. E.g. differences in tidal amplitude can play an important role in tidal pumping and localization of the turbidity maximum in estuaries (Uncles et al. 2006). Tidal amplitude, channel width, wet cross section and bathymetrical depth are all calculated from the cubature as described in the (Vandenbruwaene et al. 2012) for (at least) mean low and high tide. Within this report the average for mean high and low tides are each time represented.

The averaged depth is calculated as the wet cross section divided by the channel width. By consequence lower depth corresponds to a more shallow estuarine area with an increased contact surface between the pelagic and benthic compartment (fig. 5).

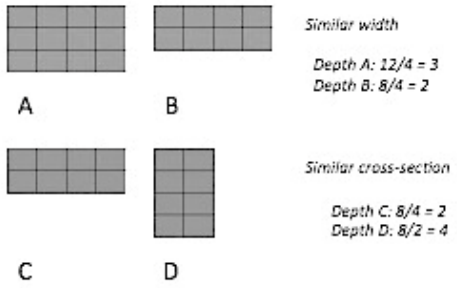


Fig. 5 Effects of different cross section and width for the average depth calculation. Lower depth corresponds to a higher contact surface between the pelagic and benthic compartment.

If only the absolute bathymetrical depth was considered, there would be no discrimination between estuarine areas with similar bathymetrical depth, one being narrower than the other compartment. By using averaged depths, less deep areas indeed imply increased biological and chemical processes (e.g. more primary production, mineralization, nitrification, denitrification…); potentially more re-suspension of sediments (which can influence the light climate and primary production) and more space for shallow water habitats.

Nevertheless, bathymetrical depths are also given, because they represent mixing depth in a well-mixed system, such as the macro-tidal estuaries examined in this report. Bathymetrical depth is the thalweg depth relative to the low water level at the $mouth_{geo}$ as defined in (Vandenbruwaene et al. 2012) and therefore could reach positive levels at the upstream boundary as defined in TIDE (Geerts et al. 2012).

2.3 Biogeochemistry

Estuarine ecosystems comprise the complex interaction between biotic and abiotic components. To understand the underlying processes that define water quality and ecology, regular biogeochemical (table 2) and continuous oxygen data have been gathered. To compare the data of the four estuaries they were classified into different zones related to chlorinity (Venice classification, see also Geerts et al. 2012). For further details on data availability per season and estuarine zone, see table 1 and Attachment 1.

As is clear from this table, comparison for biogeochemistry for all four TIDE estuaries can only be applied on a limited set of parameters. Furthermore, not all zones are equally represented in every estuary (table 1). Comparison and analyses are performed whenever at least two estuaries have data for the parameters of interest for the research question addressed (see '*1 Introduction*').

For summary statistics: number (n), mean, median, standard error, minimum and maximum of all variables

- in general for a whole year,
- in general for winter and summer season,
- & per estuarine zone according to the Venice-classification,

see Attachment 2.

Table 2 Summary overview of biogeochemical data availability per estuary (x* very few data points, x deduced data, x(!) chlorophyll extract for the Humber estuary, chlorophyll a data not available)

Parameter	Elbe	Scheldt	Humber	Weser
Chlorinity (CL)	x	x	x	x
Temperature (T)	x	x	x	x
pH	x	x	x	x
Conductivity (COND)	x	x	x	x
Dissolved oxygen (DO)	x	x	x	x
Dissolved oxygen saturation (DOsat)	x	x	x	x
Ammonium (NH4)	x	x	x	x
Nitrate (NO3)	x	x	x	x
Nitrite (NO2)	x	x	x	x
Organic nitrogen (ORG_N)	***x***	***x***	***x** **	***x***
Total dissolved inorganic nitrogen (TDIN)	***x***	***x***	***x***	***x***
Suspended particulate matter (SPM)	x	x	x	x
Chlorophyll a (CHL_A)	x	x	x (!)	x *
Phosphate (PO4)	x	x	x	x
Total phosphorus (TP)	x	x		x
Dissolved silica (DSI)	x	x	x *	x *
Biological oxygen demand (BOD)	***x***	x	x	x
Phaeopigments (PHAE)	x	x		x *
Dissolved organic carbon (DOC)	x	x		x
Particulate organic carbon (POC)	x	x		***x***
Total organic carbon (TOC)	***x***			x

2.3.1 General parameters

Spatial and temporal distribution of temperature, pH, chlorinity and suspended particulate matter are discussed for each TIDE estuary. Surfer plots were made for suspended particulate matter concentrations for the Elbe, Scheldt and Humber estuary for the time period studied. Because of differences between sampling campaigns in the three estuaries, surfer plots were based upon seasonal (3 month) averages for each TIDE-km sampled. Spring corresponds to March, April and May. Summer includes June, July and August. Autumn comprises September, October, November and winter corresponds to December, January and February. For the Weser suspended particulate matter concentrations are represented as six-yearly averages on a yearly, summer and winter basis per sampling point.

Furthermore, light climate is discussed by approximation of euphotic depth and mixing depth. Euphotic depth is calculated from suspended particulate matter concentrations with the following formulas according to Holzhauer et al. 2011:

Kd = 0,053 SPM + 2,27

Zeuph = (-1/Kd) * ln(0,01) ~ 4,6/Kd

Mixing depth is approximated by the bathymetrical depth, as calculated from the cubature (Vandenbruwaene et al. 2012). This is a valid assumption in well-mixed macro-tidal estuaries.

Zmix = bathymetrical depth

2.3.2 Estuarine patterns

2.3.2.1 Correlation analyses

For all data gathered, correlation matrices were calculated within all four TIDE estuaries, wherefore Kendall's tau was used to estimate a rank-based measure of association. This more robust method is used, because not all bivariate data is normally distributed. Association is only calculated when pairs (x, y) were complete. Correlation analyses allow us to examine estuarine patterns within each estuary to a maximum extent.

2.3.2.2 Multivariate analyses

A more extensive and equilibrated examination of estuarine functioning per zone and season in different estuaries was performed using a multivariate analysis technique, principal component analysis. For this, data is necessary for all zones and seasons. Since for the Weser only data was available from 2004 to 2009 for mostly the freshwater and oligohaline zone, the Weser could not be further included in this analysis. Shared data between the Elbe, Scheldt and Humber include the following 13 variables: temperature, chlorinity, pH, suspended particulate matter, dissolved oxygen, dissolved oxygen saturation, nitrate, nitrite, total dissolved inorganic nitrogen, ammonium, phosphate, dissolved silica and chlorophyll *a*. Some missing chlorophyll *a* data in the Elbe estuary has been filled in using the linear relationship found with biological oxygen demand (R^2 = 0.72). Missing dissolved silica data for the Humber estuary has been filled in using the linear relationship found with nitrate (R^2 = 0.28). Chlorophyll data in the Humber represents chlorophyll extract and not chlorophyll *a* data. Nevertheless, after normalization and standardization the latter should also indicate chlorophyll's importance in the Humber estuary.

Separate principal component analyses (PCA, Dolédec and Chessel 1987; Thioulouse et al. 2004) were performed for each estuary. Between-class analyses revealed the structuring influence for year, zone and season. The assessment involves a Monte-Carlo procedure based on 999 random permutations of the lines of the data table returning 999 simulated values of inertia, plus the observed one; the significance of the effect is then tested by the proportion of simulated values greater than the observed one (Heo and Gabriel 1999).

The partial triadic analysis (PTA, Thioulouse and Chessel 1987; Blanc et al. 1998; Thioulouse et al. 2004) is a sophisticated within-group analysis whereby the influence of a given factor (e.g. salinity zone or season here) is masked. In this multi-table approach, a set of *k* tables are seen as *k* clouds of points between which structural similarities are investigated. Its application here is especially relevant since the data form a cube defined by fully matched tables (e.g. same seasons × same descriptors × same zones). The columns of each table are initially centered (value minus mean value) so that all the clouds of point have a common geometric origin, and by this way, the considered factor is masked and the amplitude of each cloud of point is conserved. The procedure comprises two main steps:

(1) The construction of a correlation matrix summarizing the strength of multidimensional similarity between the tables; this step is called "interstructure", and consists in identifying the most similar / deviant patterns by mean of a correlation circle; the statistics used is the *Rv* coefficient correlation (Robert and Escoufier 1976), and its significance is tested based on 999 random permutations of the lines of the tables.

(2) The construction of a system of axes encompassing the common processes between the tables as a common model, called "compromise". As a second sub-step, the projection of the lines and columns of the different tables on the axes provides a mechanistic understanding of the similarities / deviations highlighted in the so-called "intrastructure".

2.3.3 Nutrients

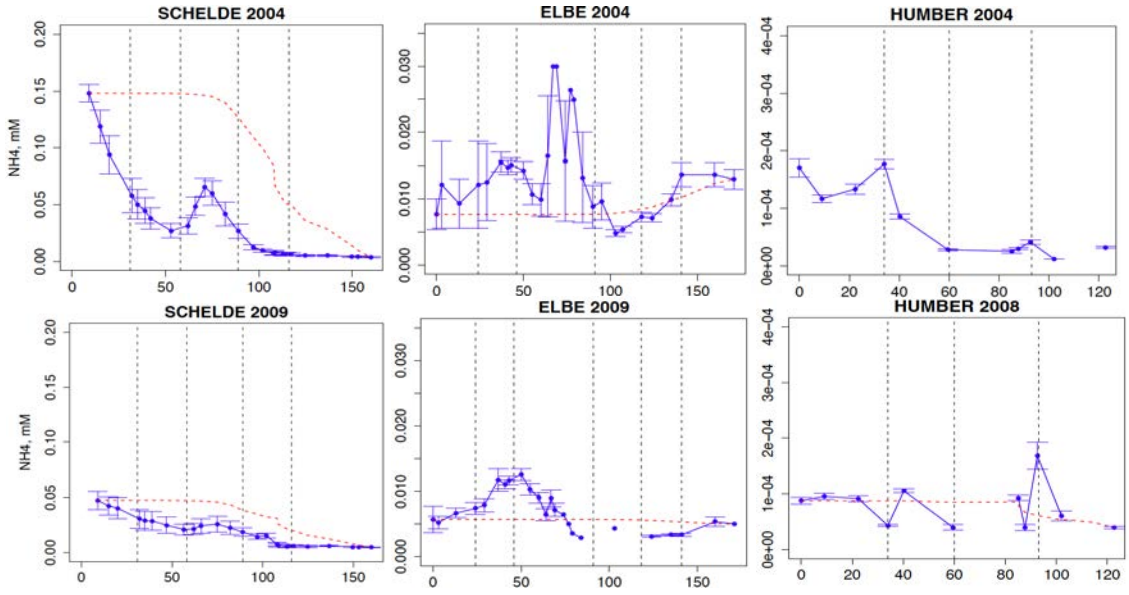
2.3.3.1 Time-distance surfer plots

Surfer plots were made for dissolved inorganic nutrients (total dissolved inorganic nitrogen, ammonium, nitrate, phosphate, dissolved silica) for the Elbe, Scheldt and Humber estuary for the time period studied. Because of differences between sampling campaigns in the three estuaries, surfer plots were based upon seasonal (3 month) averages for each TIDE-km sampled. Spring corresponds to March, April and May. Summer includes June, July and August. Autumn comprises

September, October, November and winter corresponds to December, January and February. The Weser sampling campaign only comprises three consequent sampling points, of which two in the freshwater zone and one in the oligohaline zone. Therefore, it was not possible to include surfer plots for the latter estuary. For the Weser nutrient concentrations are represented as overall six-yearly, summer and winter averages per sampling point.

2.3.3.2 Mixing plots

For each sampling point along the estuarine gradient the expected concentration by interpolation was calculated according to the conservative mixing theory as described in Eyre (2000). This is based on the chlorinity gradient and the fresh- and saltwater end member concentrations of the substrate (N, P, DSi or DO) considered. In TIDE the outer sea limit for the different estuaries studied has not always been defined up to 35 ‰. Therefore, the interpolation has been performed per set of three sampling points. Actually, chlorinity is used to calculate a weighed concentration by interpolation between each up- and downstream sampling point. Thus, formula (2) is deduced from the original formula (1) according to Eyre et al. (2000) (fig. 6). Next, to calculate the so-called 'gain' or 'loss' with respect to the expected concentration by interpolation, a difference is made between the observed and expected concentration. This was corrected for the distance between the sampling points and has been plotted as time-distance surfer plots. Green zones represent areas of gain, while red zones show areas of loss. The conservative mixing gives the concentration as expected when only dilution due to tidal mixing is observed. Hence, any deviation from these calculated concentrations, positive (gain) or negative (loss), could represent estuarine processes e.g. denitrification or direct input or removal, e.g. tributary input or freshwater discharge respectively.



$$S_{mix} = [1- (CL_x - CL_{min})/(CL_{max} - CL_{min})] \cdot S_{fw} + (CL_x - CL_{min})/(CL_{max} - CL_{min}) \cdot S_{sw} \quad (1)$$

$$S_{mix} = [1- (CL_x - CL_{us})/(CL_{ds} - CL_{us})] \cdot S_{us} + [(CL_x - CL_{us})/(CL_{ds} - CL_{us})] \cdot S_{ds} \quad (2)$$

Fig. 6 Example of the observed concentration and theoretical expected ammonium concentrations in µM, according to the conservative mixing theory, calculated as given in formula (1); the conservative mixing plots (see "Results" further) are calculated according to formula (2) for reasons explained in the text above; <u>Abbreviations:</u> S_{mix}: theoretical expected concentration of "S" due to conservative mixing between salt and fresh water; CL_x: chlorinity at position of interest x; CL_{min}: minimum chlorinity measured at most upstream sampling point; CL_{max}: maximum chlorinity measured at most downstream sampling point; S_{fw}: concentration of "S" at most upstream sampling point; S_{sw}: concentration of "S" at most downstream sampling point; CL_{us}: chlorinity measured at the first upstream sampling point; CL_{ds}: chlorinity measured at the first downstream sampling point; S_{us}: concentration of "S" at the first upstream sampling point; S_{ds}: concentration of "S" at the first downstream sampling point; Blue line: observations; error bars represent standard error; Red dotted line: theoretical expected concentration gradient as calculated with formula (1).

To have a more overall view, this gain or loss has also been multiplied with freshwater discharge, hence total gain or loss can be compared between estuaries. This has been performed for the whole estuarine gradient and per zone. Filter efficiencies have been calculated in percentage as the gain or loss according to the input concentration. The input concentrations per zone are defined as the most upstream concentration of that zone.

Residence time can reach up to about maximum 40 days in the freshwater zone (Elbe) and about maximum 50 days in the polyhaline zone (Scheldt) in summer. Thus, seasonal gain or loss can be considered. However, a yearly average can be considered more accurate, since transient effects are attenuated in this way.

2.3.4 Oxygen and primary production

2.3.4.1 Dissolved oxygen concentration and saturation

Surfer plots were made for dissolved oxygen concentrations for the Elbe, Scheldt and Humber estuary for the time period studied. Furthermore, dissolved oxygen saturation concentrations larger than 100% are indicated with diamonds. Because of differences between sampling campaigns in the three estuaries, surfer plots were based upon seasonal (3 month) averages for each TIDE-km sampled. Spring corresponds to March, April and May. Summer includes June, July and August. Autumn comprises September, October, November and winter corresponds to December, January and February. For the Weser dissolved oxygen concentrations and dissolved oxygen saturation concentrations are represented as six-yearly general, summer and winter average per sampling point.

2.3.4.1.1 Oxygen, gain and loss

The conservative mixing principle is applied similarly as for the nutrient concentrations, described earlier (see "*2.3.2.2 Mixing plots*"). This method only works for dissolved constituents. Although oxygen is gaseous, it can be considered fully dissolved and thus behaving much in a similar way as transport of nutrients.

2.3.4.2 Biological oxygen demand

Surfer plots were made for biological oxygen demand for the Elbe and Scheldt estuaries for the time period studied. In the Elbe the biological oxygen demand is measured over a period of 7 days. Within the boundary sampling station 'Schnackenburg', which is located upstream the weir and thus in the riverine part of the Elbe, biological oxygen demand has been measured for several time periods, of which also over 5 days and 7 days. The average seasonal ratio of '(biological oxygen demand over 5 days)/(biological oxygen demand over 7 days)' for this station has been used to calculate the approximate biological oxygen demand over 5 days for the other sampling points, hence the Elbe biological oxygen demand can now be compared with the Scheldt estuary. Because of differences between sampling campaigns in the two estuaries, surfer plots were based upon seasonal averages per distance sampled. In both the Weser and Humber estuaries biological oxygen demand has not been measured.

2.3.4.3 Chlorophyll a concentration

Surfer plots were made for chlorophyll *a* concentrations for the Elbe, Scheldt and for chlorophyll extract concentrations for the Humber estuary for the time period studied. Because of differences between sampling campaigns in the three estuaries, surfer plots were based upon seasonal (3 month) averages for each TIDE-km sampled. Spring corresponds to March, April and May. Summer includes June, July and August. Autumn comprises September, October, November and winter corresponds to December, January and February. For the Weser chlorophyll *a* concentrations were only measured at the boundary station Bremen Hemelingen and are therefore not represented.

2.3.4.4 Gross primary production

Primary production is not linearly correlated to chlorophyll *a* concentrations. Often estimates of primary production are made based upon ^{14}C-incorporation. However, this method is time-consuming, expensive and bottle-effects may underestimate true primary production. Using a Fourier transformation can decompose periodic components from continuous oxygen data series.

Assuming diurnal patterns in oxygen time series are mainly effect of primary production, applying the Fourier-method as described in detail in Cox et al. (in prep.) allows estimation of gross primary production (GPP) (fig. 7).

$$\overline{GPP(t)} \approx 2\omega_1 A_{O_2} \frac{\sin\theta - \theta\cos\theta}{\theta - \frac{1}{2}\sin 2\theta}$$
$$\text{with } \theta = \pi f_{DL}$$

Fig. 7 Fourier-method for gross production (GPP) estimation according to Cox et al. (in prep.) (ω1 = angular frequency of the Fourier transformation; AO_2 = continuous oxygen data series measured from the field; f_{DL} = fraction of daylight over a 24h time-period)

A truncated sinusoid (fig. 8) relation is applied between the time average and Fourier amplitude, which is function of the fraction of daylight. This transformation assumes a constant daylight fraction. Therefore, only time series of 14 days are considered at once.

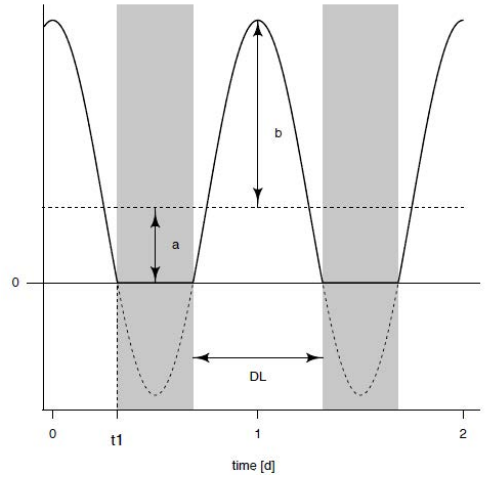


Fig. 8 Gross primary production assumed as a truncated sinusoid GPP(t) =max(0; a + bcos(ωt)), the parameters a and b are related to the relative fraction of light hours during the day (fDL = DL/24h). From the figure: the number of daylight hours DL = 2t1. (Cox et al. in prep.)

The method is less applicable when the estuarine system is stratified, shallow, subject to short residence times, experiencing strong air-water exchange and/or bubble formation. These deviations can give overestimation or underestimation of GPP (Cox et al. in prep.).

2.3.4.5 Nutrient ratios

When measured, molar nutrient ratios of nitrogen-phosphate, nitrogen-dissolved silica and phosphate-dissolved silica were calculated and are represented as overall six-yearly, summer and winter averages per sampling point. Nitrogen within each ratio refers to the sum of dissolved inorganic nitrogen. Redfield ratios (C/N/P/Si~106/16/1/16) are displayed as well to detect potential nutrient limitations for diatoms. However, potential nutrient limitation does not necessarily imply actual nutrient limitation. E.g. the nutrient ratio for nitrogen to phosphorus could be lower than 16, indicating a potential limitation for nitrogen. Nonetheless, nitrogen concentration could be sufficient to sustain the diatom population, since other factors, e.g. light, could inhibit algal growth and not all nitrogen and phosphorus are used up to the limit.

3. Results

3.1 Physics

3.1.1 Hydrodynamics

3.1.1.1 Freshwater discharge

As can be observed in fig. 9, the Elbe has clearly the highest freshwater discharge in general, with its maximum in spring 2006 (1 395 m^3/s). In the Weser a maximum freshwater discharge of 587 m^3/s is observed in winter 2007. Lowest discharges are in general observed within the Scheldt estuary (maximum in winter 2007, 189 m^3/s). In the Humber a clear peak can be observed in 2006 of 178 m^3/s. Peaks within the Elbe tend to occur in spring. However, in the Scheldt peaks can be observed earlier in winter. It has to be noticed that peaks are less likely to be pronounced, since seasonal averages are displayed. Lowest discharges are observed in summer. Summer discharges seem to differ more strongly in the Elbe estuary, while they stay relatively constant within the Scheldt estuary.

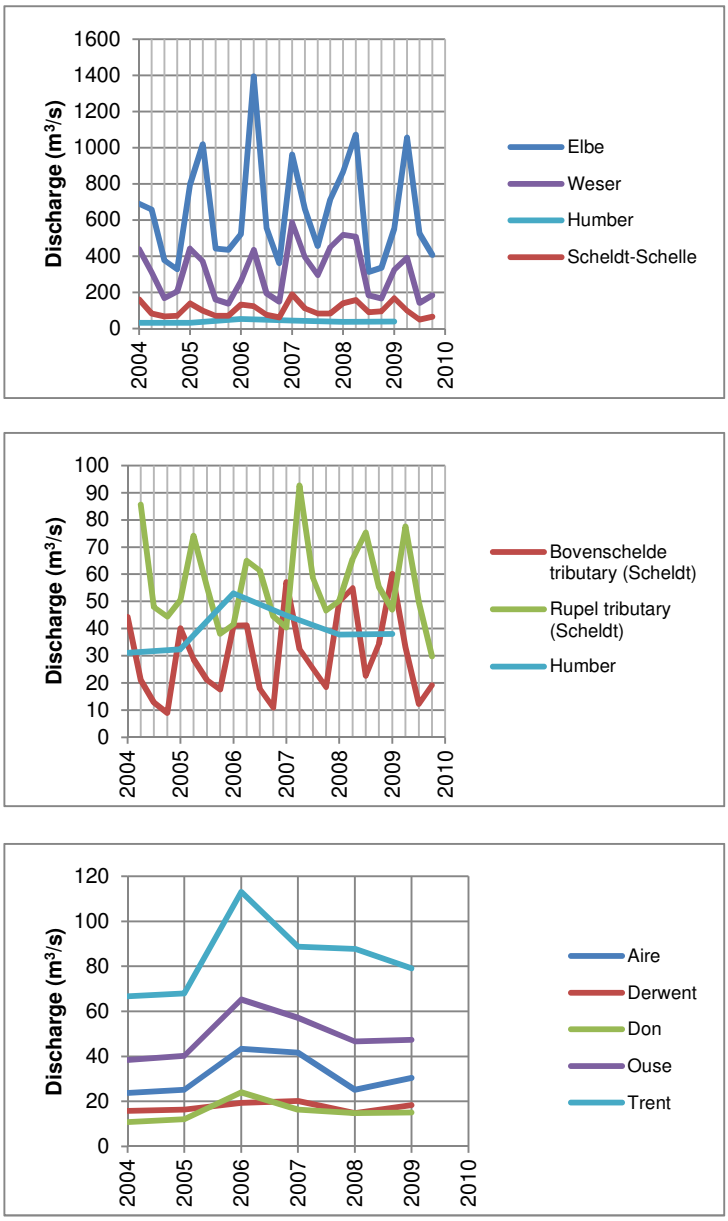


Fig. 9 Seasonal freshwater discharges (m^3/s) for the Elbe at Neu Darchau (35 km upstream from Geesthacht weir); for the Scheldt at Schelle (TIDE km 68) including discharges from Bovenschelde, Rupel, Dender and Durme; yearly freshwater discharges for the Humber summarizing discharges from Ouse and Trent; and seasonal freshwater discharges for the Weser at Intschede (about 20 km upstream from TIDE km 0). For the Humber only yearly averages were available. Discharges from main tributaries of the Scheldt (Rupel and Bovenschelde) and Humber (Aire, Derwent, Don, Ouse & Trent) are presented separately.

3.1.1.2 Residence time

In general, the higher residence times are observed in summer for all four estuaries. Remarkable from fig. 10 is the reversed pattern in Elbe and Weser compared to Scheldt and Humber. In Elbe and Weser residence times decrease towards the polyhaline zone, while in Scheldt and Humber residence times rather seem to increase towards the polyhaline zone. Furthermore, the difference between summer and winter residence time decreases towards the polyhaline zone in Elbe and Weser, while in Scheldt and Humber this difference between summer and winter persists. This can in part be explained by the method of calculation (Vandenbruwaene et al. 2012). For the Elbe and Weser the limit near the sea is set at 151 and 89 TIDE km respectively, while in fact the polyhaline zone is much larger (but could not be calculated, because of sudden estuarine widening). Hence, residence times (days) are underestimated in the Elbe and Weser estuary. When normalized for the length of each zone (in days/km), we can observe slightly more similar patterns along the estuarine gradient per estuary. Even though we can still see a decrease in residence time towards the sea in the Elbe and Weser, after normalization for length per zone, residence times are higher in the oligo- and mesohaline zone for all estuaries. Taking into account all zones, highest residence times are found in the mid-estuary of the Scheldt. When comparing residence times in the freshwater zone solely, higher values are found in the Elbe estuary, while lower values are observed in the Scheldt estuary.

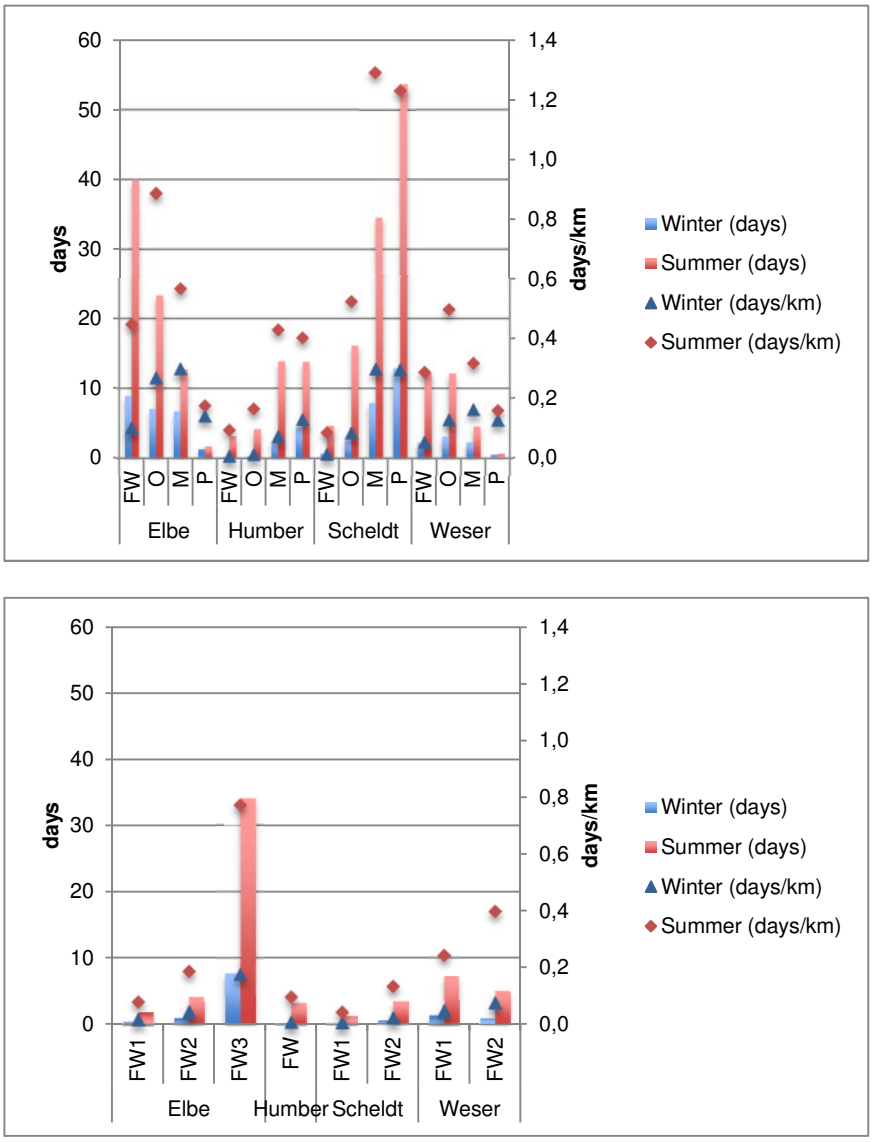


Fig. 10 Winter and summer residence time per zone (days) and normalized for the length of each zone (days/km) of the Elbe, Humber, Scheldt and Weser estuaries calculated according to the fractal freshwater method (Guo et al. 2000, see Vandenbruwaene et al. 2012). The freshwater zone residence times are presented in more detail according to the zonation as decided in (Geerts et al. 2012).

3.1.2 Morphology

3.1.2.1 Intertidal and subtidal areas

In all estuaries absolute intertidal area, marshes and subtidal area appears to increase in a proportional similar way towards the sea (fig. 12). Only in the Scheldt a decline in intertidal area and marshes from the meso- to polyhaline zone can be observed. The highest increase is usually observed from the oligohaline zone towards the polyhaline zone; however in the Elbe there is also a high amount of intertidal and subtidal area observed within the freshwater zone. Most marsh and intertidal area can be found within the Weser estuary; in all of its zones the relative amount of intertidal flats and marshes is higher than the subtidal area (except for the most upstream freshwater zone). The least amount of intertidal area and marshes can be found within the Humber estuary; however the Humber estuary is also the smallest estuarine area considered (± 31 270 ha). In the Humber there is always relatively more subtidal than intertidal flats and marshes. Nevertheless, this is mostly shallow to moderately deep subtidal area. In fact, the Humber estuary shows relatively the least amount of subtidal deep. Contrarily, the Scheldt comprises relatively the most subtidal deep and intertidal steep in general along the estuarine gradient. Furthermore, the relative least intertidal mudflat can be observed in the freshwater zone of the Scheldt estuary.

3.1.2.2 Geometry

Tidal amplitude (TA)

The largest tidal amplitude is observed within the Scheldt oligohaline zone (5.5 ± 0.1 m). Next, the Humber has the largest tidal amplitude with its maximum in the mesohaline zone (4.4 ± 0.2 m). The maximum tidal amplitudes within the Elbe and Weser are for both estuaries found within the freshwater zone (table 3; 3.6 ± 0.04 m and 3.8 ± 0.1 m, respectively).

Channel width (W)

Width for all estuaries increases from the freshwater to the polyhaline zone. The Scheldt and Humber are both the more narrow estuaries, while the Elbe is the widest estuary (table 3).

Wet cross-section (A)

Cross-section follows the same trend as channel width and gradually increases towards the polyhaline zone (table 3). The Elbe clearly has the highest cross section. The Scheldt, Humber and Weser all have similar cross-sections. The larger width of within the Weser indicates that this is a more shallow estuarine system.

Averaged depth (D) & bathymetrical depth (D bath)

In general bathymetrical depth increases towards the sea in all estuaries (fig. 11). The Elbe is clearly the deepest estuary along the whole estuarine gradient, while the Humber and Scheldt are shallower. In the Elbe and Weser depth increases gradually, except for the freshwater zone 3 within the Elbe. In the Humber and Scheldt depth increases more abruptly from the oligohaline zone towards the meso- and polyhaline zone.

When average depth is considered, in which cross-section and width are taken into account, it is clear that despite the Weser being deeper, in fact the Scheldt is less wide and thus can be considered as the ‘deeper’ estuarine system from an ecological point of view from the oligohaline towards the polyhaline zone (fig. 11).

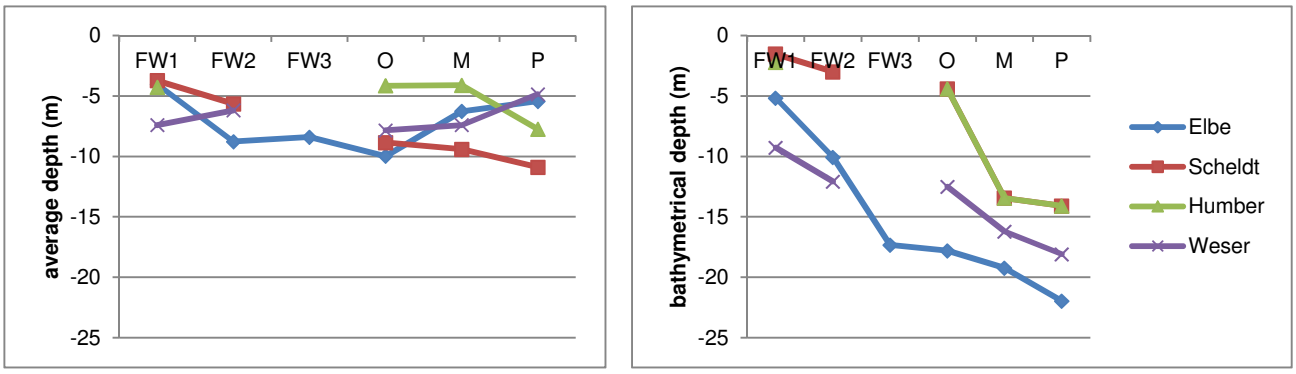
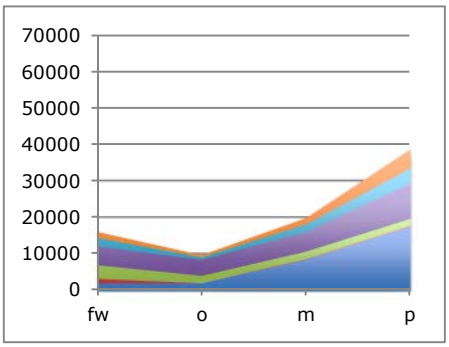


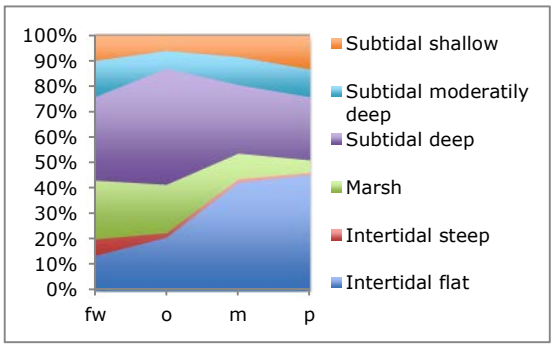
Fig. 11 Averaged depth calculated as wet cross-section divided by channel width (left) and bathymetrical depth relative to the geo mouth as defined and calculated according to the method as described in (Vandenbruwaene et al. 2012).

Table 3 Summary statistics of geometry data per estuary. TA = tidal amplitude, W = tidal channel width, A = wet cross-section, D = averaged depth: cross-section/width, D bath = bathymetrical depth

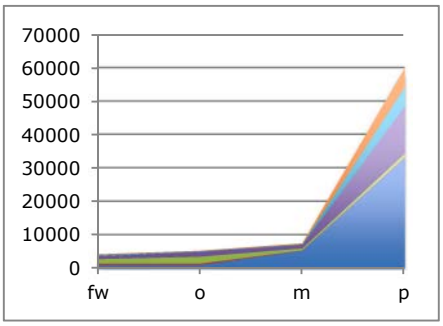
		Scheldt					Elbe				
Zone		**TA**	**W**	**A**	**D**	**D bath**	**TA**	**W**	**A**	**D**	**D bath**
FW1	n	156	145	145	145	151	97	97	97	97	97
	m	2.7	61.7	251.9	-3.7	-1.5	3.4	358.3	1502.7	-4.0	-5.2
	sd	0.9	17.9	108.8	1.1	1.7	0.1	74.5	346.9	0.6	1.3
FW2	n	135	135	135	135	133	64	64	64	64	62
	m	4.7	141.7	826.6	-5.7	-3.0	3.6	328.7	3311.1	-8.8	-10.1
	sd	0.6	59.3	351.2	0.9	2.1	0.0	134.8	2442.0	3.6	4.9
FW3	n						72	72	72	72	74
	m						3.07	1962.86	16059.15	-8.41	-17.33
	sd						0.20	547.28	3966.68	1.47	1.54
O	n	113	113	113	113	62	47	47	47	47	47
	m	5.5	381.2	3499.2	-8.9	-4.4	2.8	2575.0	24695.8	-10.0	-17.8
	sd	0.1	97.7	1318.5	2.1	2.1	0.0	665.6	2532.8	1.5	1.9
M	n	92	92	92	92	51	21	21	21	21	21
	m	5.2	1722.0	14481.4	-9.4	-13.4	2.9	7739.6	42550.4	-6.3	-19.2
	sd	0.2	978.9	5800.2	1.8	3.4	0.0	3158.1	13009.3	1.0	3.2
P	n	144	144	144	144	27	9	9	9	9	9
	m	4.4	4759.3	52388.8	-10.9	-14.1	2.9	13572.7	72213.4	-5.4	-22.0
	sd	0.3	1227.7	19129.7	2.3	3.1	0.0	1733.7	15469.3	0.4	3.9
		Humber					**Weser**				
FW1	n	167	167	167	167	284	61	61	61	61	61
	m	1.7	50.9	225.7	-4.3	-2.2	3.8	342.8	2670.3	-7.4	-9.3
	sd	0.6	15.1	108.2	1.0	2.0	0.1	96.0	1096.5	1.9	2.5
FW2	n						26	26	26	26	26
	m						3.6	827.8	4297.4	-6.2	-12.1
	sd						0.0	311.6	671.6	1.0	0.8
O	n	121	121	121	121	62	50	50	50	50	50
	m	3.4	168.4	691,7	-4.2	-4.4	3.5	1028.2	7724.5	-7.9	-12.5
	sd	0.3	55.0	210.1	1.2	2.1	0.1	157.9	1408.8	1.5	1.6
M	n	64	64	64	64	51	27	27	27	27	27
	m	4.4	1862.7	8326.6	-4.1	-13.4	3.2	2969.9	15010.1	-7.4	-16.2
	sd	0.2	674.5	3991.1	0.9	3.4	0.1	1816.2	5245.6	1.7	1.8
P	n	72	72	72	72	27	10	10	10	10	10
	m	3.6	5297.1	41030.5	-7.7	-14.1	3.1	8000.6	33505.5	-4.9	-18.1
	sd	0.2	2589.4	19493.6	1.2	3.1	0.0	702.8	3544.5	0.6	1.4



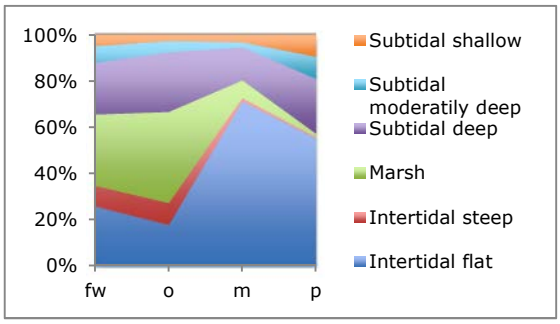
Absolute area Elbe



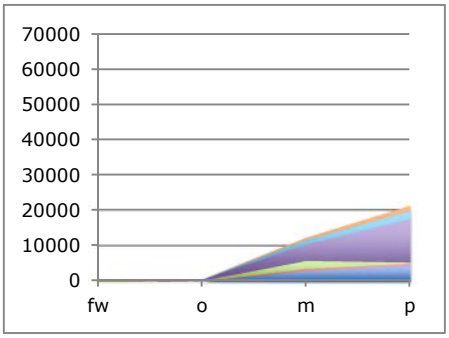
Relative area Elbe



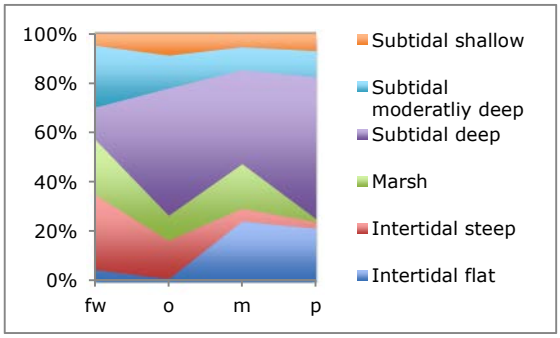
Absolute area Weser



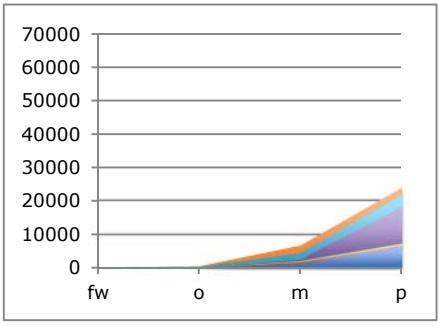
Relative area Weser



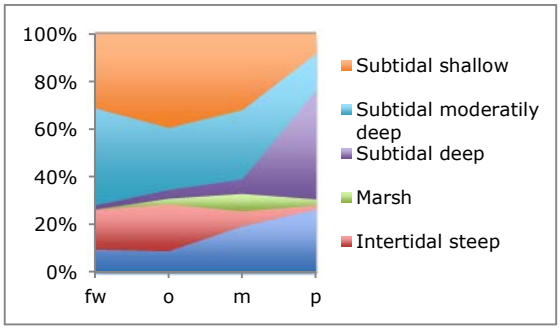
Absolute area Scheldt



Relative area Scheldt



Absolute area Humber



Relative area Humber

Fig. 12 Absolute and relative intertidal area per zone and estuary calculated based on high and low water levels (see Vandenbruwaene et al. 2012)

3.2 Biogeochemistry

3.2.1 General parameters

In general **temperature** (Attachment 2) is observed to be highest within the Scheldt estuary (13.2 ± 0.2 ℃) and lowest within the Humber estuary (10.9 ± 0.3 ℃). In winter temperature is lowest within the Elbe (4.62 ± 0.2 ℃). When considering whole estuarine seasonal temperature differences, the Elbe shows the largest difference between winter and summer temperature. On a yearly basis, temperature decreases towards the sea in all estuaries.

Chlorinity (fig. 13) intrudes up the furthest in the Elbe estuary, next in the Scheldt estuary and least in the Weser estuary. The Elbe estuary has a very extended freshwater zone (0-91 km). The maximum chlorinity (Attachment 2) for Elbe, Scheldt and Humber lay more or less in the same range, indicating a similar estuarine gradient is considered for data comparison (17 800 ± 151.4 mg CL/l; 17 929,3 ± 247.9 mg CL/l; 21 319 ± 426.8 mg CL/l; respectively). For the Weser there are mostly three sampling stations during the time period studied in TIDE, of which two are located in the freshwater zone.

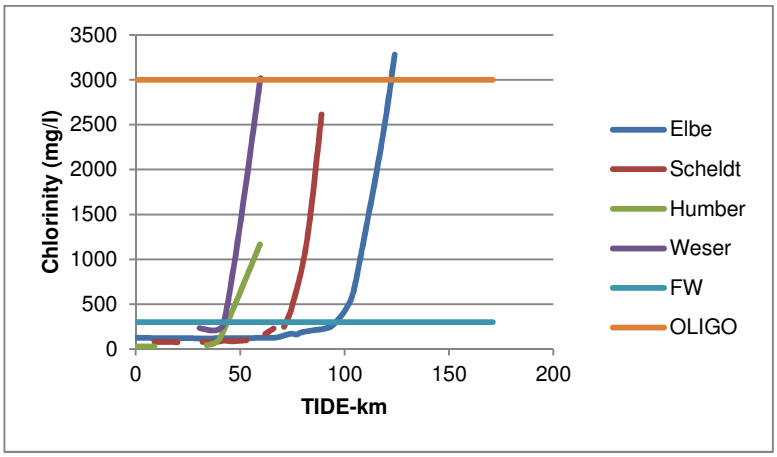


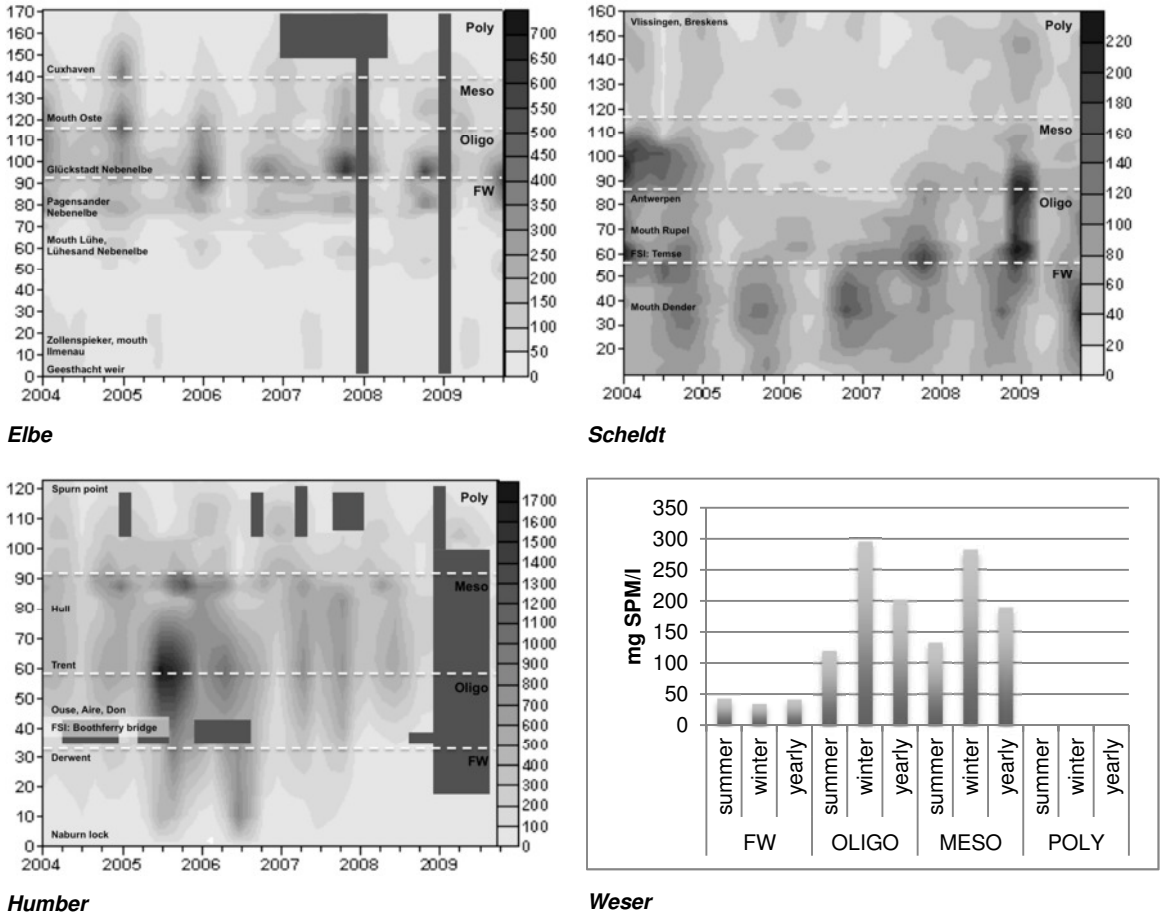
Fig. 13 Six-yearly averaged chlorinity (mg/l) according to distance (TIDE-km). The freshwater threshold (300 mg/l) indicates how far the salt intrudes up in the estuary (FW = freshwater, OLIGO = oligohaline).

Overall the whole estuarine gradient, **pH** (Attachment 2) is observed to be highest within the Elbe estuary (8.0 ± 0.01) and lowest within the Humber estuary (7.78 ± 0.01). Difference between summer and winter is most pronounced within the Elbe estuary ($pH_{summer} - pH_{winter}$ = 0.11), next within the Scheldt estuary (0.08). In the Humber there is no difference in pH between summer and winter. In all estuaries pH is high within the freshwater zone, decreases in the oligohaline zone and again increases towards the polyhaline zone.

Suspended particulate matter (Attachment 2) is clearly the highest within the Humber estuary (on average 268.1 ± 18.1 mg/l; maximum 2082.0 mg/l). The lowest values can be observed within the Scheldt estuary (65.3 ± 2.0 mg/l). In general suspended matter concentrations appear to be higher in winter than in summer for the Elbe, Scheldt and Weser estuary (SPM_{winter} - SPM_{summer} = 75.8; 28.4 & 31.9 mg/l resp.). In the Humber summer concentrations are slightly higher than in winter, showing a reverse pattern. However, the difference between summer and winter is less pronounced than for the other estuaries (SPM_{winter} - SPM_{summer} = **-**24.2 mg/l). In the Elbe suspended matter concentrations seem to increase towards the oligohaline zone and decrease again towards the freshwater zone. In the Humber highest suspended matter concentrations usually can be found along the stretch of the oligo- and mesohaline zone. Also in the Weser highest concentrations are observed within the oligo- and mesohaline zone. Within the Scheldt the highest concentrations are often observed within the freshwater zone, sometimes also within the oligohaline stretch (fig. 14). Estuarine patterns are clearly different.

Based upon suspended matter concentrations, **euphotic depth** can be estimated and compared with bathymetrical depth. Bathymetrical depth can be considered as mixing depth in well-mixed macro-tidal estuaries. In general euphotic depth is highest in the polyhaline and next, the freshwater zone of all estuaries. Within the Elbe it can be observed that as mixing depth increases, euphotic depth clearly decreases (fig. 15) and although deeper, that towards the polyhaline zone

euphotic depth is increasing again. From all four estuaries, euphotic depths are highest in the polyhaline and freshwater zone of the Elbe (1.4 m and 1.2 m resp.). However, self-shading effects of algae are not considered in the formula that is used to deduce euphotic depth (see '*2 Material and Methods*'). Within the Scheldt estuary, euphotic depth is lower within the oligohaline zone than in the freshwater zone (even more pronounced in winter). From the oligohaline zone towards the mesohaline zone, euphotic depth abruptly increases again. Within the Humber, euphotic depth rapidly decreases from the upper boundary into the freshwater zone up to polyhaline zone. It is not until the end of the polyhaline zone that euphotic depth is increasing again. Euphotic depths are observed to be lowest in the Humber estuary (0.2 m in the oligohaline zone). Within in the Weser to few data points are monitored to really see a trend in euphotic depth with mixing depth (fig. 15).

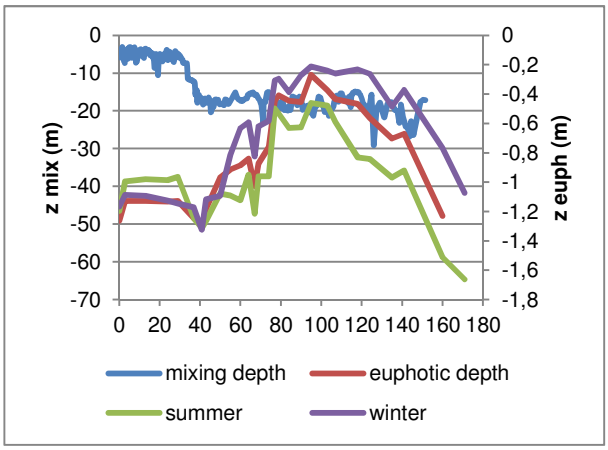


Elbe ***Scheldt***

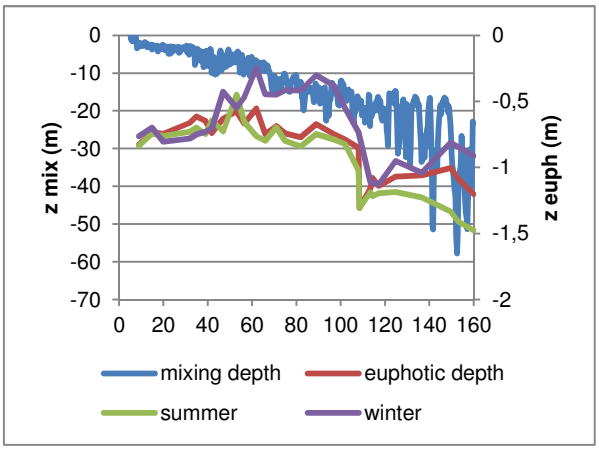
Humber ***Weser***

Fig. 14 Spatial (TIDE km) temporal (years) distribution of suspended particulate matter (SPM; mg/l) for the Elbe, Scheldt, Humber and Weser. Main tributaries and recognizing sampling points are shown in the surfer plots. For the Weser not enough sampling stations covered the estuarine gradient to represent the data as a surfer plot. Therefore averages per zone are displayed for yearly, summer and winter period. Missing data in the time-distance plots are represented as solid filled rectangles.

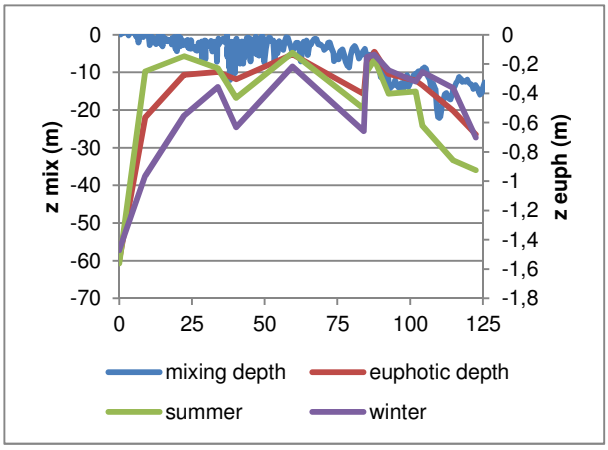
Euphotic depth, mixing depth ratios taking a six-yearly average on a yearly, summer and winter basis are in general highest in the freshwater zone. Fig. 16 reveals that ratios are highest in the freshwater zone of the Scheldt estuary (0.49). Ratios are lowest within the oligohaline zone of the Elbe (0.02) and mesohaline zone of the Humber (0.01). Even within the Elbe freshwater zone (FW3) ratios are very low (0.04), because of the very large bathymetrical depth. Differences between winter and summer are relatively limited (fig. 16).



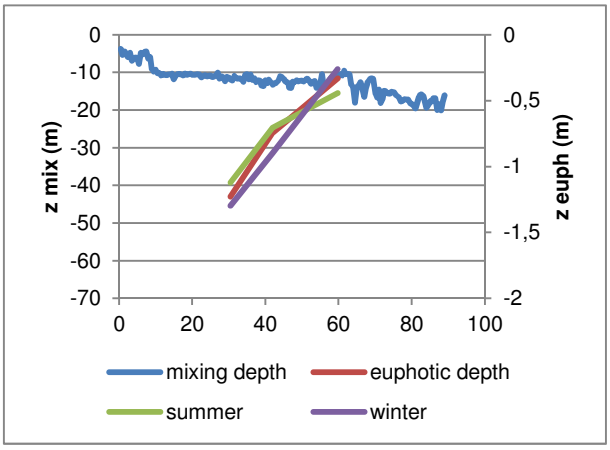
Elbe



Scheldt



Humber



Weser

Fig. 15 Mixing depth approximated by bathymetrical depth as defined in 'Material and Methods' with reference to the geo-mouth as defined in (Vandenbruwaene et al. 2012). Yearly, summer and winter average for euphotic depth, calculated based on suspended particulate matter concentrations. Applied for the Elbe, Scheldt, Humber and Weser estuaries.

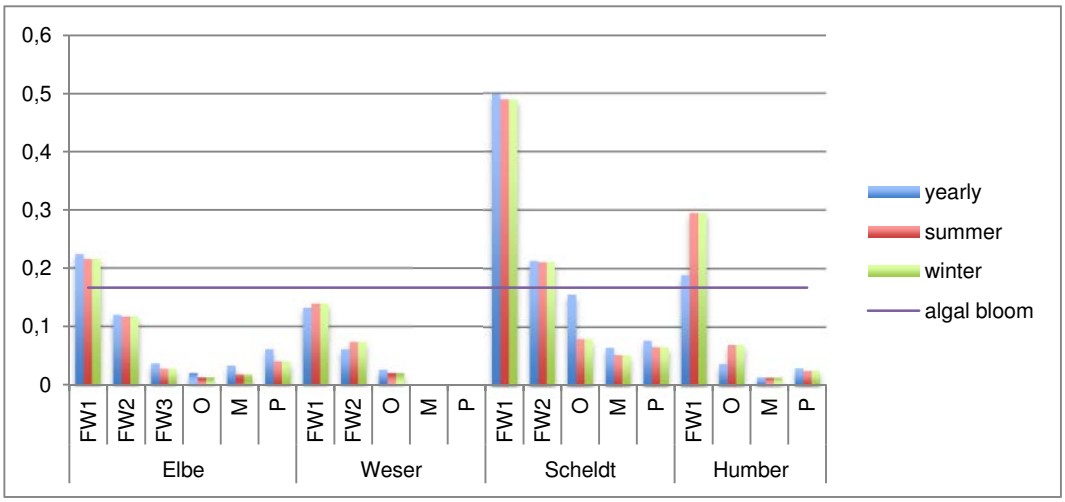


Fig. 16 Six-yearly averaged euphotic depth – mixing depth ratio (Zeuph/Zmix) per zone and estuary upon yearly, summer and winter basis. When the Zeuph/Zmix depth is larger than 1/6, algal blooms can occur (Underwood & Kromkamp 1999).

3.2.2 Estuarine patterns

3.2.2.1 Correlation analyses (Elbe, Scheldt, Humber & Weser)

Correlations larger than r = 0.50 found in **all four estuaries** (Attachment 3), include chlorinity with conductivity, dissolved oxygen with dissolved oxygen saturation and total dissolved inorganic nitrogen with nitrate. The first indicates a pure physical relationship that is created within estuaries due to mixing with seawater. The second, between oxygen parameters is rather obvious. However, the third correlation in all four estuaries observed, between total dissolved inorganic nitrogen and nitrate, indicates that most of total dissolved inorganic nitrogen consists of nitrate and in all estuaries nitrification and mineralization are the most important processes over denitrification and primary production. The correlation is clearly lower in the Scheldt estuary, possibly indicating, that denitrification and/or primary production are more pronounced within this estuary.

Correlations found in almost all estuaries, include dissolved oxygen with temperature and suspended matter concentration with total phosphorus. Dissolved oxygen and temperature are correlated by physics, since less oxygen can dissolve with increasing temperature. Absence of this physically regulated correlation larger than 0.50 within the Scheldt estuary might indicate the larger importance of other oxygen influencing processes over the physical ones compared to the other estuaries in TIDE. The correlation between suspended particulate matter and total phosphate in the Elbe, Scheldt and Weser, while there is a lack of correlation between suspended matter and phosphate in these estuaries, show that a large part of suspended particulate matter consists out of organic phosphorus. This correlation presumably also exist within the Humber estuary, as can be seen from the phosphate dynamics (see further); however total phosphorus was not measured within this estuary. Correlation is less pronounced in the Scheldt estuary. Further correlation with organic carbon compounds with suspended matter was also only found within the Elbe and Weser. In the Humber no organic carbon compounds were measured during the six-year period studied.

Furthermore, some **characteristic correlations per estuary** could be found. In the Scheldt there was a clear negative correlation of dissolved constituents (dissolved organic carbon, nitrate, phosphate, …) with chlorinity. In the Elbe estuary there is a clear correlation between chlorophyll *a*, biological oxygen demand and phaeopigments, likely indicating that chlorophyll *a* represents a large part of the organic matter input within the estuary. The Weser and Humber strongest correlations mostly reflect physical ones, such as between temperature and dissolved oxygen.

3.2.2.2 Multivariate analyses (Elbe, Scheldt & Humber)

(with contribution of Olivier Beauchard)

A more extensive and equilibrated examination of estuarine functioning per zone and season in different estuaries was performed using a multivariate analysis technique, principal component analysis. Data is needed for all zones and seasons. Since for the Weser only data was available from 2004 to 2009 for mostly the freshwater and oligohaline zone, the Weser could not be further included in this analysis. Shared data between the Elbe, Scheldt and Humber include the following 13 variables: temperature, chlorinity, pH, suspended particulate matter, dissolved oxygen, dissolved oxygen saturation, nitrate, nitrite, total dissolved inorganic nitrogen, ammonium, phosphate, dissolved silica and chlorophyll *a* (however, chlorophyll data in the Humber represents chlorophyll extract and not chlorophyll *a* data; nevertheless it should indicates its importance in this type of analysis). Because of data gaps, only the years 2004 to 2006 could be included in the analysis.

Spatial and temporal differences of physic-chemical processes per estuary

In a first step, three separate principal component analyses per estuary were performed (fig.17). For all three estuaries a clear **upstream-downstream gradient from the freshwater to the polyhaline zone can be found**. The freshwater is characterized by high nutrient concentrations, decreasing gradually towards the polyhaline zone. The polyhaline zone on the contrary is characterized by high pH values and high dissolved oxygen concentrations (fig. 17; A-C & D-F). Furthermore, also the opposition between winter and summer season is clearly displayed for all three estuaries (fig. 17; G-I). However, the physico-chemical processes defining this seasonality, differ markedly between estuaries. In the Scheldt winter to summer seasonality is defined by

increasing temperature and chlorophyll *a* concentrations, meanwhile in the Elbe winter to summer seasonality is defined by increasing phosphate concentrations and decreasing chlorophyll *a* concentrations. In the Humber estuary the winter to summer seasonality is mostly defined by an increase in temperature and a decrease in ammonium (fig. 17; A-C & G-I).

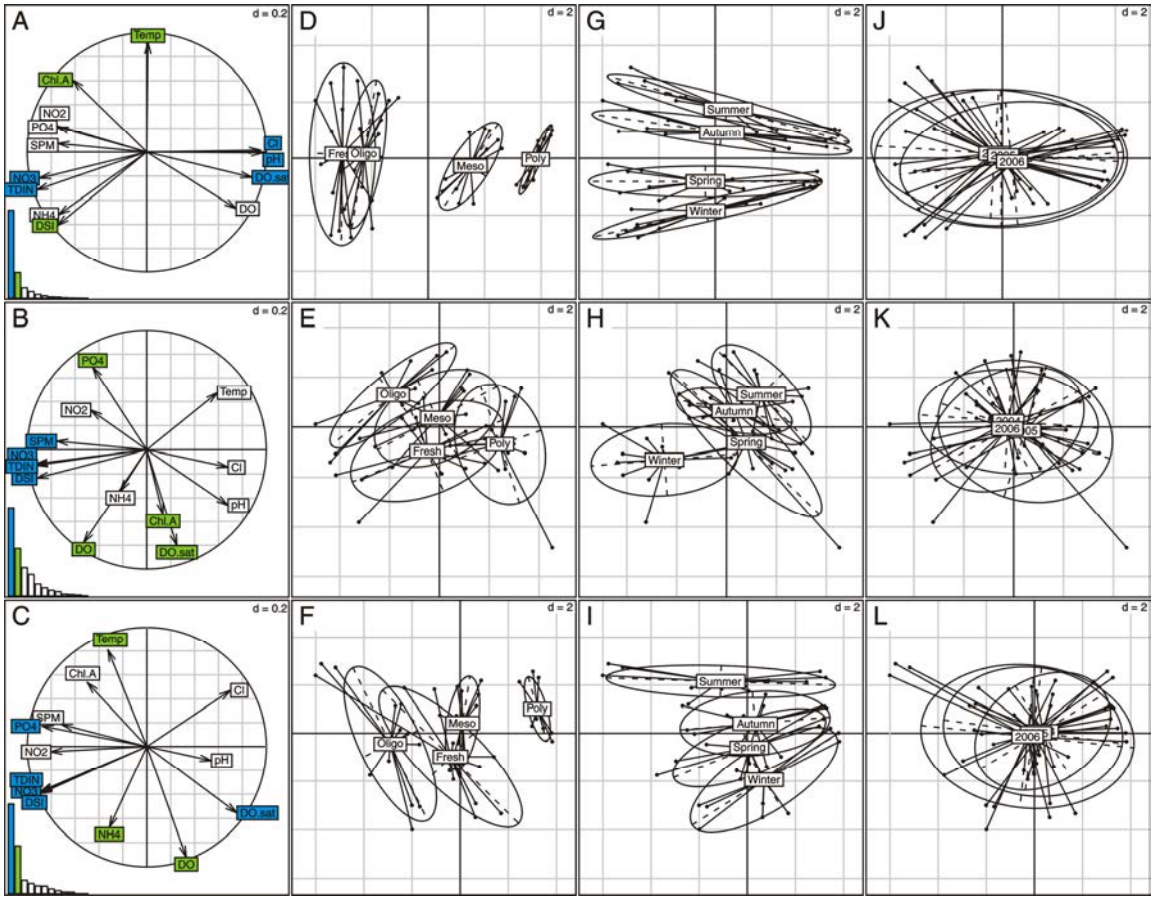


Fig. 17 Separate PCA performed on each estuarine dataset: first row, Scheldt; second row, Elbe; third row, Humber. A – C) Correlation circles and eigenvalues diagrams; blue labels indicate the variables which contribute to 50 % of the first axis variance; green labels indicate the variables which contribute to 50 % of the second axis variance. D – F) Statistical units (salinity zone × season × year) grouped per salinity zone. G – I) Statistical units grouped per season. J – L) Statistical units grouped per year. "d" indicate the grid scale.

Between analyses per estuary reveal that the most significant structuring factor is salinity, next seasonality (fig. 18; $p<0.01$). For the three years examined, no significant year effect could be found for any of the estuaries.

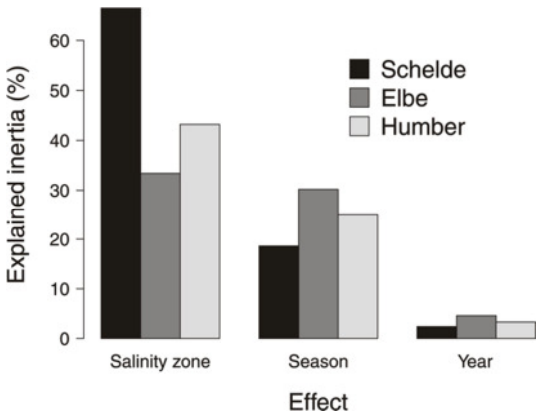


Fig. 18 Between-class analyses. "Explained inertia" provides the amount of multidimensional variance structured by the considered factor. According to the permutation tests, all the effects were significant ($p < 0.01$) in the three datasets, except the year effect ($p > 0.05$).

To further examine how **zones** differ from each other in physico-chemical processes for the different estuaries, a partial triadic analysis has been performed. Respectively to each zone, a table is defined by the physico-chemical descriptors measured three times (2004-2006) during the four seasons (season-year in lines × descriptor in columns). Next, correlations are made between all estuarine zones. The correlation matrix (table 4) and circle (fig. 19) between estuarine zones exhibits a majority of significant Rv coefficients, indicating that many of them share similar seasonal patterns of processes. Most differences with respect to the other estuarine zones are to be found in the freshwater and oligohaline zones of the Scheldt and Humber estuaries.

Table 4 Partial Triadic Analysis (PTA), Rv coefficients between estuarine zone tables. Labels: "Sch", Scheldt; "Elb", Elbe; "Hum", Humber; "F", freshwater; "O", oligohaline; "M", mesohaline; "P", polyhaline. Significance levels: *, 0.01 < p < 0.05; **, 0.001 < p < 0.01; ***, p < 0.001.

	Sch.F	Sch.O	Sch.M	Sch.P	Elb.F	Elb.O	Elb.M	Elb.P	Hum.F	Hum.O	Hum.M
Sch.O	0.73 ***										
Sch.M	0.39 *	0.51 **									
Sch.P	0.30 *	0.40 *	0.81 ***								
Elb.F	0.24 *	0.35 *	0.29 **	0.48 ***							
Elb.O	0.26	0.45 *	0.53 ***	0.45 **	0.58 ***						
Elb.M	0.21	0.35 *	0.59 ***	0.59 ***	0.60 ***	0.77 ***					
Elb.P	0.13	0.20	0.30 *	0.51 ***	0.56 ***	0.38 ***	0.74 ***				
Hum.F	0.10	0.24	0.23	0.17	0.16	0.21 *	0.25 *	0.19 **			
Hum.O	0.16	0.26 *	0.27 *	0.23	0.10	0.15	0.22 *	0.17 *	0.53 ***		
Hum.M	0.15	0.20	0.38 **	0.46 ***	0.20 **	0.29 **	0.41 ***	0.29 ***	0.10	0.25 **	
Hum.P	0.24 *	0.32 *	0.43 **	0.49 **	0.27 ***	0.33 **	0.42 ***	0.38 ***	0.18	0.29 *	0.31 ***

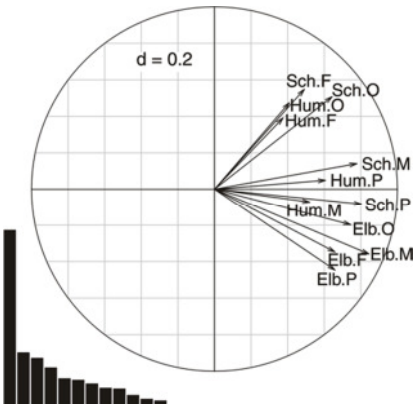


Fig. 19 PTA, Correlation circle of the interstructure. The eigenvalues diagram indicates a highly dominant first value (41,6 %) evidencing common structural similarities among the estuarine zones (contiguous vectors). For labels, see table 4. "d" indicates the grid scale.

The average estuarine pattern that can be found from this analysis is represented in the compromise structure (fig. 20). The first axis reflects the opposition between winter and summer. Summer is characterized by high temperatures and salinities. Winter rather shows high dissolved silica, dissolved oxygen, total dissolved inorganic nitrogen and nitrate concentrations.

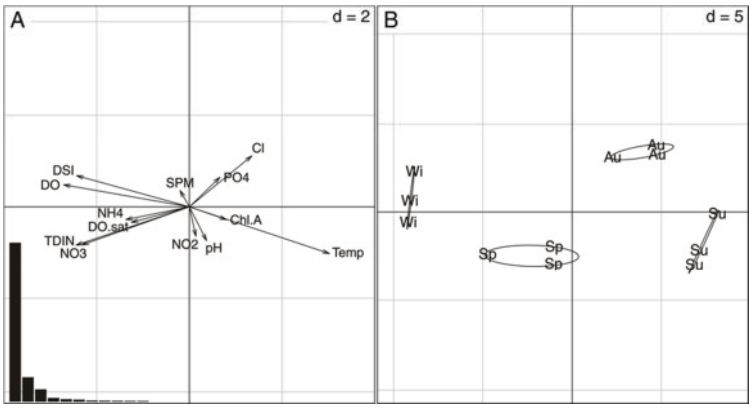


Fig. 20 PTA, Compromise. A) Descriptors and eigenvalues diagram; first axis (horizontal), 79.0 %; second axis (vertical), 11.7 %. B) Statistical units grouped per season (three years per season). "d" indicates the grid scale.

In the intrastructure, distinct seasonal (fig. 21) and physico-chemical (fig. 22) patterns for the Scheldt and Humber estuaries become clear. The Humber estuary is marked by high suspended matter concentrations in summer and autumn, and absence of seasonal variations in chlorophyll *a* and dissolved silica concentrations in the low salinity zones (fig. 21; I-L & fig. 22; I-L). The Scheldt freshwater zone mainly differs from the Elbe by its peak of primary production, occurring rather in autumn than in spring (fig. 21; A-D & fig. 22 A-D). A general remarkable aspect that can be observed between zones within an estuary is the decrease in seasonal amplitude of the physico-chemical processes in the polyhaline zone. Only within the Scheldt estuary, this decrease can be observed to be gradual along the estuarine gradient (fig. 22; A-D).

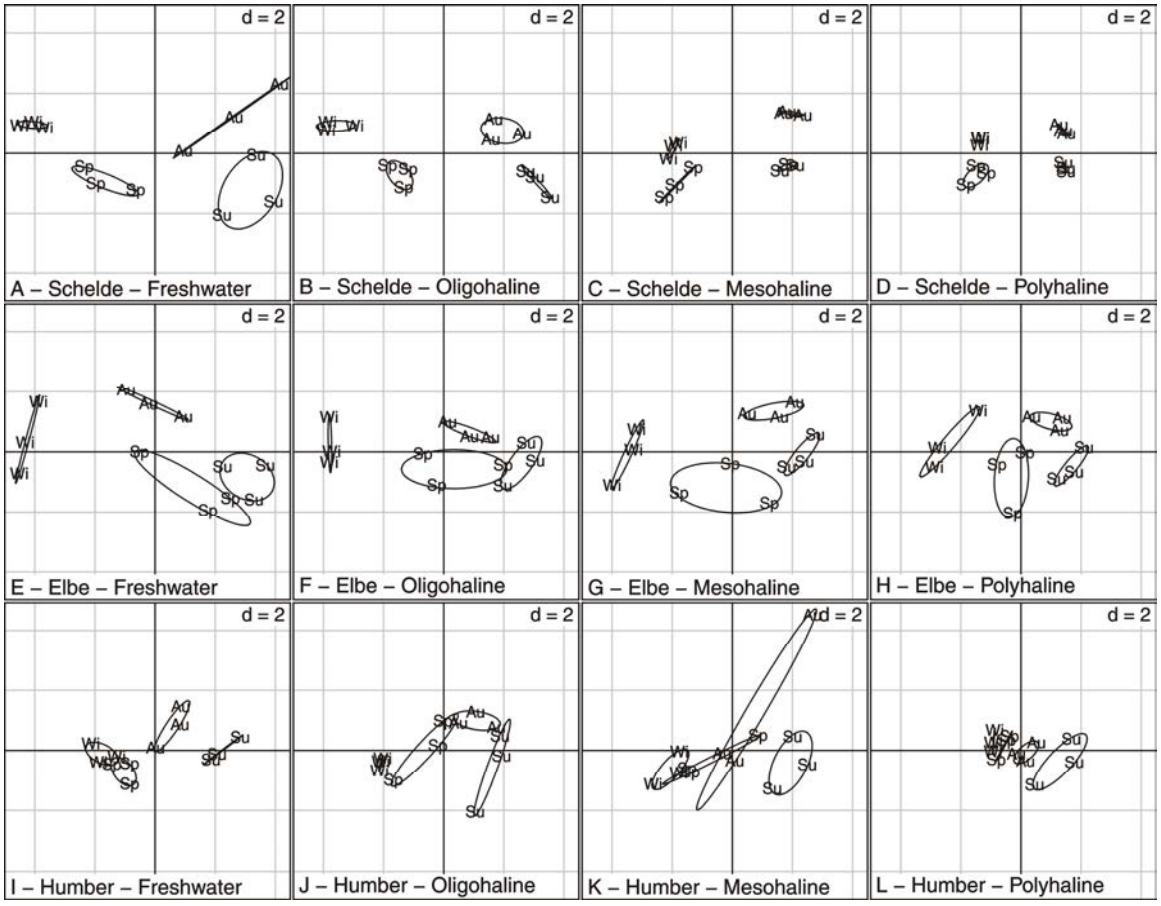


Fig. 21 PTA, intrastructure. It consists in the projection of the lines of the initial tables (season × year) as passive elements on the axes of the compromise. Complementarily to the interstructure, the intrastructure provides structural information determining how tables (cloud of points) deviate from each other and from the compromise. Here, the patterns exhibited by the Humber zones are clearly more deviant from those of the other estuaries. "d" indicates the grid scale.

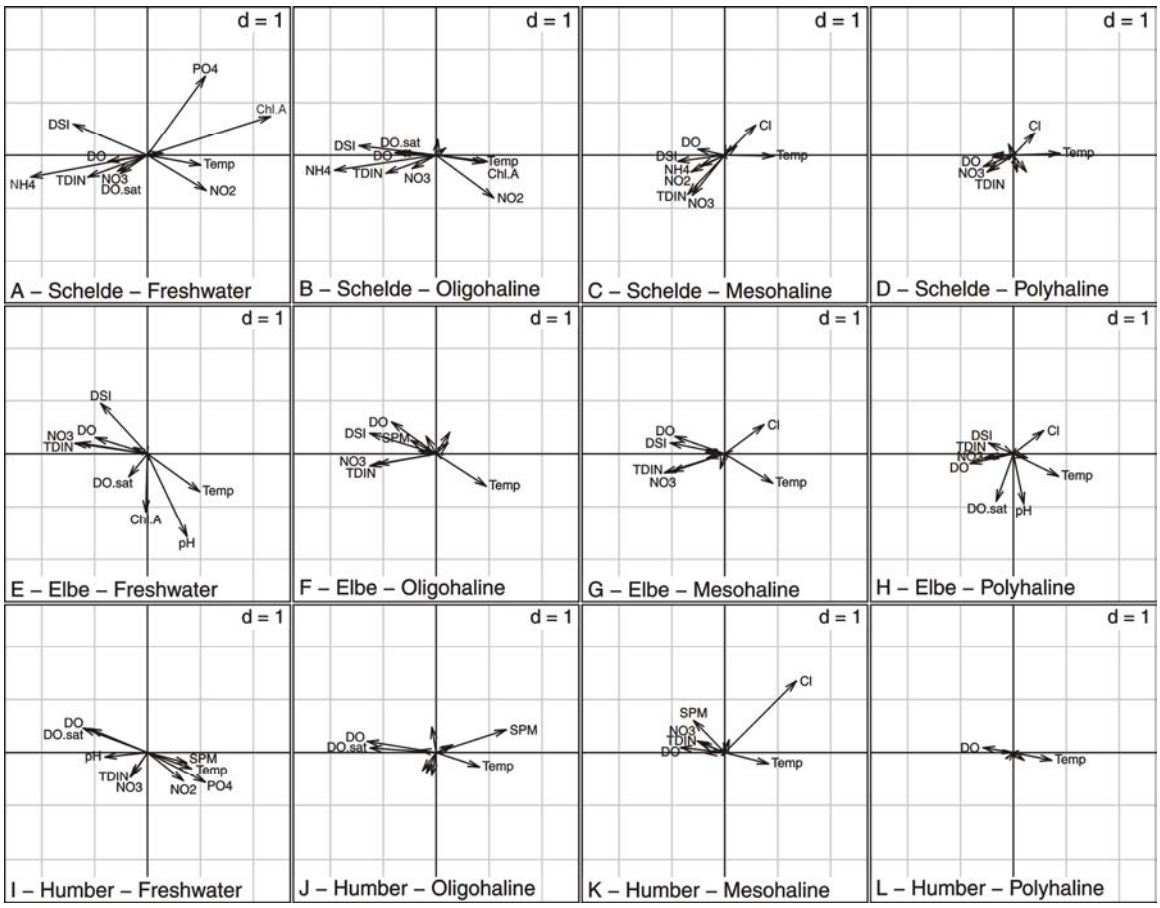


Fig. 22 PTA, intrastructure, descriptors. It consists in the projection of the columns of the initial tables (physicochemical descriptors) as passive elements on the axes of the compromise. Combined to figure 19, vectors positions indicate the physicochemical context, and vector lengths indicate the extent of the variations between seasons. For clarity, only the labels of the most contributing variables are indicated. "d" indicates the grid scale.

To further study how **seasons** differ from each other in physico-chemical processes between zones, a similar (partial triadic) analysis has been performed. However, now for each season, a table is defined by the physico-chemical descriptors measured three times (2004-2006) for the four different spatial units (zone-year lines × descriptors in columns). Again a correlation matrix (table 5) and circle (fig. 23) are created, but this time displaying correlations between seasons for an average estuarine pattern.

Table 5 PTA, Rv coefficients between estuarine seasonal tables. Significance levels: *, 0.01 < p < 0.05; **, 0.001 < p < 0.01; ***, p < 0.001.

	Spring	Summer	Autumn
Summer	0.70 ***		
Autumn	0.70 ***	0.78 ***	
Winter	0.74 ***	0.57 ***	0.74 ***

All Rv coefficients are significant (table 5), indicating similar patterns for all seasons. Nevertheless, the winter-spring and summer-autumn opposition can be seen from the correlation circle (fig. 23).

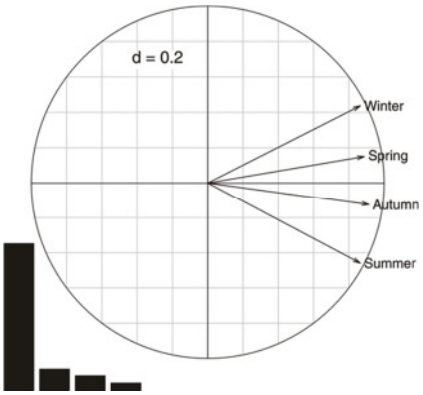


Fig. 23 PTA, Correlation circle of the interstructure. The eigenvalues diagram indicates a highly dominant first value (41.6 %) evidencing common structural similarities among seasons for different estuarine zones (contiguous vectors). "d" indicates the grid scale.

Again, from the compromise it is clear that the upstream parts of Scheldt and Humber (freshwater and oligohaline zone resp.) are most distinct from the other estuarine spatial units (fig. 24).

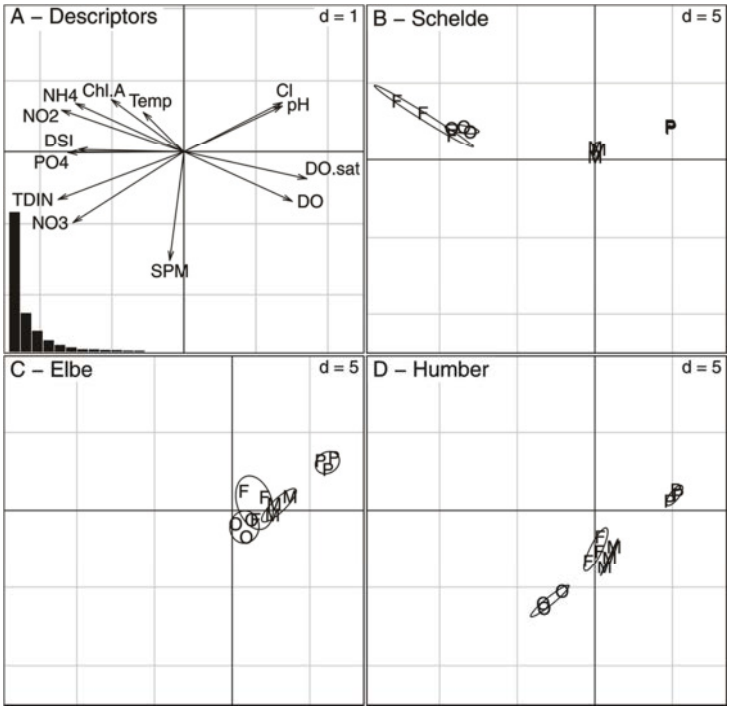


Fig. 24 PTA, Compromise. A) Descriptors and eigenvalues diagram; first axis (horizontal), 79.0 %; second axis (vertical), 11.7 %. B) Statistical units grouped per zone (three years per estuary). "d" indicates the grid scale.

Although Rv coefficients are significant, from the intrastructure it can be observed that estuarine patterns between zones are most alike for all seasons in the Elbe. In the Humber differences in estuarine patterns between zone decrease in winter, while in the Scheldt a distinction between zones persists throughout the seasons (fig. 25). In all estuarine zones and seasons dissolved constituents (nitrogen species, phosphate) decrease and pH and dissolved oxygen concentrations increase with chlorinity increasing. Ammonium concentrations decrease with increase in temperature and chlorophyll *a* in summer and autumn, mostly in the Scheldt. The Humber differentiates itself from the other estuaries by its low dissolved silica concentrations and absence of chlorophyll dynamics in summer. The Elbe differentiates itself from the other estuaries by its lower nutrient concentrations in general (fig. 25).

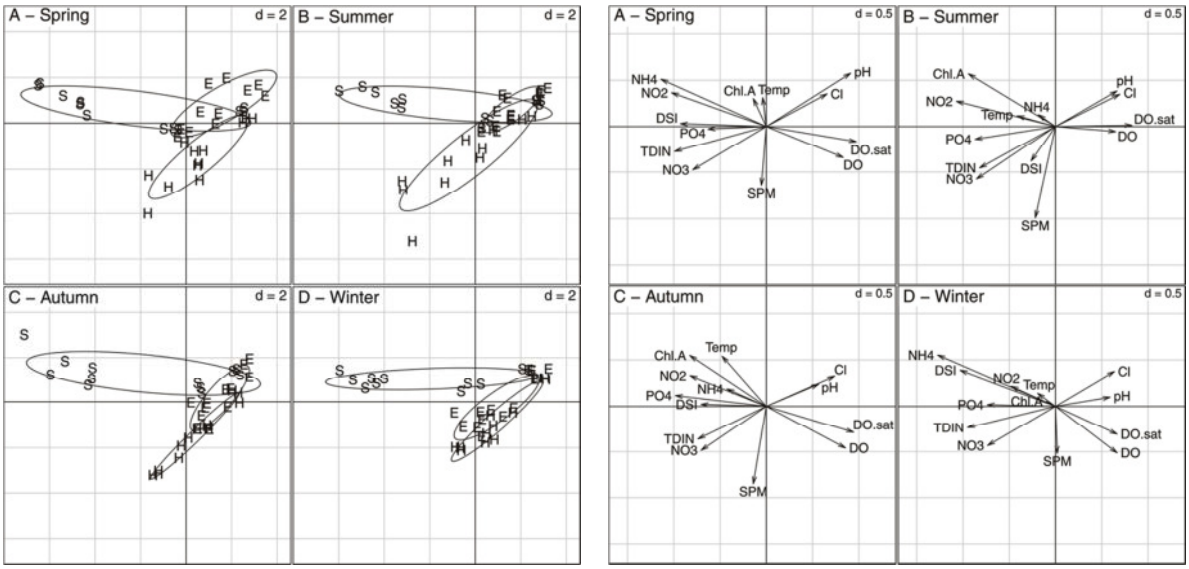


Fig. 25 PTA, intrastructure <u>Left:</u> It consists in the projection of the lines of the initial tables (zone × year) as passive elements on the axes of the compromise. Complementarily to the interstructure, the intrastructure provides structural information determining how tables (cloud of points) deviate from each other and from the compromise. Here, the patterns exhibited by seasonality in the Scheldt are clearly more deviant from those of the other estuaries. "d" indicates the grid scale. In the Elbe patterns do not seem to change between seasons, while in the Humber parameter variability decreases towards the winter season. "d" indicates the grid scale. <u>Right:</u> It consists in the projection of the columns of the initial tables (physico-chemical descriptors) as passive elements on the axes of the compromise. When left and right graphs are combined, vectors positions (right) indicate the physico-chemical context, and the clouds of points (left) indicate the extent of the variations between seasons. For clarity, only the labels of the most contributing variables are indicated. "d" indicates the grid scale.

3.2.3 Nutrients

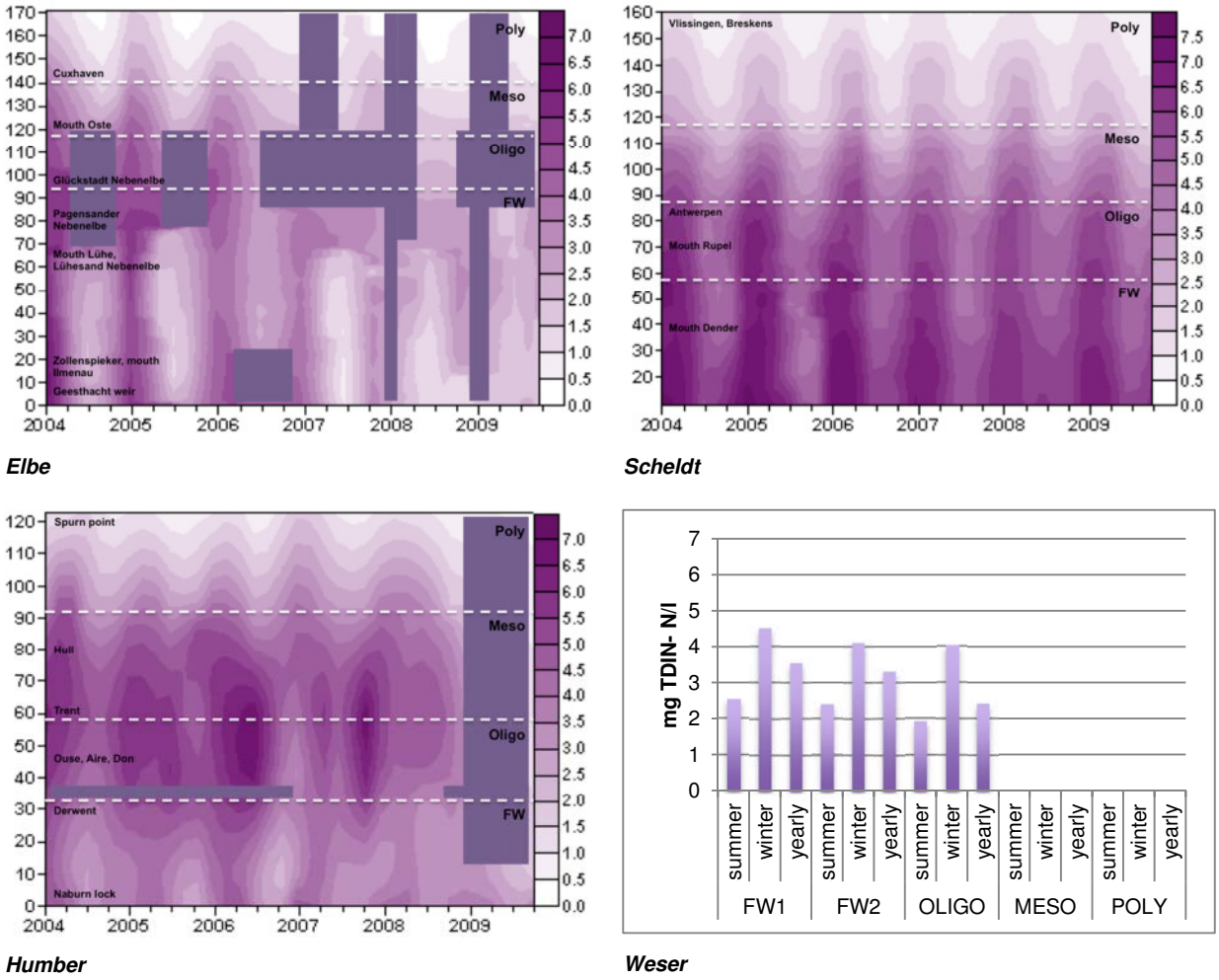
(with contributions of Tom Maris, Stefan Van Damme, Karline Soetaert)

3.2.3.1 Nitrogen

Total dissolved inorganic nitrogen (TDIN)

Total dissolved inorganic nitrogen concentrations (fig. 26) do not change drastically for the time period studied. However, we can see clearly different spatial patterns for the Elbe, Scheldt and Humber estuaries. The spatial distribution of the Weser could not be considered because total dissolved inorganic nitrogen was measured in only three, occasionally four sampling stations, within the freshwater, oligohaline and sometimes the polyhaline zone. The concentrations however, seem to be in the same order of magnitude then those for the Elbe estuary.

The concentrations of total dissolved inorganic nitrogen (Attachment 2) averaged over the six-year period studied, are highest within the Scheldt estuary (4.2 ± 0.09 mg N/l) and lowest within the Elbe estuary (3.0 ± 0.08 mg N/l). The highest concentrations in the Elbe, Scheldt, Humber and Weser are observed in the oligohaline, freshwater, oligohaline and freshwater zone respectively. In the Scheldt a gradual decrease towards the sea can be observed, while in the Elbe and Humber local peaks and valleys are displayed (fig. 26). In all estuaries total dissolved inorganic nitrogen concentrations are highest in winter (Attachment 2). The six-yearly average difference between winter and summer concentration for the zone of highest total dissolved nitrogen concentration per estuary is observed to be highest within the Elbe estuary (2.73 mg N/l), next the Weser estuary (2.01 mg N/l) and the Scheldt estuary (1.88 mg N/l) and lowest within the Humber estuary (0.05 mg N/l). However, taking into account the missing data in the Elbe estuary, this summer winter difference is likely to be higher in the freshwater zone than the oligohaline zone.



Elbe ***Scheldt***

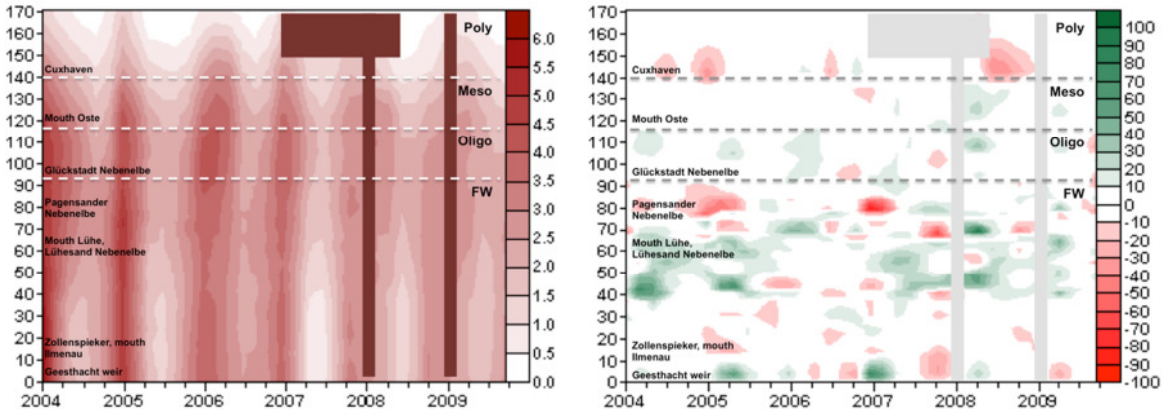
Humber ***Weser***

Fig. 26 Spatial (TIDE km) temporal (years) distribution of total dissolved inorganic nitrogen (TDIN; mg N/l) for the Elbe, Scheldt, Humber and Weser. Main tributaries and recognizing sampling points are shown in the surfer plots. For the Weser not enough sampling stations covered the estuarine gradient to represent the data as a surfer plot. Therefore averages per zone are displayed for yearly, summer and winter period. Missing data in the time-distance plots are represented as solid filled rectangles.

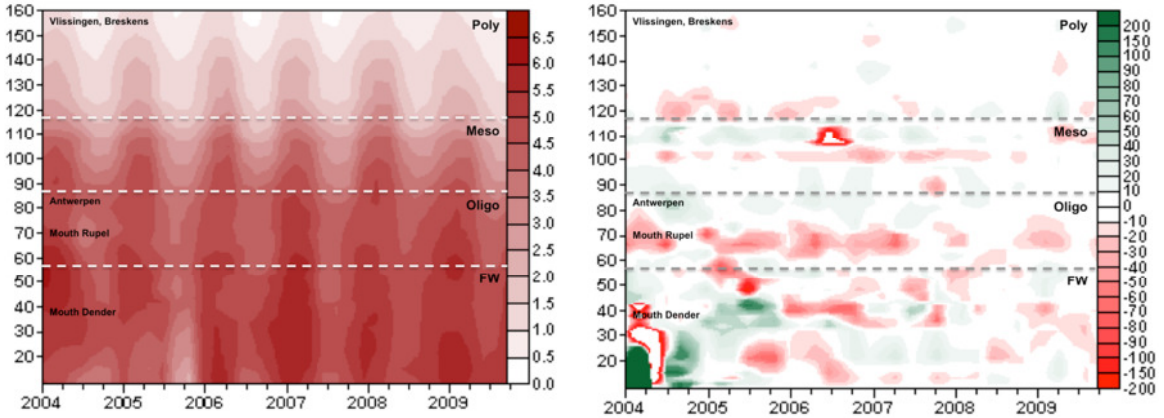
To understand these different patterns, a closer study of ammonium and nitrate concentrations (see further) is performed, the two species mostly involved within biogeochemical processing for nitrogen. Besides concentrations, also deviations from the expected concentrations due to conservative mixing are considered here. This gives insight into the sink and source function per zone. Unfortunately sink and source functions could not be studied for the Weser estuary, since not enough data were available along the estuarine salinity gradient to apply this method.

Nitrate and ammonium dynamics

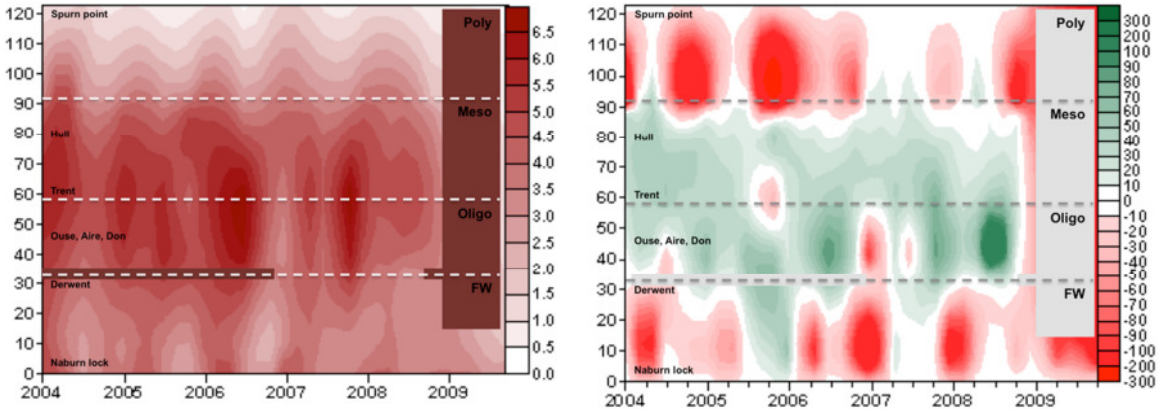
In general, along the overall estuarine gradient, highest average nitrate concentrations (Attachment 2) are reached in the Scheldt and Humber estuary (3.67 ± 0.07 mg N/l and 3.67 ± 0.10 mg N/l resp.). Lowest average nitrate concentrations can be observed in the Elbe estuary (2.60 ± 0.05 mg N/l). In both Scheldt and Elbe nitrate concentrations appear to decrease towards the sea. In the Humber concentrations seem to reach a maximum along the oligo- to mesohaline stretch (fig. 27). Nitrate concentrations are also highest in winter within the same zones as observed for total dissolved inorganic nitrogen (see earlier). The six-yearly average difference between winter and summer concentration for the zone of highest nitrate concentration per estuary is observed to be highest within the Elbe estuary (2.25 mg N/l), next the Weser estuary (1.92 mg N/l) and the Scheldt estuary (0.87 mg N/l) and lowest within the Humber estuary (0.20 mg N/l). Considering the surfer plots of gain and loss of observed nitrate concentration relative to the expected concentration due to mixing, in Elbe and Scheldt gain and loss seem to alternate along the estuarine gradient, while in the Humber there are clear patches of nitrate gain and loss displayed (fig. 27).



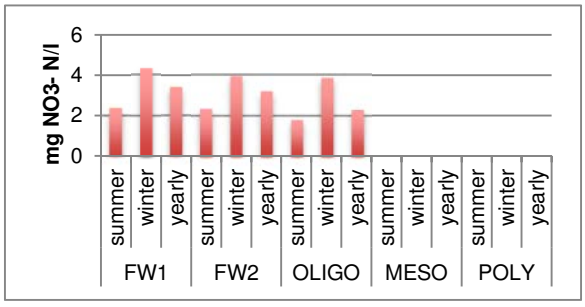
Elbe



Scheldt



Humber



Weser

Fig. 27 Spatial (TIDE km) temporal (years) distribution of nitrate concentration (NO3; mg N/l; left) and of nitrate gain and loss as calculated according to the conservative mixing principle (µg/l*km; right) for the Elbe, Scheldt, Humber and Weser. Main tributaries and recognizing sampling points are shown in the surfer plots. For the Weser not enough sampling stations covered the estuarine gradient to represent the data as a surfer plot or to calculate gain and loss. Therefore only average nitrate concentrations per zone are here displayed for yearly, summer and winter period. Missing data in the time-distance plots are represented as solid filled rectangles.

Gain and loss multiplied with freshwater discharge, averaged per zone for the six-year period studied on a yearly basis (fig. 28) shows that most nitrate is gained within the freshwater zone of the Elbe estuary (91 ton N/yr*km) and least nitrate is gained within the freshwater zone of the Scheldt (1 ton N/yr*km). Nitrate loss is highest within the mesohaline zone of the Humber estuary (-95 ton N/yr*km). In general, in summer there is a tendency for nitrate gain, while in winter there is rather nitrate loss. Except for the oligohaline zone of the Humber, and all zones from the oligohaline zone towards the sea in the Scheldt, where there is nitrate gained in both summer and winter. Taking into account the input concentration, as the concentration of the most upstream point per zone, one can have an idea of the filter efficiency per zone, by dividing gain or loss by its input. On a yearly basis, nitrate is most efficiently removed within the mesohaline zone of the Humber estuary (-1.94 %/km). However, nitrate is also mostly produced within the same estuary, within the oligohaline zone (+ 0.90 %/km). Whether it concerns gain or loss, the filter appears to be more competent in summer than in winter, except for the mesohaline zone of the Humber estuary, in which nitrate is more efficiently removed in winter.

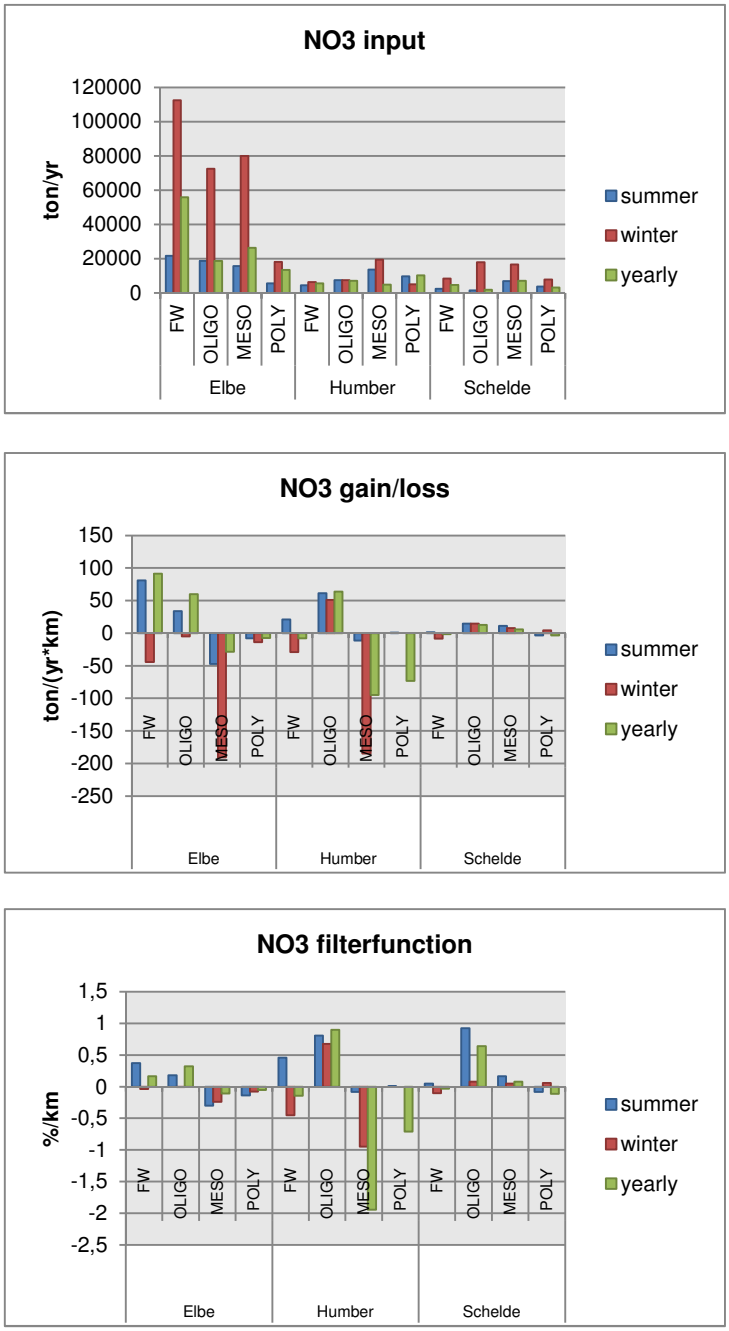
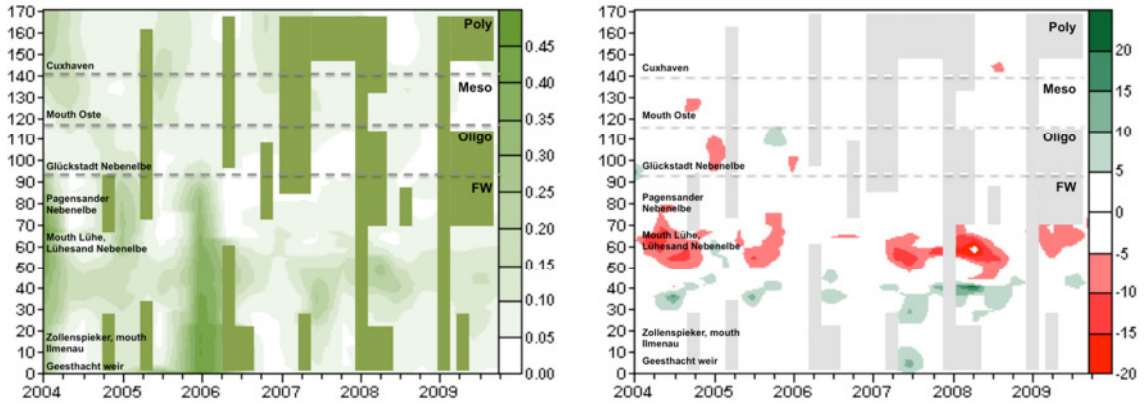


Fig. 28 Six-yearly average of nitrate input (ton/yr), gain and loss (ton/(yr*km)) and filter efficiency (%/km) per zone for Elbe, Scheldt and Humber, on a yearly, winter and summer basis. Summer = June, July, August; winter = December, January and February.

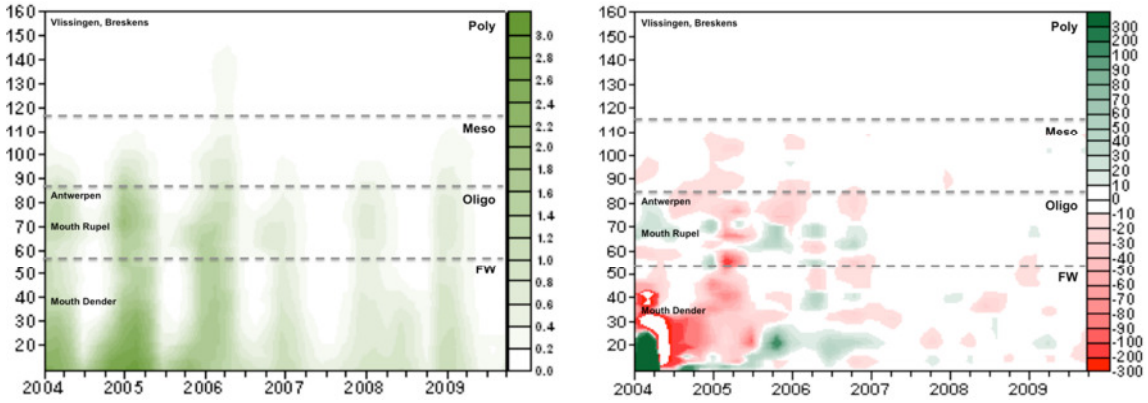
Like for nitrate, also highest **ammonium** concentrations (Attachment 2) as observed in general, along the overall estuarine gradient can be found within the Scheldt estuary (0.44 ± 0.03 mg N/l), having their maximum within the freshwater zone (0.82 ± 0.05 mg N/l) and next gradually decreasing towards the sea (fig. 29). The difference between the estuaries is much more strikingly for ammonium than for nitrate. Even though ammonium concentrations have decreased most pronounced within the Scheldt estuary (fig. 29), six-yearly averaged concentrations are about three times higher than within the Elbe, Weser and Humber estuaries (Attachment 2). Although, in the Elbe there is quite a lot of data missing in time and space, it seems concentrations are highest within the freshwater zone (0.14 ± 0.01 mg N/l). Noteworthy are the high concentrations observed in 2006 (fig. 29). In the Humber estuary, ammonium concentrations are higher within the oligohaline zone (0.14 ± 0.02 mg N/l). However, study of the surfer plot shows there is a second peak more downstream at the border of the meso- and polyhaline zone. Furthermore, it appears that the first peak of ammonium within the oligohaline zone shifted more downstream to the mesohaline zone from 2006 to 2007 (fig. 29). In the Weser estuary highest ammonium concentrations can be observed within the oligohaline zone (0.13 ± 0.01 mg N/l). However, it has to be noticed only limited data for the Weser was available (n = 21). Again concentrations for ammonium are like for nitrate higher in winter than in summer. The difference between winter and summer for the zone of maximum concentration is highest within the Scheldt estuary (1.05 mg N/l), followed by the Humber (0.16 mg N/l), Elbe (0.13 mg N/l) and Weser estuaries (0.03 mg N/l).

Compared with nitrate mixing plots, ammonium mixing plots seem to be more defined by distinct zones of gain and loss (fig. 29).

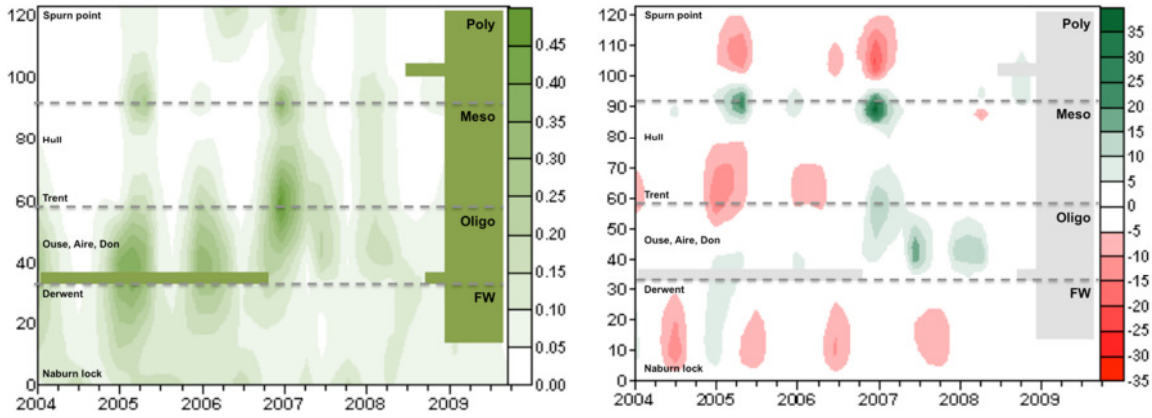
Based upon a six-yearly average, gain of ammonium is highest within the oligohaline zone of the Humber estuary (18 ton N/ yr*km), loss is highest within the oligohaline zone of the Scheldt estuary (-13 ton/yr*km) (fig. 30). Within the Scheldt ammonium is lost in both winter and summer season and on a yearly basis along almost the whole estuarine gradient. Loss is most pronounced during winter season. Within the Humber ammonium is lost in winter and gained in summer. On a yearly basis, ammonium is produced within the Humber along the whole estuarine gradient (fig. 30), despite large patches of ammonium loss observed in the freshwater, meso- and polyhaline zone (fig. 29). Within the Elbe ammonium is gained within the freshwater zone, while lost in the other zones (fig. 30). Considering also the input into every zone, ammonium is gained mostly within the Humber estuary within the oligo- and mesohaline zone, while being most efficiently removed within the oligohaline zone of the Scheldt estuary. Either gain or loss is effectively limited in the Elbe estuary, or ammonium gain is immediately balanced by loss (e.g. ammonium from organic matter mineralization is immediately nitrified) (fig. 30).



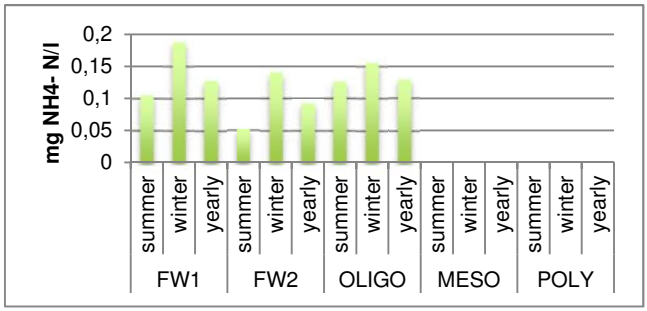
Elbe



Scheldt



Humber



Weser

Fig. 29 Spatial (TIDE km) temporal (years) distribution of ammonium concentration (NH4; mg N/l; left) and of ammonium gain and loss as calculated according to the conservative mixing principle (µg/l*km; right) for the Elbe, Scheldt, Humber and Weser. Main tributaries and recognizing sampling points are shown in the surfer plots. For the Weser not enough sampling stations covered the estuarine gradient to represent the data as a surfer plot or to calculate gain and loss. Therefore only average ammonium concentrations per zone are here displayed for yearly, summer and winter period. Missing data in the time-distance plots are represented as solid filled rectangles.

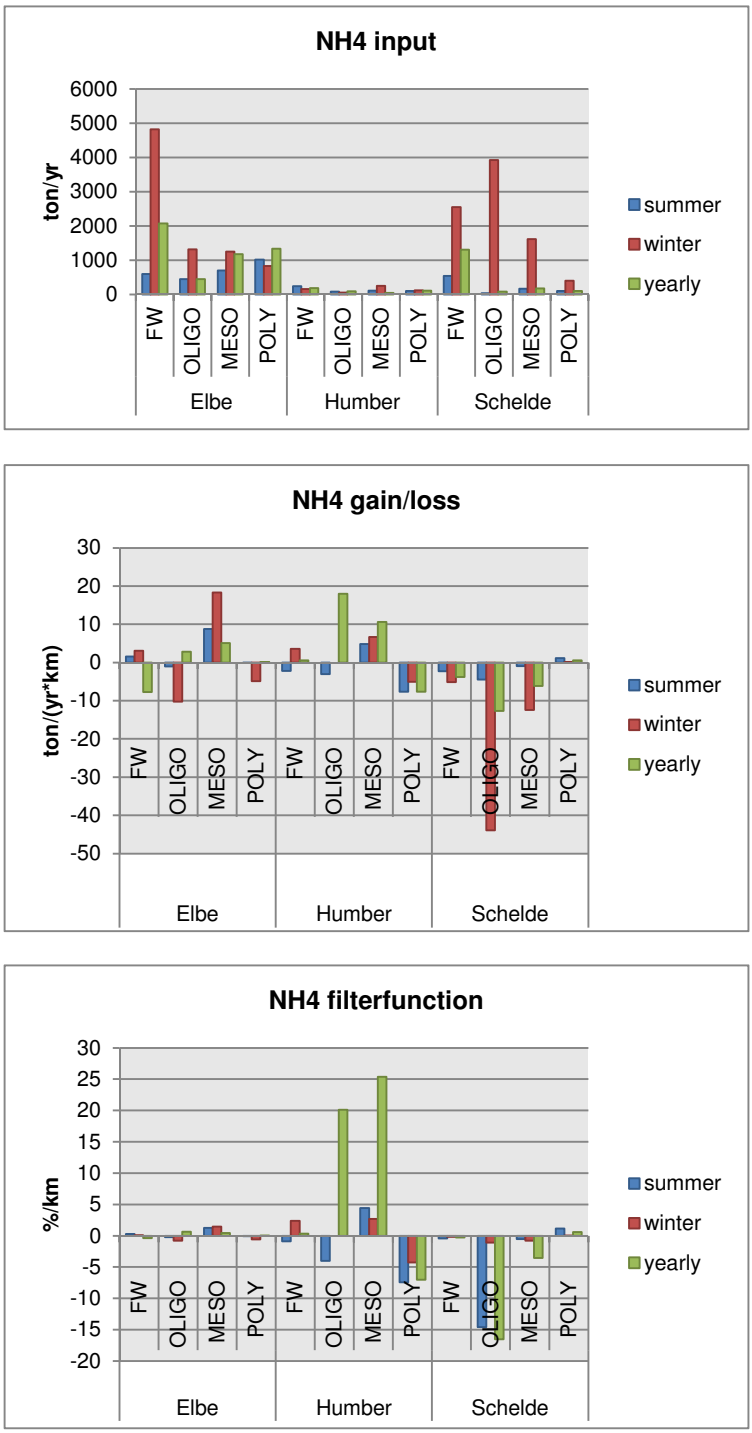
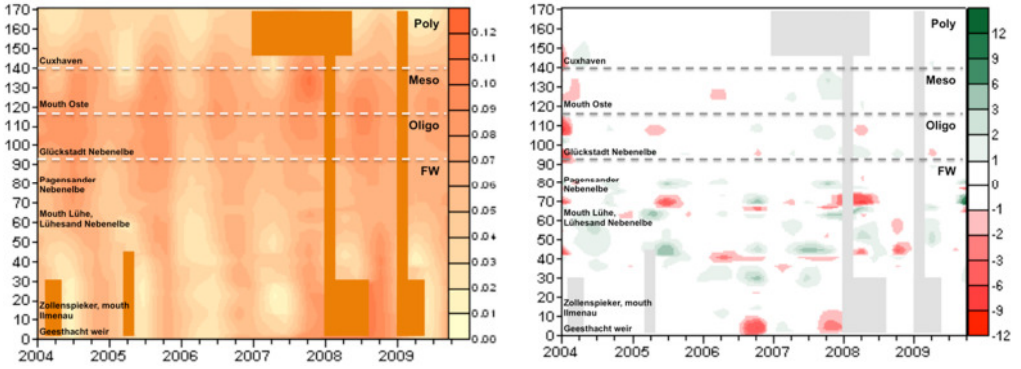


Fig. 30 Six-yearly average of ammonium input (ton/yr), gain and loss (ton/(yr*km)) and filter efficiency (%/km) per zone for Elbe, Scheldt and Humber, on a yearly, winter and summer basis. Summer = June, July, August; winter = December, January and February.

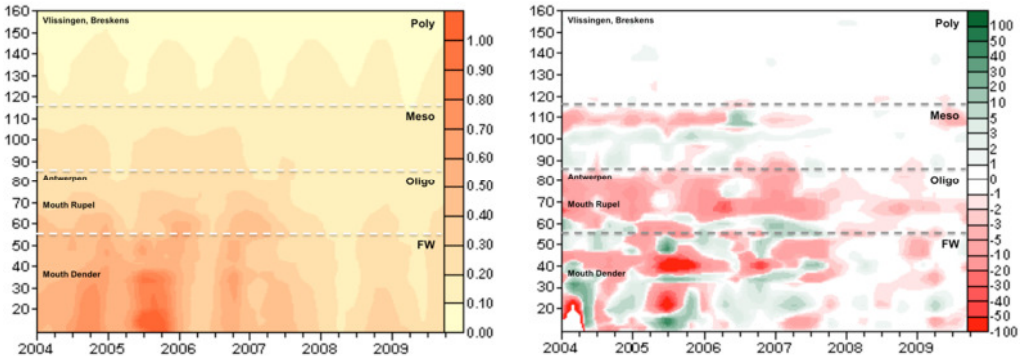
3.2.3.2 Phosphate

Phosphate concentrations (Attachment 2) are highest within the Scheldt estuary (0.26 ± 0.01 mg P/l), next within the Humber estuary (0.18 ± 0.01 mg P/l). They are about three to four times higher than within the Elbe and Weser estuaries (0.06 ± 0.002 mg P/l and 0.07 ± 0.002 mg P/l resp.). Phosphate concentrations in the Scheldt are highest in the freshwater zone (0.43 ± 0.01 mg P/l), gradually decreasing towards the sea. Within the Humber highest concentrations are observed along the oligo- and mesohaline stretch (0.28 ± 0.01 mg P/l & 0.20 ± 0.01 mg P/l resp.). Within the Elbe estuary, phosphate concentrations are highest in the oligo- and mesohaline zone. However, they do not differ much along the whole estuarine gradient. Within the Weser phosphate

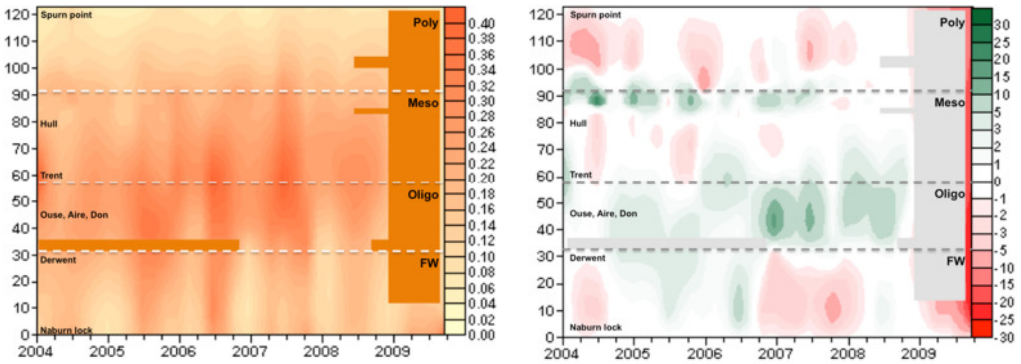
concentrations are in the same order of magnitude than within the Elbe and do not differ greatly between zones either (fig. 31). Only slight differences between winter and summer season are observed, except within the Humber estuary in which phosphate concentrations are higher in summer (Attachment 2).



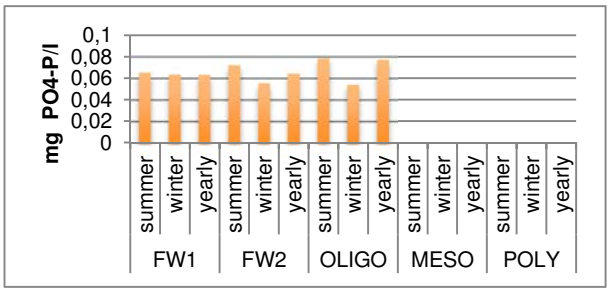
Elbe



Scheldt



Humber



Weser

Fig. 31 Spatial (TIDE km) temporal (years) distribution of phosphate concentration (PO4; mg P/l; left) and of phosphate gain and loss as calculated according to the conservative mixing principle (µg P/l*km; right) for the Elbe, Scheldt, Humber and Weser. Main tributaries and recognizing sampling points are shown in the surfer plots. For the Weser not enough sampling stations covered the estuarine gradient to represent the data as a surfer plot or to calculate gain and loss. Therefore only average phosphate concentrations per zone are here displayed for yearly, summer and winter period. Missing data in the time-distance plots are represented as solid filled rectangles.

On a yearly basis, phosphate is gained most within the oligo- and mesohaline zone of the Humber estuary (10 ton/yr*km) and lost most within the oligohaline zone of the Scheldt estuary (-2 ton/yr*km). Usually, losses are higher in winter than in summer for all estuaries, except for the oligohaline zones of the Elbe and Humber estuaries, in which phosphate is gained more during winter than during summer. In general phosphate is lost along the whole estuarine gradient of the Scheldt and gained along most of the estuarine gradient of the Humber (fig. 32). Taking into account input concentrations per zone, phosphate is mainly lost within the upstream parts of the Scheldt estuary and produced within the middle part of the Humber estuary. Dynamics are clearly lower within the Elbe estuary (fig. 32).

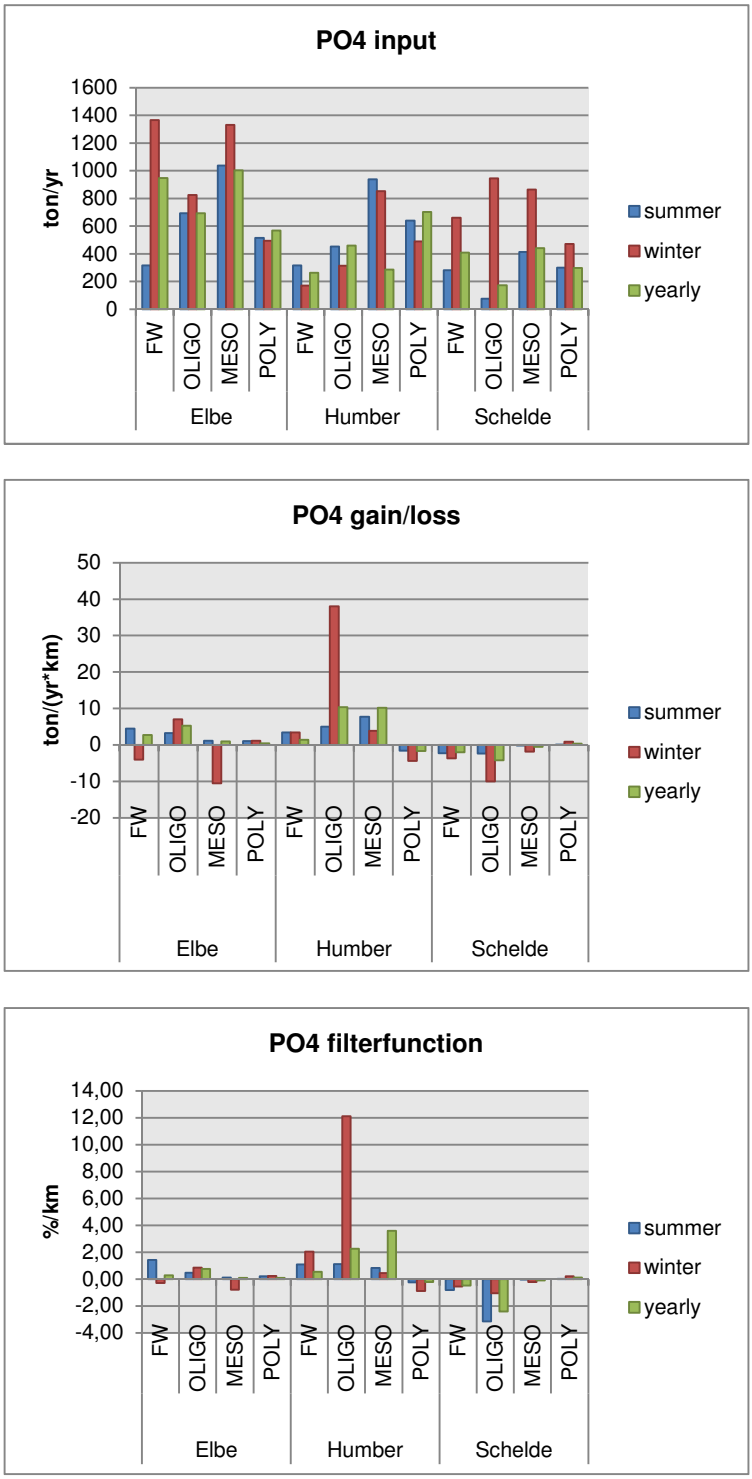


Fig. 32 Six-yearly average of phosphate input (ton/yr), gain and loss (ton/(yr*km)) and filter efficiency (%/km) per zone for Elbe, Scheldt and Humber, on a yearly, winter and summer basis. Summer = June, July, August; winter = December, January and February.

3.2.3.3 Dissolved silica

Dissolved silica concentrations (Attachment 2) are highest within the Scheldt estuary (3.43 ± 0.10 mg DSI/l), followed by the Elbe estuary (2.26 ± 0.12 mg DSI/l). Nevertheless, in the Elbe freshwater zone dissolved silica concentrations fall frequently below 0.3 mg DSI/l, while this only occurs once within the freshwater zone of the Scheldt (fig. 33). Furthermore, in both Scheldt and Elbe concentrations also can fall under 0.3 mg DSI/l within the polyhaline zone. Silica limitation in the Elbe occurs in spring, in the Scheldt in summer. Since 2007 in the Scheldt no limitations occurred anymore, at least not if seasonal averages were considered. The low dissolved silica concentrations in the Weser are result of limited sampling within only the polyhaline zone. Also in the Humber sampling appears to be rather limited in time and space (fig. 33). In both Scheldt and Humber the dissolved silica concentration is highest in the freshwater zone, gradually decreasing towards the sea. Concentrations are higher in winter than summer (Attachment 2). Difference between average winter and summer dissolved silica concentration within the freshwater zone is slightly higher in the Elbe than in the Scheldt estuary (Scheldt: 5.29 mg DSI/l; Elbe: 4.55 mg DSI/l).

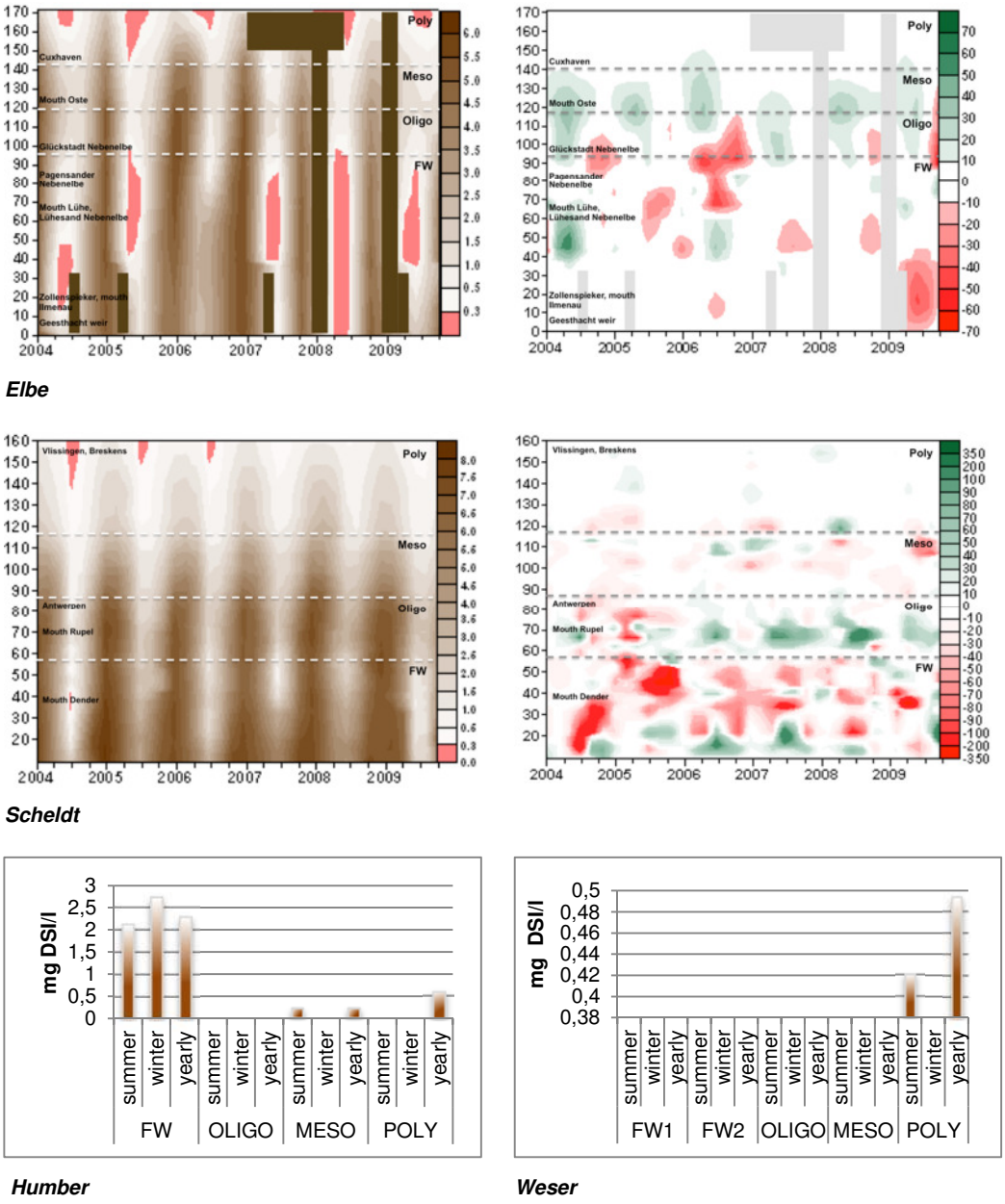


Fig. 33 Spatial (TIDE km) temporal (years) distribution of dissolved silica concentration (DSI; mg DSI/l; left) and of dissolved silica gain and loss as calculated according to the conservative mixing principle (µg DSI/l*km; right) for the Elbe and Scheldt. Main tributaries and recognizing sampling points are shown in the surfer plots. For the Humber and Weser not enough sampling stations covered the estuarine gradient to represent the data as a surfer plot or to calculate gain and loss. Therefore only average dissolved silica concentrations per zone are here displayed for yearly, summer and winter period. Missing data in the time-distance plots are represented as solid filled rectangles.

The method to calculate gain and loss could only be applied upon the Scheldt and Elbe estuary. In both estuaries clear patches of gain and loss can be distinguished (fig. 33).

In the Elbe dissolved silica is gained within the mid part of the estuary. In the Scheldt dynamics are limited and rather a small loss of dissolved silica can be observed in the mid-estuarine part. Taking input concentration per zone into account, only within the oligohaline part of the Elbe estuary a clear increase of dissolved silica can be seen (8.27 %/km). Mostly there is not that much difference between gain and loss in summer and winter (fig. 34). However, when looking at the mixing plots, it can be noted that dissolved silica is gained in winter and lost in summer (fig. 34).

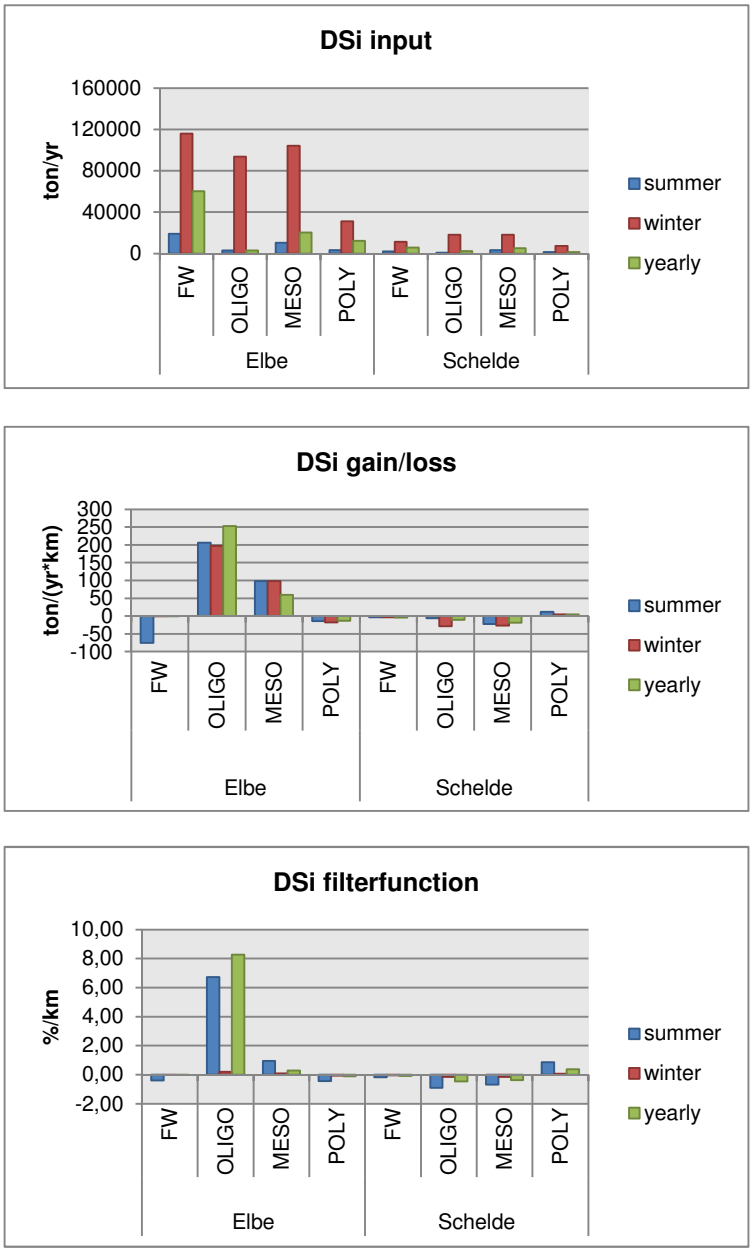


Fig. 34 Six-yearly average of dissolved silica input (ton/yr), gain and loss (ton/(yr*km)) and filter efficiency (%/km) per zone for Elbe and Scheldt, on a yearly, winter and summer basis. Summer = June, July, August; winter = December, January and February.

3.2.3.4 Different sink and source functions for the Elbe, Scheldt and Humber estuaries

Total dissolved inorganic nitrogen

Averaging gain and loss along the whole estuarine length for Elbe, Scheldt and Humber shows that the Elbe is exporting the most amount of inorganic nitrogen (76 ton/yr*km), while most is removed within the Scheldt estuary (-3 ton/yr*km). In the Humber nitrogen is also exported on a

yearly basis (18 ton/yr*km). Nitrogen loss appears to be high in winter, while gain is rather high in summer (fig. 35). Taking the starting concentration into account, total dissolved inorganic nitrogen gain has more effect upon the Elbe and Humber estuaries, than removal has upon the Scheldt estuary (fig. 35).

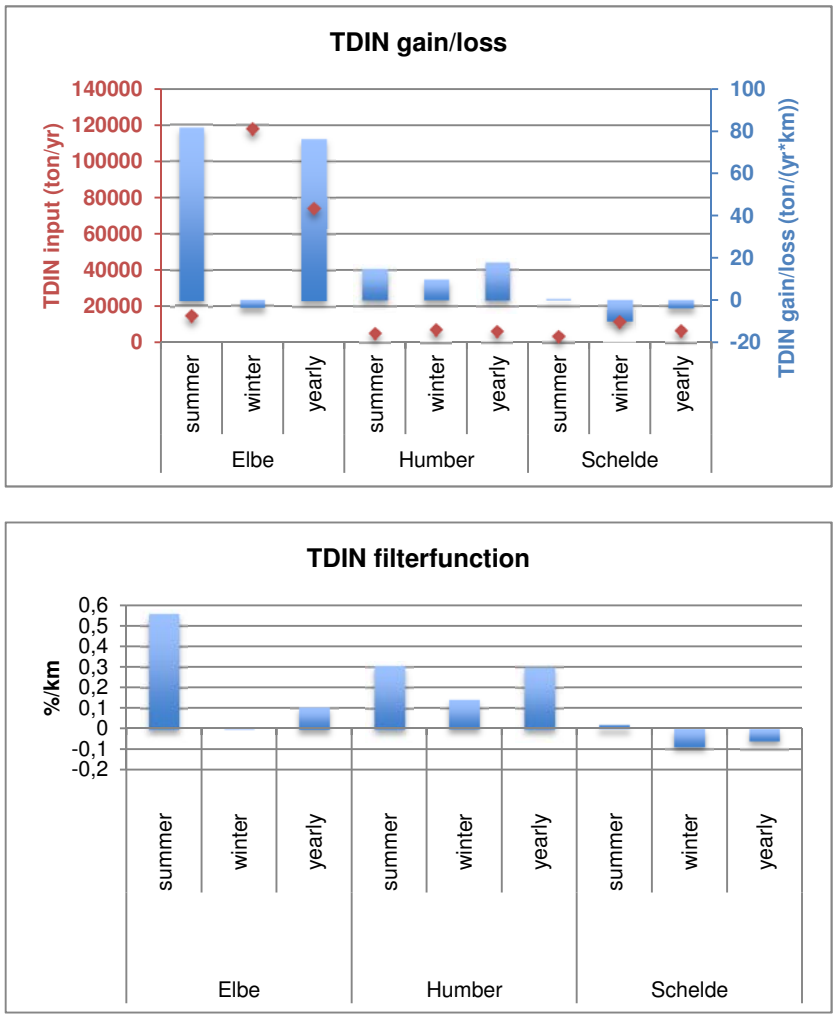


Fig. 35 Sink and source function for total dissolved inorganic nitrogen (TDIN) in the Elbe, Scheldt and Humber estuary, calculated as six-year average along the whole estuarine gradient on a yearly, summer and winter basis. In the upper graph, input (ton/yr) and gain/loss (ton/(yr*km)) are given. In the lower graph, contribution of gain/loss relative to the initial input (starting concentration) is displayed (%/km). Summer = June, July, August; winter = December, January and February.

Nitrogen input

Nitrogen import (fig. 36) in the Elbe estuary is obviously the highest compared with the other estuaries (78 kton/yr, nitrate ammonium and organic nitrogen combined). Also much organic nitrogen is mainly imported in the Elbe. Next, much nitrogen is imported in the Weser estuary (47 kton). Input seems to be lowest within the Scheldt estuary. At the Rupel, nitrogen import in the Scheldt is clearly elevated. Import is highest in winter. Difference between winter and summer import is highest in the Weser and within the Scheldt near the Rupel (3.7 and 3.3 times more input in winter, respectively). Difference is lowest in the Humber estuary (only 10 % more input in winter).

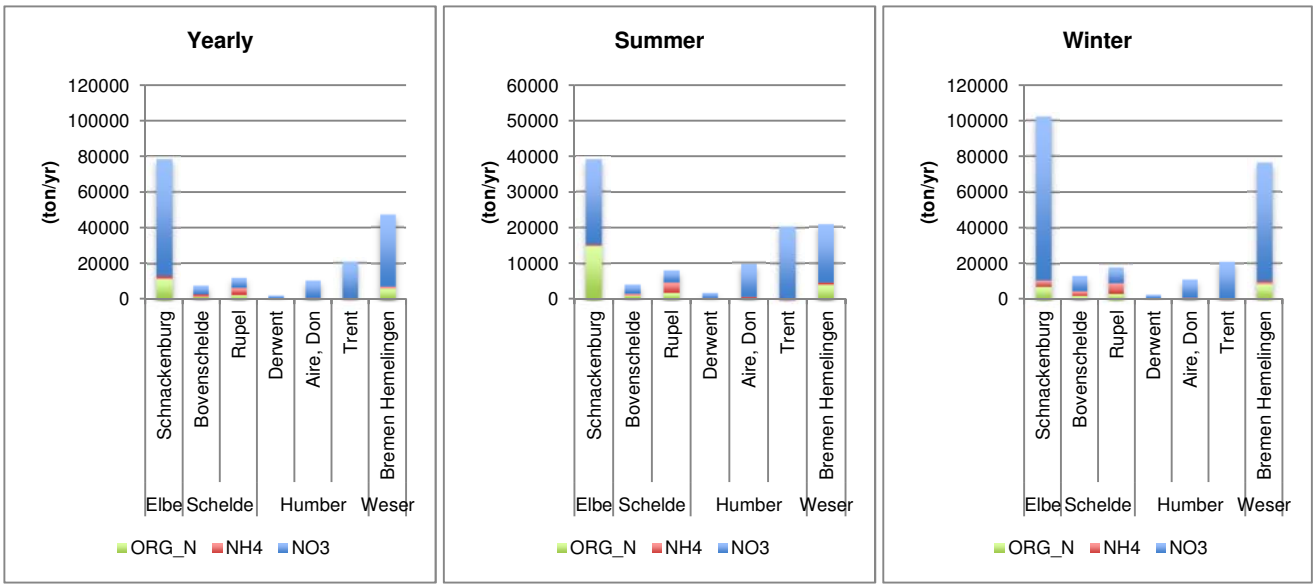


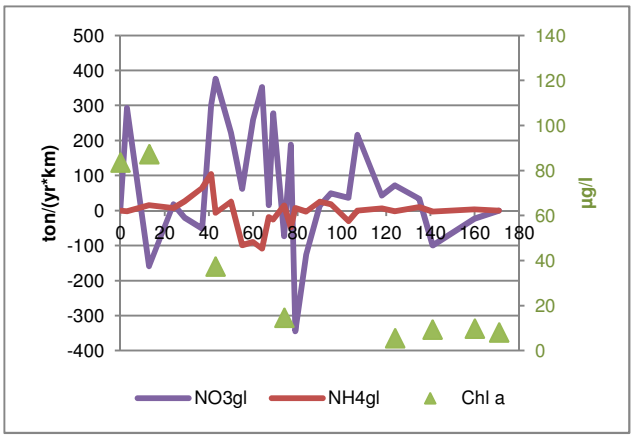
Fig. 36 Six-year average nitrogen input (nitrate, ammonium and organic nitrogen in ton/yr) from the upper boundaries and main tributaries for Elbe, Scheldt, Humber and Weser on a yearly basis and for winter and summer period. Summer = June, July, August; winter = December, January and February.

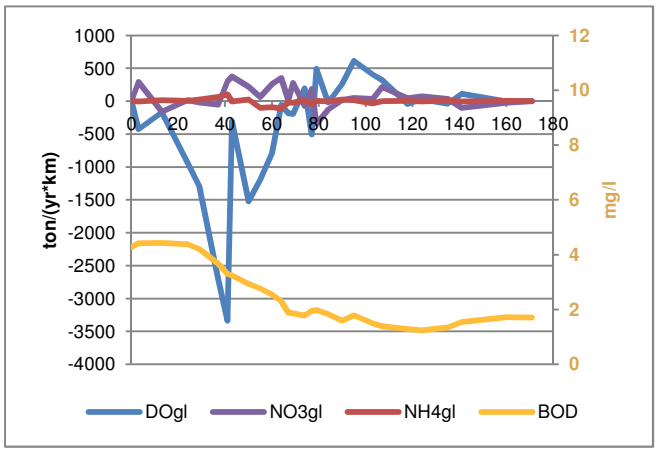
Estuarine processing

Ammonium and nitrate are successively gained in the freshwater zone of the Elbe estuary. As biological oxygen demand decreases towards the sea, also gain and loss dynamics for nitrogen seem to decrease. As biological oxygen demand decreases, probably more organic matter is mineralized to ammonium, which is further nitrified to nitrate, explaining the successive gain of ammonium and nitrate. Chlorophyll *a* concentrations measured, are highest in the freshwater zone, but seem not to be very clear correlated with nitrogen dynamics. It appears biological oxygen demand as indicator for organic matter and ammonium input is the main indicator for nitrogen dynamics. A peak of nitrate gain can be observed near the mouth of the Lühe, while a peak of nitrate loss can be observed near Pagensander Neben Elbe shallow water zone (fig. 37).

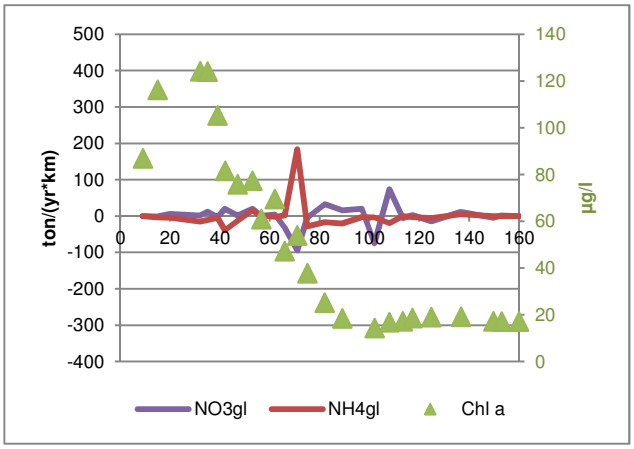
In the Scheldt, also chlorophyll *a* concentrations are very high in the freshwater. However, again there is not a very clear correlation with nitrogen dynamics. In general they are higher than within the Elbe estuary. Most nitrogen gain and loss occurs near the mouth of the Rupel. A clear peak of ammonium gain coincides with a peak of nitrate loss. Near the Rupel also a peak of oxygen loss and a peak of biological demand is observed. It would be expected that ammonium gained from organic matter mineralization is further nitrified to nitrate, giving a peak of nitrate gain. However, a peak of nitrate loss is observed indicating nitrate removal. Together with the low oxygen concentrations observed near the Rupel (see fig. 44, further), it is likely a zone of coupled nitrification-denitrification can be found in the pelagic here. Oxygen and biological oxygen demand again show to be the main indicators for nitrogen dynamics (fig. 37). At the border between Belgium and the Netherlands, where the Zeeschelde proceeds into the Westerschelde (at kilometer 100), peaks of consecutively nitrate loss and nitrate gain are observed. This seems to correspond to consecutive peaks of dissolved oxygen gain and loss respectively, indicating a zone of increased nitrification. Although only measured up to the border, there seems to be no difference in biological oxygen demand in this zone.

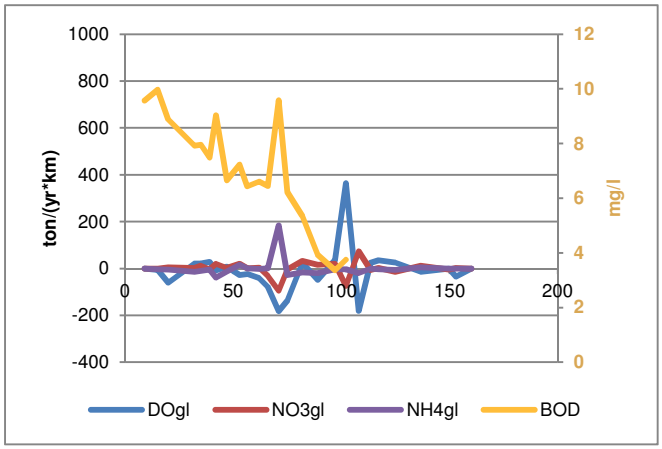
Within the Humber, peaks of nitrate, ammonium and dissolved oxygen are observed near kilometer 90, where the mesohaline zone ends and proceeds to the polyhaline zone (fig. 37). Within this zone also dissolved oxygen oversaturation is frequently observed (also see fig. 44). Chlorophyll extract is not represented here, since the values are only very low within this very turbid estuarine system and hence are not very likely to affect nitrogen dynamics.



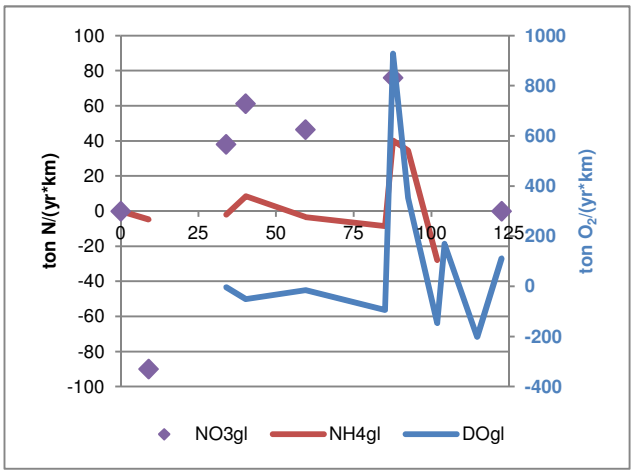


Elbe





Scheldt



Humber

Fig. 37 Relation between nitrate & ammonium gain and loss in ton N/(yr*km) with chlorophyll a (µg/l), biological oxygen demand (mg/l) and dissolved oxygen gain and loss in ton O_2/(yr*km) for Elbe, Scheldt and Humber.

Phosphate

The Humber is the most phosphate-exporting estuary (4 ton/yr*km), while most is removed in the Scheldt estuary (-1 ton/yr*km). In winter in both Elbe and Scheldt more phosphate is lost. However, in the Humber more phosphate is gained in winter (fig. 38). However, considering input concentrations it is clear that phosphate losses in winter have more effect in the Scheldt than in the Elbe estuary. Nevertheless, it is the gain of phosphate within the Humber estuary that is most effective (fig. 38).

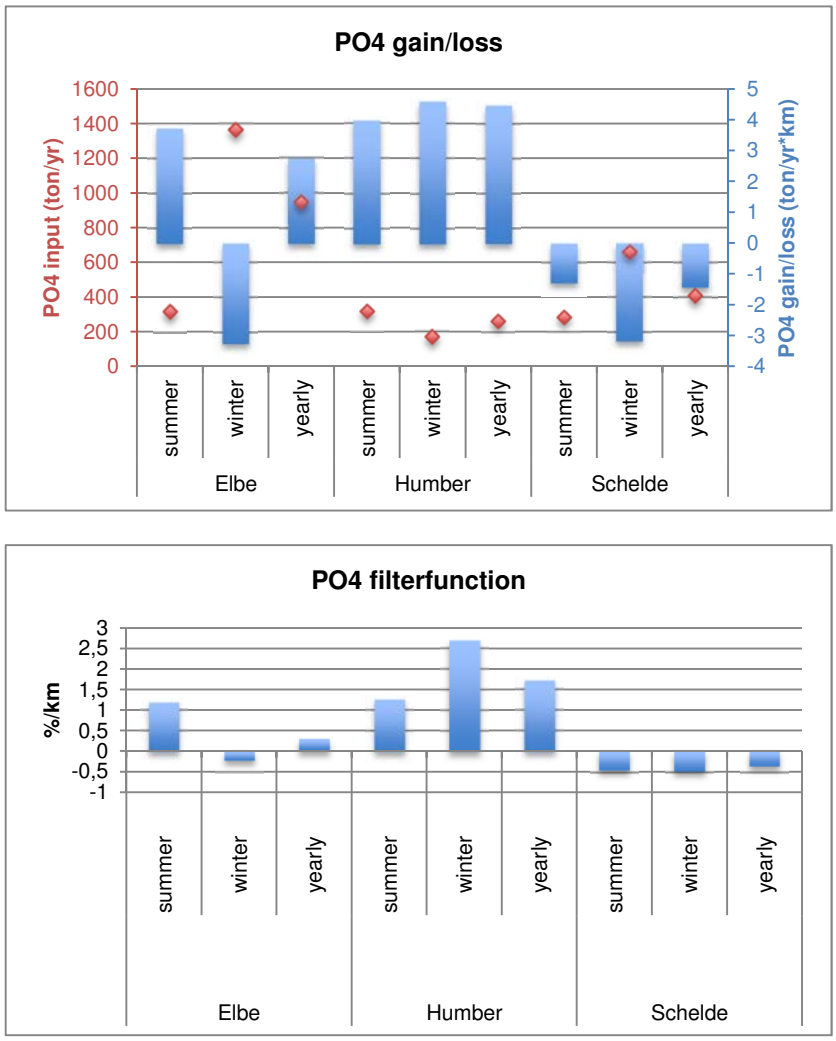


Fig. 38 Sink and source function for phosphate (PO4) in the Elbe, Scheldt and Humber estuary, calculated as six-year average along the whole estuarine gradient on a yearly, summer and winter basis. In the upper graph, input (ton/yr) and gain/loss (ton/yr*km) are given. In the lower graph, contribution of gain/loss relative to the initial input (starting concentration) is displayed (%/km). Summer = June, July, August; winter = December, January and February.

Phosphorus input

Like for nitrogen, also phosphorus input (fig. 39) is highest within the Elbe estuary (3.0 kton/yr total phosphorus input). In the Elbe there appears also to be a relatively higher input of total phosphorus concentration, and thus organic phosphorus, compared with the other two estuaries (in the Humber total phosphorus is not measured). Next, the highest phosphate input is observed within the Humber estuary (1.8 kton/yr phosphate input), at the mouth of the Trent. Input of phosphate in the Scheldt and Weser estuaries are in the same order of magnitude. Although, total phosphorus input is higher in the Weser. Within the Scheldt, again input is elevated near the mouth of the Rupel. In general, also input of phosphorus is highest in winter. However, differences between summer and winter are smaller than for nitrogen. Difference between winter and summer concentrations for solely phosphate are highest in the Elbe (more than 6 times more input in winter). For total phosphorus, difference is highest in the Bovenschelde (more than 2 times more input in winter).

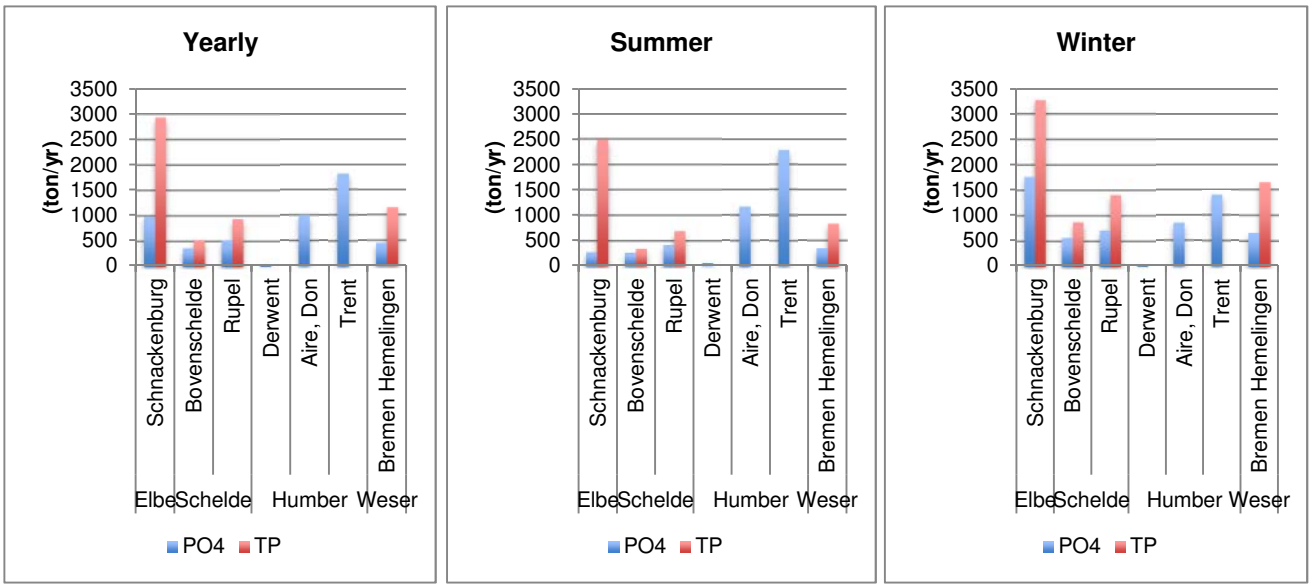
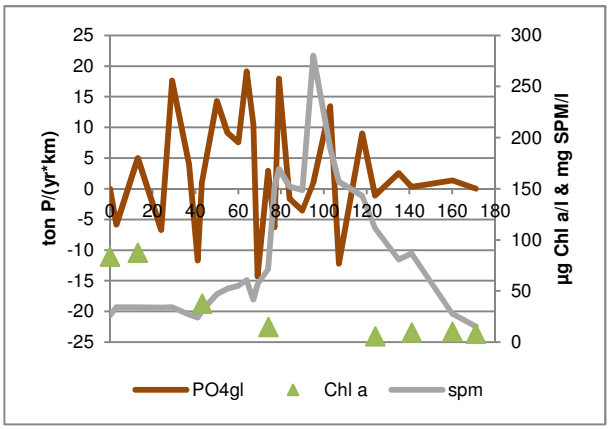
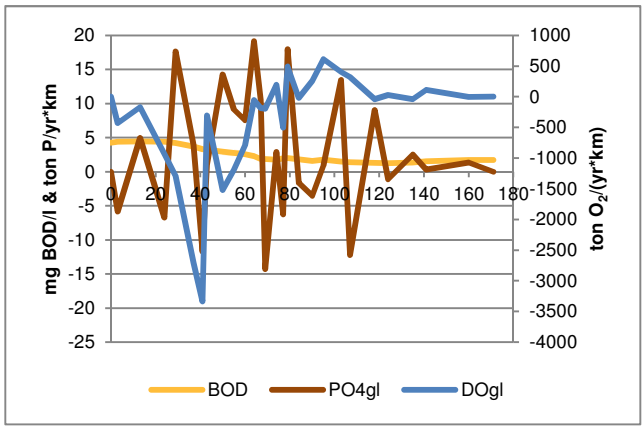


Fig. 39 Six-year average phosphorus input (phosphate, PO4 and total phosphorus, TP in ton/yr) from the upper boundaries and main tributaries for Elbe, Scheldt, Humber and Weser on a yearly basis and for winter and summer period. For the Humber total phosphorus was not measured. Summer = June, July, August; winter = December, January and February.

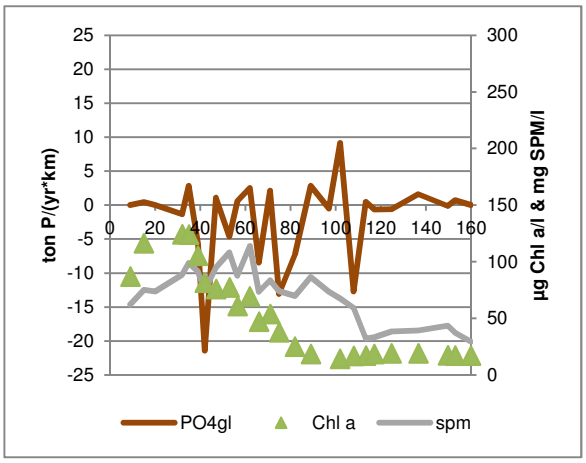
Estuarine processing

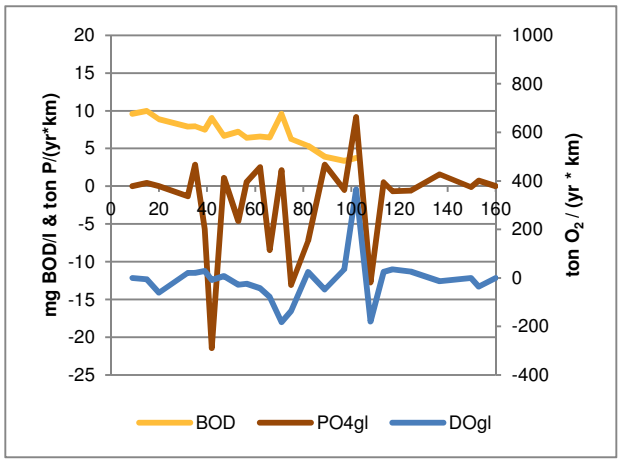
In both the Elbe and Scheldt estuaries, phosphate is subsequently gained and lost along the estuarine gradient (fig. 40). Phosphate dynamics decrease abruptly from the mid-mesohaline zone towards the sea. These patterns do not seem to show any clear correlation, with oxygen dynamics, chlorophyll *a* concentrations, suspended particulate matter distribution or biological oxygen demand in the Elbe estuary. In the Scheldt estuary, a decrease in chlorophyll *a* concentrations and more elevate suspended particulate matter concentrations in the upper reaches of the estuary could be related to a phosphate loss, as it can be observed that peaks of phosphate loss are smaller heading towards the sea, together with decreasing chlorophyll *a* and suspended matter concentrations. Within the Humber estuary, a peak of suspended matter concentration and oxygen gain at kilometer 90 coincides with a peak of phosphate gain. This is the border zone between the mesohaline and polyhaline zone. It could be that phosphorus in the Humber is associated with the very high concentrations of suspended particulate matter, and is being released as it arrives in the high chlorinity zone resulting in this large peak of phosphate gain. Although this does not correspond to what is expected from the bell shaped theory in which phosphate is released in the oligohaline zone (see earlier, '*1.2.2.2 Sink and source function regulation: Phosphorus*').



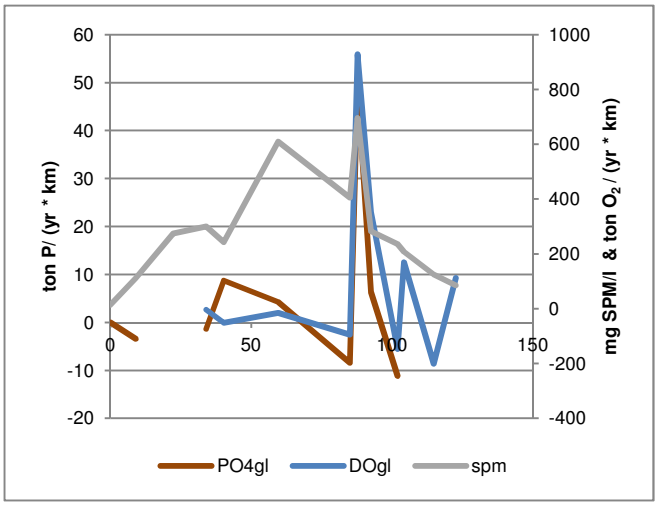


Elbe





Scheldt



Humber

Fig. 40 Relation between phosphate gain and loss with chlorophyll a, biological oxygen demand, suspended matter concentration and dissolved oxygen gain and loss for Elbe, Scheldt and Humber.

Dissolved silica

Gain and loss of dissolved silica could only be calculated for the Elbe and Scheldt estuary. The Elbe is exporting dissolved silica (36 ton/yr*km), while the Scheldt removes dissolved silica (-6 ton/yr*km). Considering initial concentrations of dissolved silica, the loss of dissolved silica seems to affect the Scheldt estuary more, than export is affecting the Elbe estuary (fig. 41).

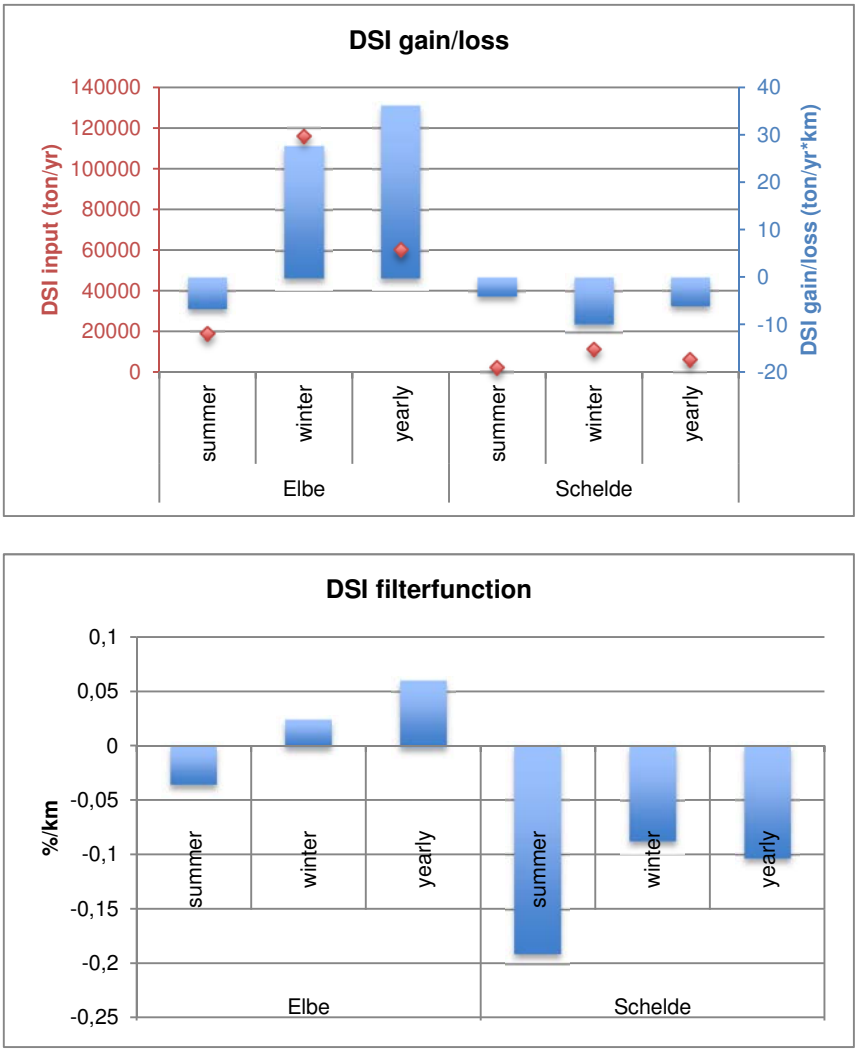


Fig. 41 Sink and source function for dissolved silica (DSI) in the Elbe and Scheldt estuary, calculated as six-yearly average along the whole estuarine gradient on a yearly, summer and winter basis. In the upper graph, input (ton/yr) and gain/loss (ton/yr*km) are given. In the lower graph, contribution of gain/loss relative to the initial input (starting concentration) is displayed (%/km). For the Humber estuary to few data points were available to calculate gain and loss for dissolved silica. Summer = June, July, August; winter = December, January and February.

Dissolved silica input

Input of dissolved silica is highest in the Elbe estuary (fig. 42). Input in the Scheldt estuary is slightly higher than in the Humber estuary. In the Scheldt, also for dissolved silica an elevated input can be observed near the Rupel mouth. In the Humber, input is most elevated near the Trent mouth. In the Weser dissolved silica is not measured at the boundary. Like for nitrogen and phosphorus, dissolved silica inputs are higher in winter. Difference between winter and summer concentrations are most pronounced at the Elbe boundary (input is about 7 times higher in winter).

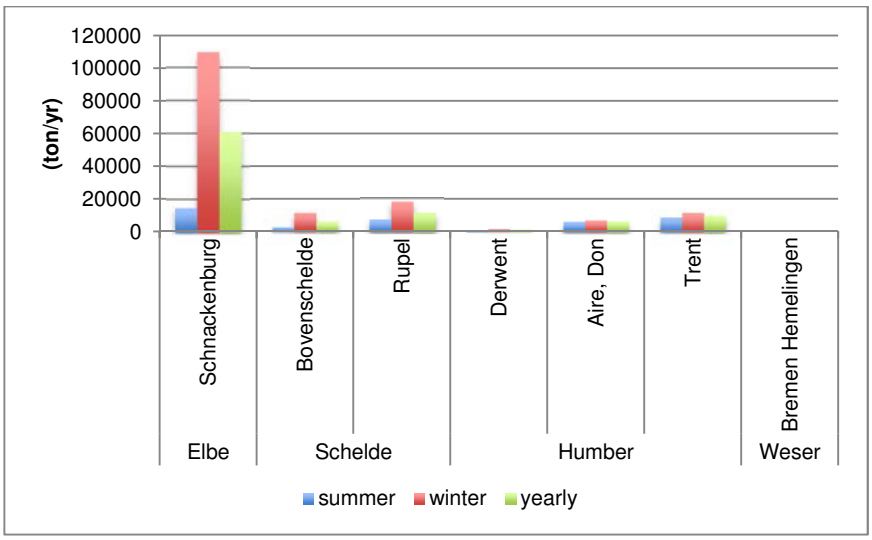


Fig. 42 Six-year average dissolved silica input (ton/yr) from the upper boundaries and main tributaries for Elbe, Scheldt, Humber and Weser on a yearly basis and for winter and summer period. Summer = June, July, August; winter = December, January and February.

Estuarine processing

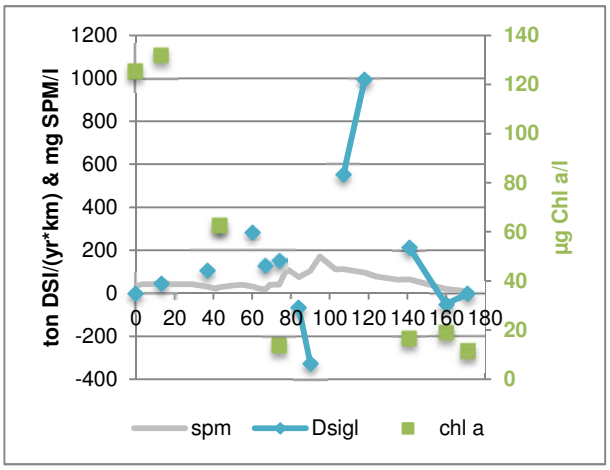
In the Humber and Weser too few data measurements were available to calculate gain and loss dynamics for dissolved silica. Here beneath dissolved silica and possible regulating factors are displayed for the Elbe and Scheldt estuaries for 6 yearly averages for a spring, summer and autumn period (fig. 43).

In general chlorophyll *a* concentrations are highest in the most upstream part of the estuary examined. In the Elbe highest values are reached in spring, while in the Scheldt highest values are attained in summer, indicating a different period of algal bloom in both estuaries. Overall highest values are found in the Scheldt estuary.

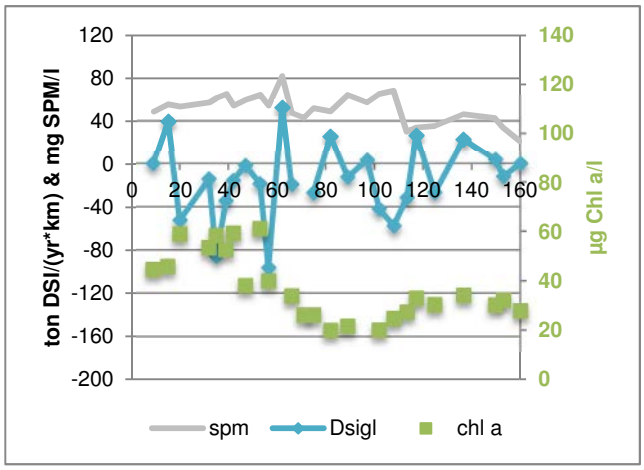
In the Elbe a sudden drop in chlorophyll *a* is observed coinciding with an increase in depth near TIDE km 40, mostly pronounced in spring (not in autumn). However, it is not until summer a loss of dissolved silica can be observed in the freshwater part. In both spring and summer, as observed to be here the period of algal activity, a peak of loss near 90 TIDE km (Glückstadter Nebenelbe) and a peak of gain near 120 TIDE km (Öste mouth) of dissolved silica can be found.

In the Scheldt a maximum in chlorophyll *a* is observed at TIDE-km 32-35 near the Dender tributary (TIDE-km 39). Although the highest peak of chlorophyll *a* is reached in summer, in spring a small peak downstream (near TIDE-km 136) can be observed. Furthermore, after decreasing from 35 TIDE-km onwards, a very short chlorophyll *a* peak is observed near TIDE-km 71. In spring, dissolved silica gain and loss dynamics are very variable along the Scheldt estuarine gradient, while in summer and autumn (the period of most algal activity), a peak of gain the most clear peak can be observed at the mouth of the Rupel (TIDE-km 60). In autumn also a large peak near TIDE-km 120 can be found.

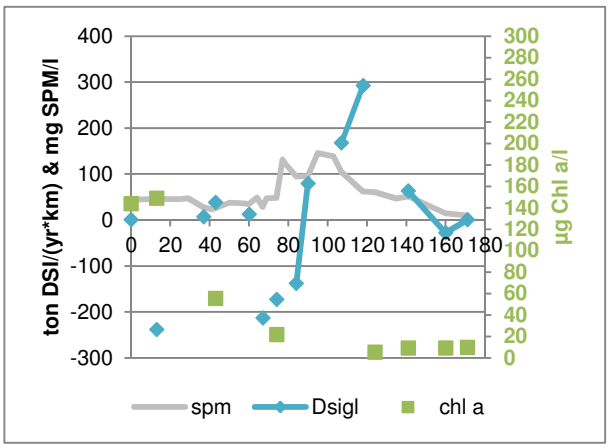
Gain or loss of dissolved silica seems to be mainly regulated by input from tributaries and boundaries, mostly observed during the period of algal activity. Algal bloom in the Elbe occurs in spring, while in summer in the Scheldt.



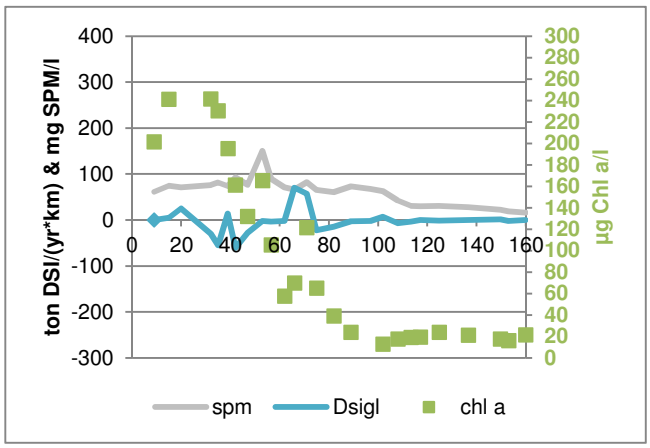
Elbe - spring



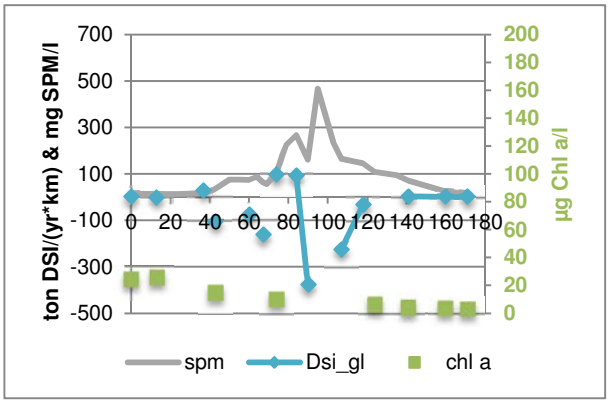
Scheldt - spring



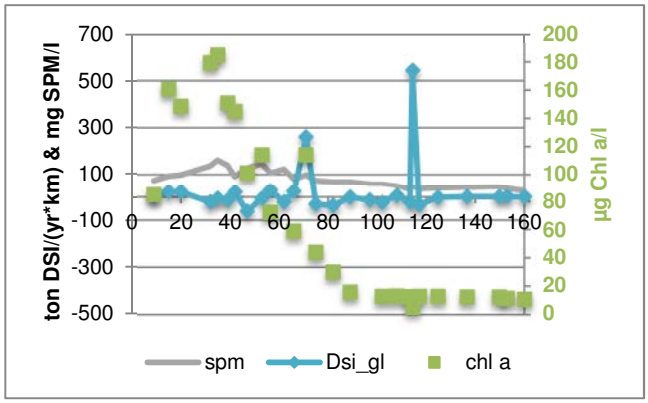
Elbe - summer



Scheldt - summer



Elbe - autumn



Scheldt - autumn

Fig. 43 Relation between dissolved silica gain and loss with chlorophyll a and suspended matter concentration for Elbe and Scheldt based on six-yearly averages for the spring, summer and autumn period (March-November).

3.2.4 Oxygen and primary production

3.2.4.1 Dissolved oxygen concentration and saturation

Highest dissolved oxygen concentrations (Attachment 2) can be found within the Weser estuary (9.5 ± 0.23 mg O_2/l). For the Weser, however, only observations within the freshwater and oligohaline zone were made (fig. 44). Next, the Humber estuary shows the highest oxygen concentrations within the freshwater zone (10.0 ± 0.21 mg O_2/l) and the mesohaline zone (9.4 ± 0.19 mg O_2/l), followed by the Elbe and the Scheldt estuaries (9.4 ± 0.10 mg O_2/l and 6.9 ± 0.10 mg O_2/l resp., on average along the whole estuarine gradient for the six-year period studied). Mainly in the Scheldt estuary dissolved oxygen concentrations drop below 5 mg O_2/l in the freshwater and oligohaline zone. However, the situation has clearly improved since 2008. In the Elbe estuary dissolved oxygen concentrations drop again below 5 mg O_2/l since the summer of 2007 within the freshwater zone after almost two years of well-oxygenated waters (fig. 43). In the Humber concentrations never drop as low as in the Scheldt and Elbe estuaries. However, in summer also within the Humber estuary, oxygen concentrations drop, here along the oligohaline and mesohaline stretch (fig. 44). In general concentrations are always lowest in summer and highest in winter in all estuaries (fig. 44). Considering dissolved oxygen saturation concentrations higher than 100%, oversaturation in the Elbe can be mainly observed within the freshwater zone upstream of the port, where water depth is lower compared to other areas, and in the polyhaline zone. In the Scheldt oversaturation is mostly observed in the polyhaline zone, however recently also observed more upstream. Within the Humber oversaturation are more dispersed along the estuarine gradient. Nevertheless, oversaturation is also consequently observed within the polyhaline zone within this estuary (fig. 44).

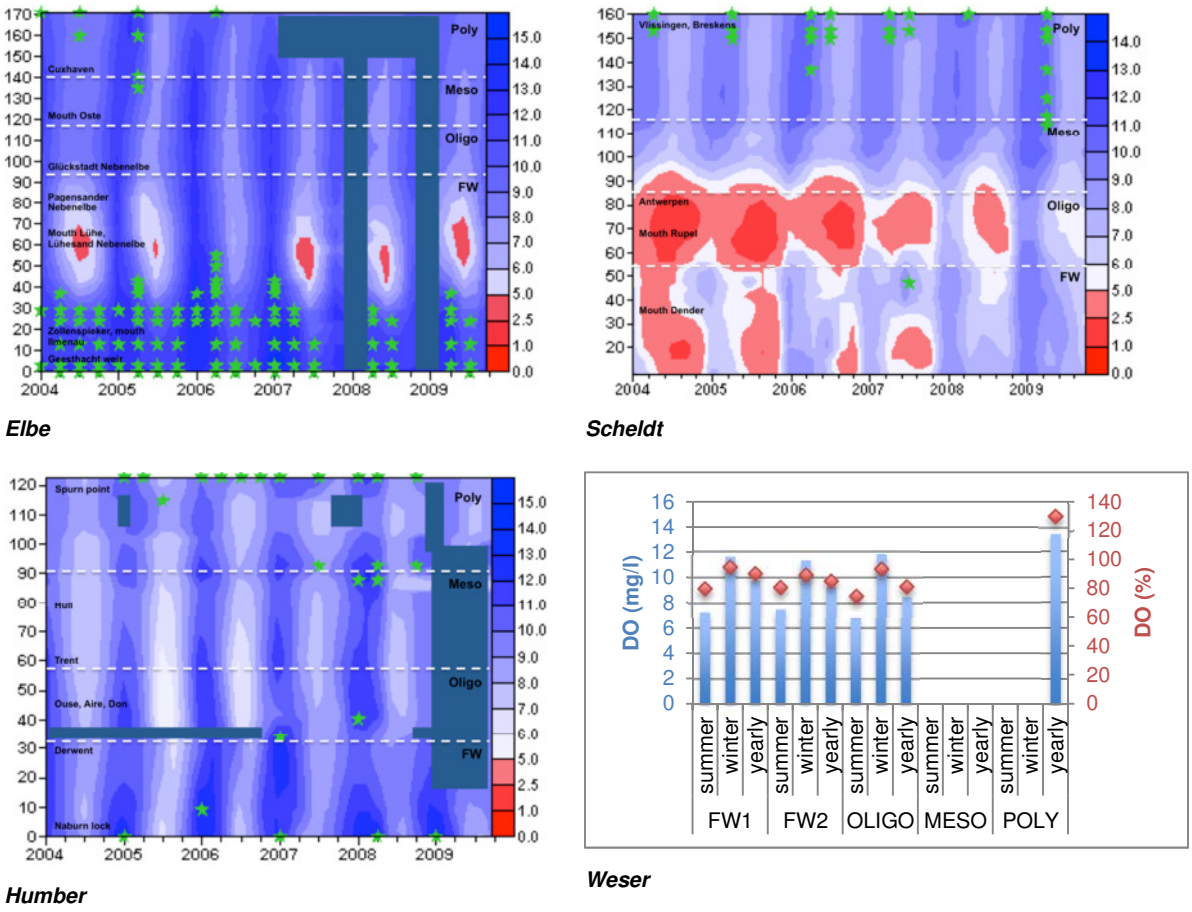


Fig. 44 Spatial (TIDE km) temporal (years) distribution of dissolved oxygen concentration (DO; mg O_2/l) for the Elbe, Scheldt, Humber and Weser. Main tributaries and recognizing sampling points are shown in the surfer plots. For the Weser not enough sampling stations covered the estuarine gradient to represent the data as a surfer plot. Therefore averages per zone are displayed for yearly, summer and winter period. Dissolved oxygen saturation larger than 100 % are indicated by green asterisks within the surfer plots for Elbe, Scheldt and Humber. Dissolved oxygen saturation concentration for the Weser are indicated on the right y-axis. Missing data in the time-distance plots are represented as solid filled rectangles.

3.2.4.1.1 Oxygen, gain and loss

The same calculation for gain and loss as made for dissolved constituents was made for oxygen concentrations, since it is also 'dissolved'. Averaging per zone (fig. 45) shows that most dissolved oxygen is gained within the mesohaline zone of the Humber estuary (327 ton/yr*km), and most is lost within the freshwater zone of the Elbe, specifically in the port area (- 600 ton/yr*km). Taking into account the starting concentration per zone, the highest oxygenation is still reached in the mesohaline zone of the Humber estuary (3.4 %/km). However, the greatest oxygen loss considering the starting concentration can now be observed within the oligohaline zone of the Scheldt estuary (- 2.2 %/km).

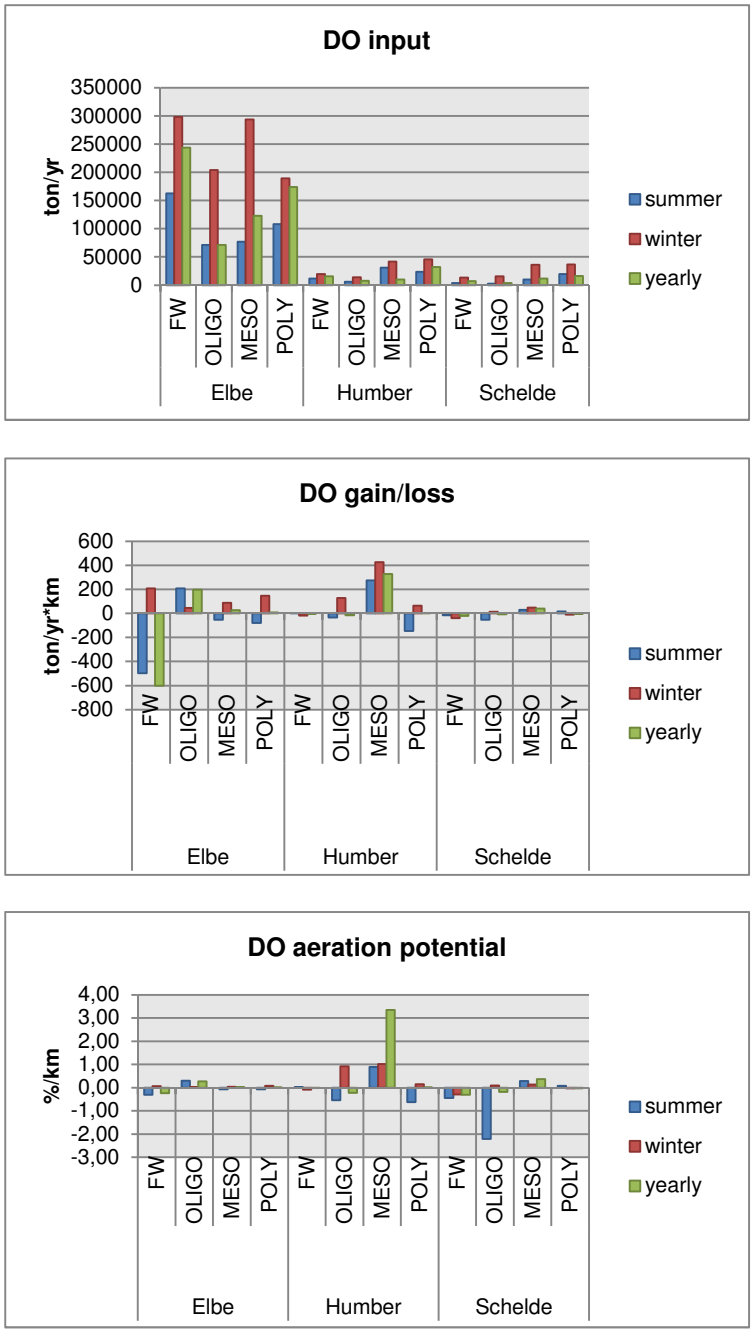
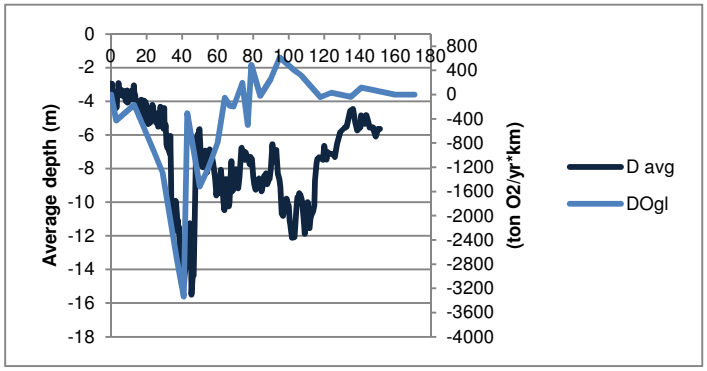


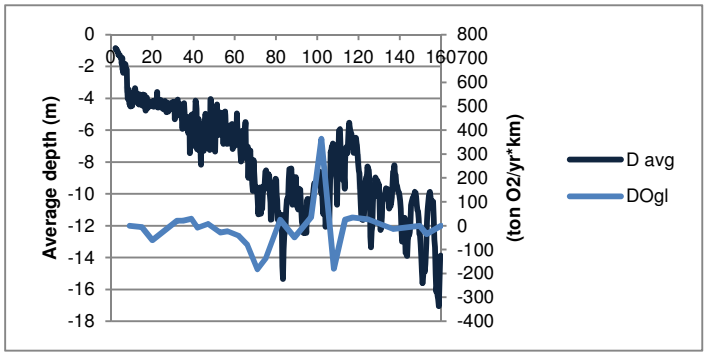
Fig. 45 Six-yearly average of dissolved oxygen input (ton/yr), gain and loss (ton/(yr*km)) and filter efficiency (%/km) per zone for Elbe and Scheldt, on a yearly, winter and summer basis. Summer = June, July, August; winter = December, January and February.

Oxygen deficiencies

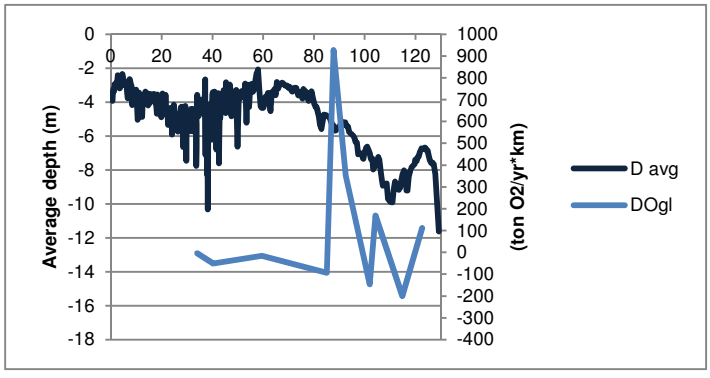
From all estuaries studied, it is mostly the Elbe now re-experiencing oxygen deficit problems within the mid-freshwater zone (within and downstream the port area). This appears to be a consequence of bathymetry (fig. 46). A peak of oxygen loss coincides clearly with the deeper part in the freshwater zone of the Elbe estuary. In the Scheldt and Humber estuaries such a pattern in bathymetry cannot be found. For the Weser, too few data measurements were available to detect a pattern between oxygen and depth. However, for the sampling points that have been measured in the Weser estuary, there seems to be no problem of any oxygen deficits, since it has the highest dissolved oxygen concentrations of all four estuaries examined (see fig. 44 earlier). Previous oxygen deficiencies in the Scheldt appear to have reduced nowadays (fig. 44). As clear from the graph below, this is not related to bathymetry in any way. However, it can be explained by nitrogen dynamics (see '*3.2.3.4 Different sink and source functions for the Elbe, Scheldt and Humber estuaries*'), and changes in organic matter and nitrogen input (see further, '*3.2.4.2 Biological oxygen demand*').



Elbe



Scheldt

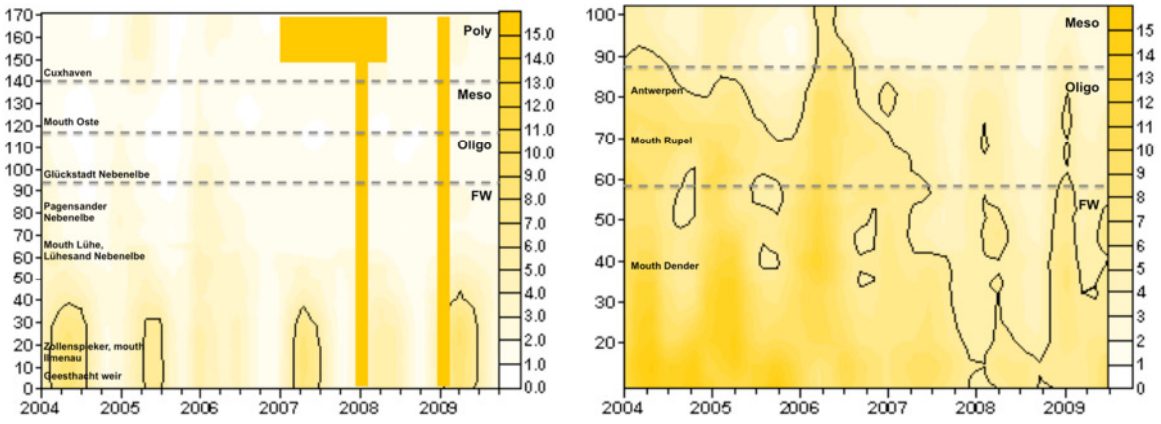


Humber

Fig. 46 Relation of oxygen gain and loss (ton O_2/yr*km; based on six-year average) to the average depth (m) along the estuarine gradient (x = TIDE km) within the Elbe, Scheldt and Humbers estuary. Average depth is calculated as the wet cross section divided by the channel width.

3.2.4.2 Biological oxygen demand

On average biological oxygen demand (Attachment 2) is clearly much higher within the Scheldt estuary (Scheldt: 6.8 ± 0.16 mg O_2/l; Elbe: 2.47 ± 0.07 mg O_2/l). The missing polyhaline zone within the Scheldt alone could not explain this large difference between these two estuaries. Although, within the Scheldt the biological oxygen demand has decreased much more during the last 6 years, as can be deduced from the extending contour of 5 mg O_2/l. In both estuaries, concentrations are highest in the freshwater zone. Biological oxygen demand is highest in winter and spring, while usually lower in summer. In summer the pattern is different from winter. In winter biological oxygen demand is gradually decreasing towards the sea. In summer, after a decrease towards the oligohaline zone, a (slight) increase can again be observed towards the sea (fig. 47).



Elbe ***Scheldt (Westerschelde not included)***

Fig. 47 Spatial (TIDE km) temporal (years) distribution of biological oxygen demand (BOD; mg O_2/l) for the Elbe and Scheldt. Main tributaries and recognizing sampling points are shown in the surfer plots. Biological oxygen demand is not measured within the Westerschelde and therefore the surfer plot for the Scheldt only goes up to the boundary between the Netherlands and Belgium. Within the Humber and Weser biological oxygen demand is not measured at all and therefore not represented here. The contours displayed here, represent a biological oxygen demand of 5 mg O_2/l. Missing data in the time-distance plots are represented as solid filled rectangles.

Decrease in biological oxygen demand in the Scheldt estuary

The decrease in biological oxygen demand in the Scheldt can be explained by changes in the nitrogen input for the time period studied (fig. 48). With decreasing ammonium input, less is to be nitrified and biological oxygen demand also has decreased. However, in general nitrate load is still increasing in both Bovenschelde and Rupel (except for a decrease in the last year of the six-year period studied).

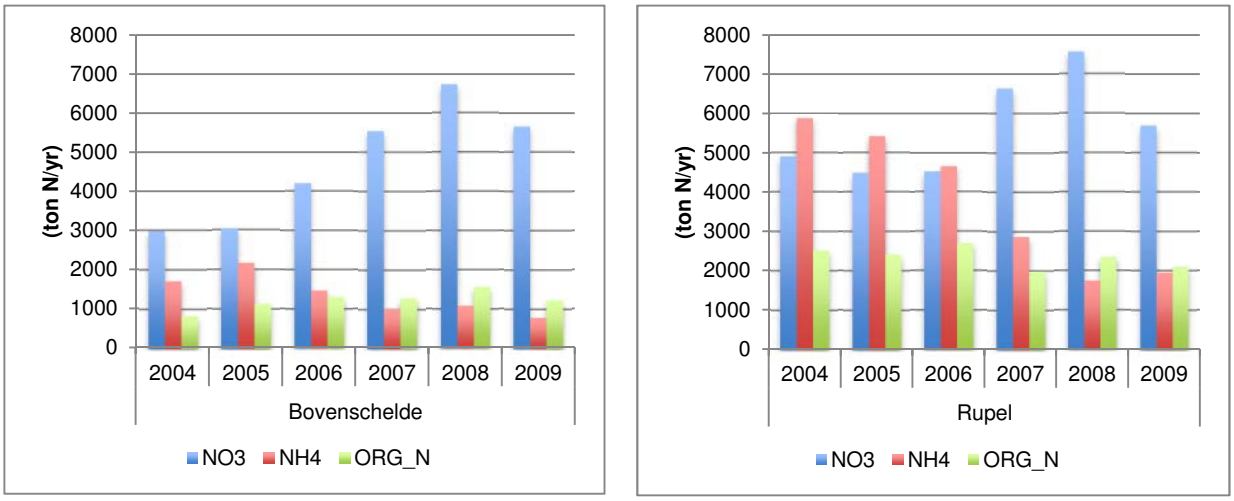


Fig. 48 Yearly changes in nitrogen input in the Scheldt estuary for the most upstream boundary (Bovenschelde) and the main tributary (Rupel) in ton N/yr.

3.2.4.3 Chlorophyll *a* concentration

Mean chlorophyll *a* concentrations (Attachment 2) are highest within the Scheldt estuary (52.1 ± 3.09 µg/l), next within the Elbe estuary (38.1 ± 4.86 µg/l). In the Humber chlorophyll extract values are very low. In both Scheldt and Elbe, concentrations are highest in the freshwater zone. However, focusing upon the freshwater zone in the Scheldt they are about almost two times higher than in the Elbe estuary (Elbe: 56.0 ± 7.05 µg/l; Scheldt: 101.1 ± 6.64 µg/l), even when you consider the fact that the Elbe freshwater zone is much more extended (max. in the Elbe: 210 µg/l; Scheldt: 468 µg/l). In the Humber chlorophyll extract values are highest along the oligo- and mesohaline stretch. In general, in summer and spring concentrations are higher than in winter (fig. 49). Differences in concentrations can be explained by differences in dissolved silica limitation, residence time and mainly euphotic depth (see also '*3.2.1 General parameters*').

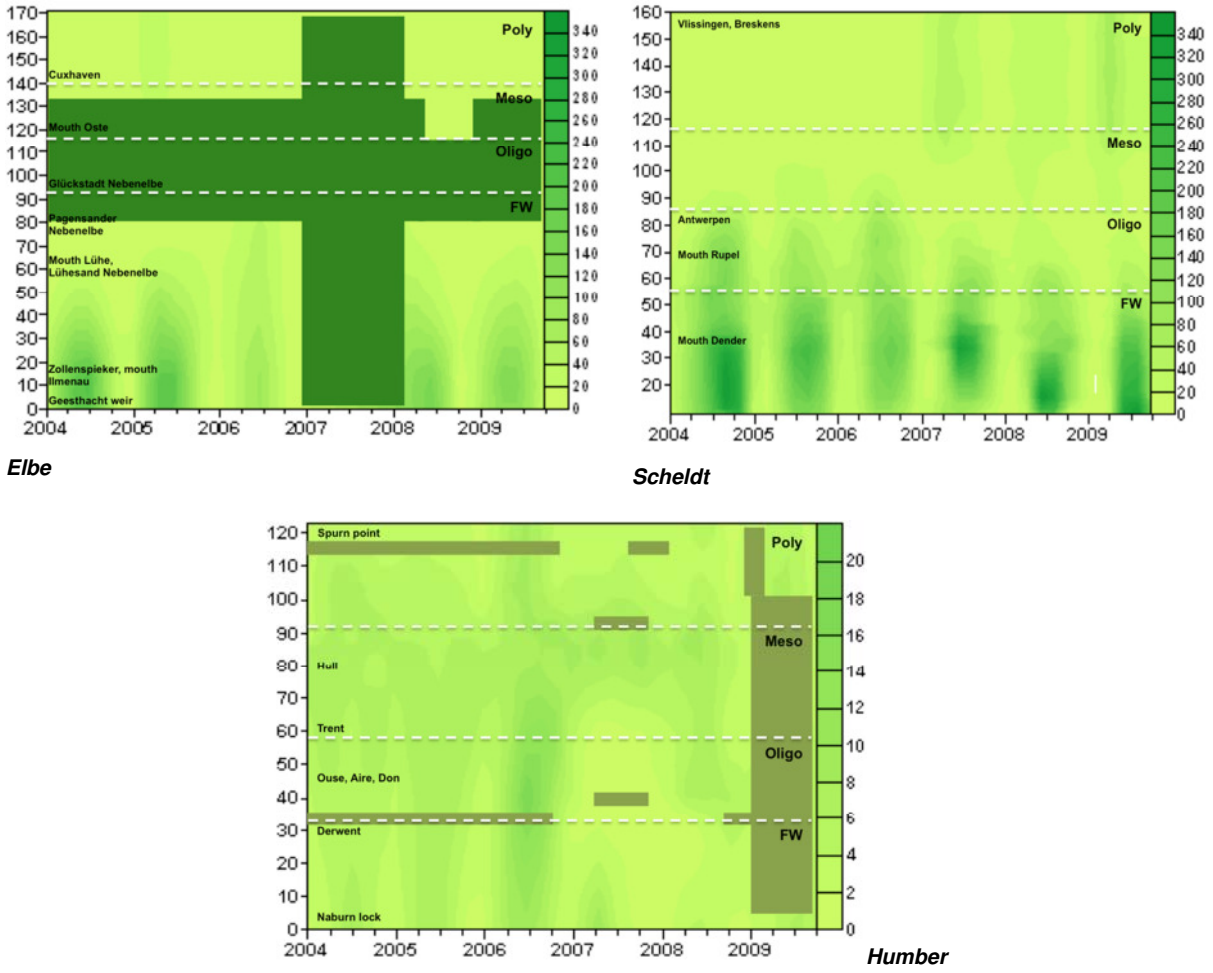


Fig. 49 Spatial (TIDE km) temporal (years) distribution of chlorophyll a concentrations in the Elbe and Scheldt; and for chlorophyll extract in the Humber estuary (CHL A; µg/l). Main tributaries and recognizing sampling points are shown in the surfer plots. Within the Weser chlorophyll pigments are only measured 6 times within only the polyhaline zone of the estuary and therefore not represented here. Missing data in the time-distance plots are represented as solid filled rectangles.

3.2.4.4 Gross primary production

(with contributions of Alexander Meire & Tom Cox)

The absolute error for estimating gross primary production (GPP) from continuous oxygen series decreases for time intervals more than 15 days. Considering longer time intervals might obscure short time fluctuations. Shorter time intervals cause overestimates of GPP (fig. 50, table 6). The signal of GPP in dissolved oxygen series also has to be large enough. Hence, a minimum of primary production is required. Therefore, GPP was estimated (1) for time intervals of 14 days and (2) from March to October, so that primary production is always higher than 15 mmol C/m^2 day. For the Humber no results are shown, since no GPP could be detected in the signal of continuous

oxygen series. Thus, from this method gross primary production within the Humber estuary in the water column could be considered insignificant. Chlorophyll *a* is not measured within the Humber. Only chlorophyll extract values are available and also these are very low compared with the chlorophyll *a* values for the Elbe and Scheldt (see earlier, '*3.2.4.3 Chlorophyll a concentration*').

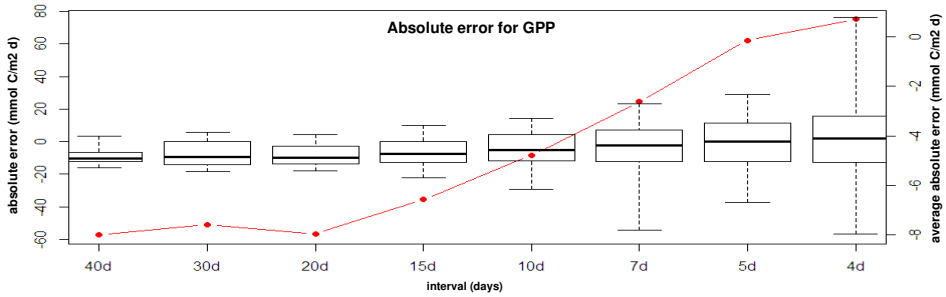


Fig. 50 Time-dependent absolute error for estimates of gross primary production (GPP) calculated for a 1-year simulated oxygen series. Boxplots represent variance of the error (GPP estimate – GPP real). The red curve displays the average absolute error on the y-axis for clarity reasons.

Table 6 Different estimates of average GPP (mmol C/m^2 d) for Elbe, Scheldt and Weser for different time intervals. Between brackets the number of estimates from which the average was calculated is given. At the bottom of the table overall mean, absolute and relative standard deviation are given.

Estuary		***Elbe***					***Scheldt***		***Weser***						
Year		***2009***					***2011***		***2007***	***2008***			***2009***		
Time interval	***Month***	***5***	***6***	***7***	***8***	***9***	***7-8***	***9-11***	***1-12***	***12-6***	***6-8***	***7-1***	***1-2***	***3***	***4-12***
30 days				123 (1)			45 (2)	18 (3)	23 (12)	56 (6)	96 (3)	9 (4)			40 (8)
20 days			189 (1)				47 (3)	17 (4)	30 (18)	62 (8)	89 (4)	9 (6)	6 (2)		41 (13)
15 days		207 (1)		122 (2)	126 (1)	119 (1)	42 (4)	18 (5)	24 (24)	70 (11)	116 (6)	12 (9)	9 (3)	13 (2)	42 (17)
10 days		207 (2)	198 (2)	114 (3)			44 (6)	22 (8)	37 (35)	70 (17)	100 (8)	20 (13)	16 (5)	15 (3)	46 (25)
7 days		199 (3)	198 (3)	124 (4)	120 (2)	113 (2)	47 (9)	25 (11)	48 (51)	77 (24)	123 (12)	23 (18)	29 (7)	18 (4)	52 (36)
5 days		214 (4)	182 (4)	132 (6)	120 (3)	123 (3)	48 (13)	23 (15)	54 (71)	81 (33)	110 (17)	40 (26)	20 (9)	24 (5)	66 (50)
3 days		223 (7)	198 (7)	142 (10)	143 (5)	121 (5)	56 (21)	27 (25)							
mean		210.1	193.2	126,2	127.3	118.9	47.2	21.4	35.8	69.2	105.6		15.8	17.4	47.5
sd		9.3	7.3	9.5	10.5	4.5	4.3	4.0	12.9	9.1	12.8		9.1	4.8	9.7
sd (%)		4.4	3.8	7.5	8.3	3.8	9.2	18.9	36.0	13.2	12.2		57.4	27.4	20.5

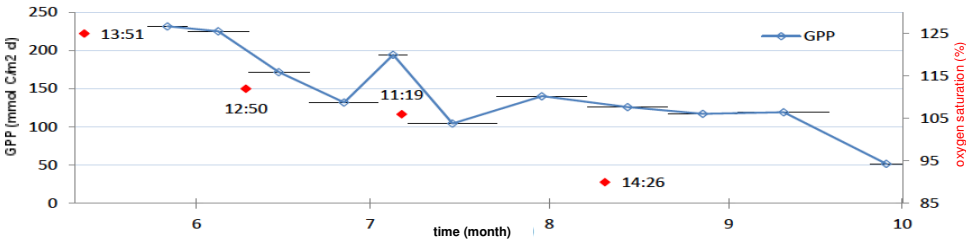
In the Elbe estuary maximum gross primary production can be observed at the end of May (223 mmol C/m^2 d). During summer GPP decreases again to values of 51 mmol C/m^2 d. Oxygen saturation concentrations seem to follow a similar trend (fig. 51).

In the Scheldt, GPP estimates were also made based on continuous pH data. Furthermore, it was compared with primary production estimates from the ^{14}C method to check validity of the GPP estimates from continuous oxygen (and pH) series. Initially, large differences between GPP estimates for pH and O_2 could be found in January and February 2009, but from March on discrepancies are limited. A large peak in June 2009 could be found for estimates from both oxygen and pH series (pH: 153 mmol C/m^2 d; O_2: 218 mmol C/m^2 d). Also in June 2010 a large peak of GPP could be detected. Both methods appear to correlate well with the ^{14}C method (Pearson's correlation for pH and O_2 are 0.80 and 0.82 resp., $p<0.001$). Most differences were to be found in spring and winter 2010, where estimates of GPP from continuous oxygen and pH series were higher than for estimates from the ^{14}C method (fig. 51). Dips in GPP in the Scheldt corresponded with dips in dissolved silica and PAR (not shown here). Effect of stratification during

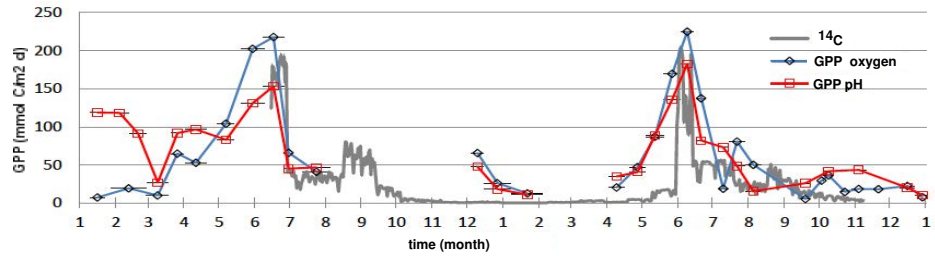
slack tide, giving a maximum gradient of 0.2 mg O_2/l, lead to a maximum difference of 2 mmol C/m^2 d in GPP estimates.

In the Weser GPP is largest in 2008. A peak of 291 mmol C/m^2 d could be found at the end of May. In summer 2007 a smaller peak of 87 mmol C/m^2 d could be observed. In 2009 primary production fluctuates from May to August around 80 mmol C/m^2 d.

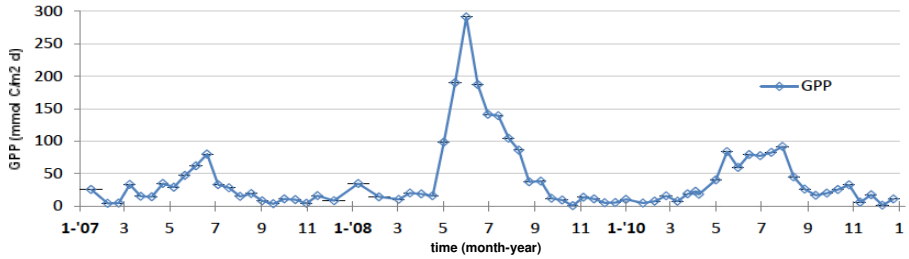
Estimates of yearly averages were not possible, because of data fragmentation and minimum time interval lengths required.



Elbe – Bunthaus (a)



Scheldt – Kruibeke (b)



Weser – Brake (c)

Fig. 51 GPP estimates from continuous oxygen data series in Elbe, Scheldt and Weser for Bunthaus, Kruibeke and Brake resp.; (a) in the Elbe, GPP is represented for the time period of 23-5-2009 to 1-10-2009; the horizontal bar displays length of the time interval considered; oxygen saturation values based on a 14day average are added in red; (b) in the Scheldt, GPP for the time period 2009 to 2010 is displayed; also GPP estimates based on pH continuous profiles and GPP calculation from 14C in situ methods are added to the graph; (c) in the Weser, the GPP estimates based continuous oxygen profiles for 2007 to 2008 are represented; horizontal bars represent time interval.

3.2.4.5 Nutrient ratios

Nitrogen phosphorus ratio

The nitrogen phosphorus ratio is highest within the freshwater zone of the Elbe estuary (181.0 ± 7.80), while lowest in the freshwater zone of the Scheldt estuary (37.5 ± 1.15). In general the nitrogen phosphorus ratio is higher in winter in all estuaries. Within the Elbe a peak can be observed near 20 and 60 TIDE km in winter and near 80 TIDE km in summer within the freshwater zone. In the Scheldt peaks can be observed near 70 and 80 TIDE km in summer and winter respectively. In the Humber, nitrogen phosphorus ratios are high in the freshwater zone and then abruptly decrease towards the sea. The Weser has too few data points to really detect a trend. However, the nitrogen phosphorus ratios are in the same order of magnitude as those in the Elbe

estuary. In all estuaries the ratio is always above the Redfield ratio (16:1), implying a relative limitation for phosphorus. This potential limitation is most pronounced within the Elbe estuary within the freshwater zone (fig. 52).

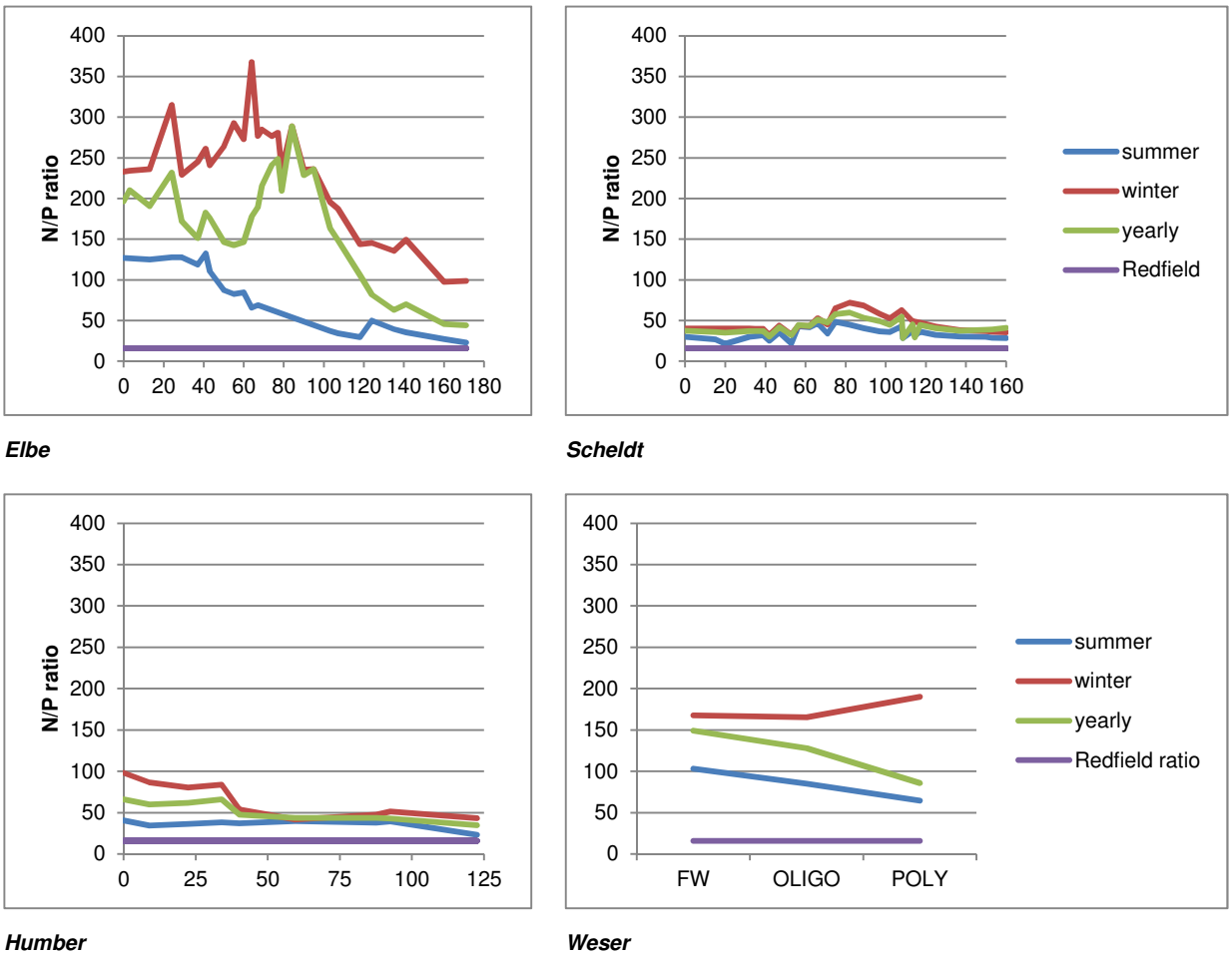
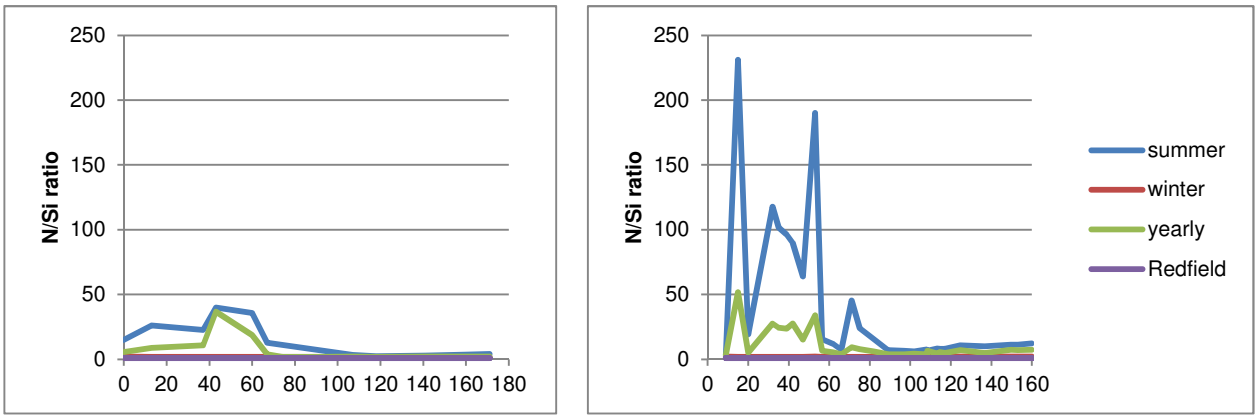


Fig. 52 Nitrogen phosphorus molar ratios, calculated as sum of inorganic dissolved nitrogen divided by phosphate concentrations based upon a six-year average, represented for a yearly, summer and winter period for Elbe, Scheldt, Humber and Weser. Summer = June, July, August; winter = December, January and February.

Nitrogen silica ratio

The nitrogen silica ratio is observed for too few data points in Weser and Humber. Therefore, here beneath only ratios for the Elbe and Scheldt are plotted (fig. 53). On average, the nitrogen silica ratio is observed to be highest in the freshwater zone of the Scheldt estuary (21.1 ± 6.50). Also in the Elbe ratios are highest in the freshwater zone (15.8 ± 3.91). In the Elbe a peak is seen near 40 TIDE km (in the port area), in the Scheldt peaks are seen near 15, 30, 50 and 70 TIDE km. In winter ratios approach the Redfield ratio (1:1), while in summer there is a relative limitation of dissolved silica. From the end of the freshwater zone towards the sea, silica limitation abruptly decreases and observed ratios approach the Redfield ratio.

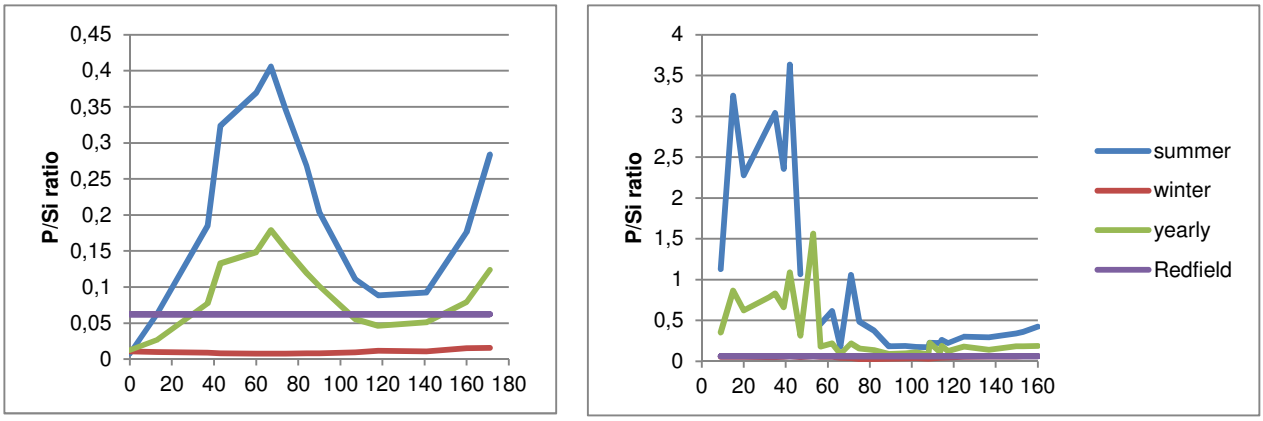


Elbe ***Scheldt***

Fig. 53 Nitrogen silica molar ratios, calculated as sum of inorganic dissolved nitrogen divided by dissolved silica concentrations based upon a six-year average, represented for a yearly, summer and winter period for the Elbe and Scheldt. For the Humber and Weser to few data points were available to represent results in this way. Summer = June, July, August; winter = December, January and February.

Phosphorus silica ratio

Phosphorus silica ratios are highest in the Scheldt estuary (Attachment 2), within the freshwater zone (0.6 ± 0.13, six-yearly average based on a yearly period). Also in the Elbe ratios are highest in the freshwater zone (0.11 ± 0.01). In general in both estuaries, ratios are higher in summer (fig. 54). In the Scheldt ratios abruptly decrease from the freshwater zone towards the sea, while in the Elbe ratios seem to increase again in the polyhaline zone. Relative to the Redfield ratio (1:16), along most of the estuarine gradient there appears to be a limitation for silica in both estuaries, except for the winter season in which there is rather a potential limitation for phosphorus along the whole estuarine gradient. In the Elbe in summer and during the year, also a potential limitation for phosphorus can occur within the upper part of the freshwater zone and within the oligo- and mesohaline zone (fig. 54).



Elbe ***Scheldt***

Fig. 54 Phosphorus silica molar ratios, calculated as phosphate divided by dissolved silica concentrations based upon a six-year average, represented for a yearly, summer and winter period for the Elbe and Scheldt. For the Humber and Weser to few data points were available to represent results in this way. Summer = June, July, August; winter = December, January and February.

4. Discussion

4.1 Estuarine patterns

In all estuaries studied, chlorinity obviously seems to be the most important structuring element. As chlorinity increases towards the sea, dissolved constituent such as nitrogen species, phosphate and dissolved silica decrease, while dissolved oxygen and pH increase. This could be found from both correlation analyses and multivariate analyses. It appears the mixing effect from sea is dominant in all estuaries. However, this structuring element is of most importance in the Scheldt where it explains 66.5 % of the variation observed ($p<0.01$). In the Humber and Elbe zonation explains only about 43.6 % and 32.5 % of the variation observed respectively ($p<0.01$). Furthermore, a correlation of total dissolved inorganic nitrogen with nitrate was found in all estuaries, implying nitrate constitutes the major part of total dissolved inorganic nitrogen. Most estuaries are currently well oxygenated. Hence, this is indeed not very surprisingly (Statham et al. 2011). This might indicate the overall importance of nitrification and mineralization processes over primary production and denitrification processes for all estuaries studied. Another correlation found in most estuaries (Elbe, Weser, Schelde) is that between suspended particulate matter and total phosphorus. Absence of a correlation with phosphate in these estuaries likely indicates an association of suspended particulate matter with organic phosphorus and consequently represents a source of phosphate by mineralization. Even though total phosphorus is not measured in the Humber estuary this correlation could also be existent within this turbid estuary. Although, sink source function of phosphate in literature is rather explained by purely physical adsorption and desorption in function of phosphate, salinity and suspended particulate matter concentration (van Beusekom & Brockmann 1998, van der Zee et al. 2007, Deborde et al. 2007), an association of suspended particulate matter with organic phosphorus could give an explanation for the large source found in the Humber at the border between the meso- and polyhaline zone. Another general aspect to be found is the opposition between winter and summer. Some obvious common winter-summer differences include higher temperatures and salinity in summer, and higher dissolved oxygen and other dissolved constituents in winter. Nevertheless, variation explained by seasonality is lower in general (Scheldt: 18.6 %; Elbe: 29.2 %; Humber: 24.7 %; $p<0.01$) and seasonal estuarine patterns often differ between estuaries. For all estuaries no significant in between year effect could be found for 2004 to 2006.

In total most variation of the estuarine patterns are explained in the Scheldt, next in the Humber estuary. Thus in the Elbe the estuarine patterns are least explained, mainly due to lack of zonation effects. In fact, where data variability (and thus intensity of ecological processes) is lower in the polyhaline zones of the Scheldt and Humber, this reduced data variability is not observed in the polyhaline zone of the Elbe estuary. This could have several reasons. Baborowski et al. (2011) also found water quality patterns in the Elbe river to be rather explained by seasonal variation (37.5 %). This is likely to be attributed to the much larger and seasonally variable freshwater discharge observed in the Elbe compared to the Scheldt and Humber (645 m^3/s on average, fig. 9), continuously disrupting the salinity gradients typically for estuaries. Aside from a sudden deepening of more than 20 m nearby the Hamburg port area in the Elbe estuary (TIDE-km 40), the Elbe still demonstrates a gradient of increasing depth as observed in the other TIDE estuaries. Hence, solely bathymetry does not explain the less conspicuous estuarine patterns observed in the Elbe. Also different patterns in residence time or euphotic depth give no conclusive answer (fig. 10 & fig. 14). It seems that indeed a reduced mixing effect from sea is the main reason for less spatially structured patterns in the Elbe. However, the tidal amplitude has been found largest in the freshwater zone of the Elbe, indicating the tide intrudes up to the freshwater end member. Nonetheless, tidal amplitude is the lowest in the Elbe (3.6 ± 0.04 m), compared to the Scheldt and Humber (5.5 ± 0.1 m and 4.4 ± 0.2 m, resp.) and effects of the sea are likely to be markedly less than in the more narrow and smaller Scheldt and Humber estuaries. Other reasons could be that other processes not included in this multivariate analysis, are more characteristic for the Elbe estuary.

Indeed, besides from general observed estuarine patterns, some characteristic patterns can be distinguished per estuary examined. Where dilution seems to be most characteristic for the Scheldt estuary, mainly physical correlations such as between temperature and dissolved oxygen concentration are to be found in the Humber and Weser estuaries. However, this rather obvious

correlation for temperature with oxygen is least pronounced in the Scheldt, reflecting the importance of other more biological oxygen influencing processes. The Scheldt is amongst the estuaries with highest dissolved inorganic nitrogen and organic matter concentrations (van der Zee et al. 2007). When comparing average concentrations (Attachment 2), indeed nitrogen, biological oxygen demand and also phosphorus concentrations are observed to be highest within the Scheldt compared to the other TIDE-estuaries. Hence, processes influencing oxygen concentrations can be expected to be most intense within this estuary. Within the Elbe a specific correlation can be found between chlorophyll *a*, phaeopigments and biological oxygen demand. This might indicate the importance of autochthonous organic matter input (from algae) in the Elbe estuary. This is in agreement with general findings in the BfG contribution in TIDE (Schöl et al. 2012). According to Quiel et al. (2011) phytoplankton peaks occur upstream in the Elbe river where they are more susceptible to grazing and are subsequently exported in a degradable form more downstream in function of freshwater discharge (Quiel et al. 2011). Nonetheless, it is not clear why chlorophyll *a* values are not higher in the Elbe than in the Scheldt. Although freshwater discharge is much higher in the Elbe, residence time is in fact higher than in the Scheldt estuary (fig. 10). Comparing euphotic depth, mixing depth ratios, this could be an explanation (fig. 16). However, more oversaturation of dissolved oxygen is observed in the most upstream part of the Elbe estuary, indicating intense primary production (fig. 44). Thus, it could be that in fact there is more primary production within the Elbe, but biomass is more effectively controlled by grazing. From the decrease in chlorophyll *a* concentrations observed, most likely algae die off in the deepened part nearby the Hamburg port area, where euphotic depth, mixing depth ratio drops about fivefold (fig. 16). From the multivariate analysis also specific differences in seasonal and spatial patterns per estuary could be discriminated. Most estuarine zones show similar estuarine patterns throughout all seasons, except for the upstream parts of the Scheldt and Humber (freshwater and oligohaline zones). The Scheldt differs from the Elbe in timing of primary production. In the Elbe a peak of primary production can be observed early in spring, while in the Scheldt in autumn. Although when absolute values in chlorophyll *a* are considered, Scheldt maxima can be rather found in summer than in autumn (fig. 43), corresponding to findings of Arndt et al. (2011). Anyway, the peak of algal bloom is observed earlier in the Elbe estuary. Mostly in the Scheldt, ammonium decreases with increase in temperature and chlorophyll *a* in autumn and summer, indicating increased primary production and nitrification. Nutrient concentrations are lower in the Elbe. As the largest river drainage basin (148 286 km^2, Grabemann & Krause 2001), the Elbe also comprises a much larger volume, both coming from upstream and from tidal exchange, compared to the other estuaries examined (fig. 9 & table 3). Hence, in general nutrients are expected to be more diluted. Furthermore, the effort for water treatment occurred at an earlier stage (80ies) than within the Scheldt (90ies), also contributing to the overall lower nutrient concentrations when both estuaries are compared at present (Soetaert et al. 2006, Schlarbaum et al. 2010). Next, in the Scheldt there are more then twice as many inhabitants per square kilometer observed (Arndt et al. 2011, Quiel et al. 2011). The Humber estuary distinguishes itself by its high suspended matter concentrations in summer and autumn, absence of seasonal chlorophyll (extract) dynamics and low dissolved silica concentrations in summer in the low salinity zones. This is in general agreement with previous literature for the Humber estuary, stating that primary production is to be considered negligible (Jickels et al. 2000) and finding only minor dissolved silica fluxes at the intertidal mudflats (Mortimer et al. 1998). Except for some obvious physical correlations, not many specific estuarine patterns could be found for the Weser. This does not imply a less ecologically relevant estuary, as high dissolved oxygen values observed (fig. 44) and gross primary production values calculated from continuous oxygen data series (fig. 51) in the upstream parts of the Weser estuary suggest. However, more data is needed to reach this conclusion.

4.2 Different sink and source functions for nutrients

4.2.1 Dissolved inorganic nitrogen

In all estuaries dynamics (both gain and loss) decrease towards the sea. The polyhaline zone is much larger in cross-section and width and is usually marked by an increase in euphotic depth. Nevertheless, the intensity of ecological processes as calculated per kilometer is highest in the upstream parts of the estuary. This can be related to the higher nutrient concentrations in the freshwater zone. Often the upstream part is also shallower. The Elbe appears to be the largest source for dissolved inorganic nitrogen, while the Scheldt can be considered a sink. Furthermore, impact of nitrogen delivery on estuarine functioning of the pelagic is ought to be higher in the Elbe, than nitrogen removal has upon the Scheldt estuary, since concentrations are lower within the Elbe estuary. Also the Humber appears to be a source for dissolved nitrogen species. ***Differences in source and sink functions of an estuary can be due to (1) differences in input (direct/indirect via organic matter degradation) and (2) differences in estuarine functioning (transformation processes) along the estuarine gradient.***

Taking into account freshwater discharge, the ***input (1)*** of dissolved inorganic nitrogen is observed to be about four times higher in the Elbe estuary than in the Scheldt estuary. Also the largest part of organic nitrogen input is observed in the Elbe estuary, likely related to decaying algal biomass. (fig. 34). Different input can be attributed to differences in freshwater discharge. The source sink functions for nitrogen can in part be explained by these differences in nitrogen input. As less dissolved inorganic nitrogen is removed by biological activity in winter, inputs at the boundaries are generally higher than in summer explaining the general observation of higher dissolved inorganic nitrogen gain in winter. Furthermore, high nitrogen concentrations in winter are often related to the fact that nitrogen sources are mostly diffuse. Hence, higher freshwater discharge in winter comes along with higher nitrogen input (Sanders et al. 1997, Statham et al. 2011). Input of dissolved nitrogen and freshwater discharge in the Humber estuary are similar to the Scheldt estuary. However, the Humber estuary is rather a limited source than it is a sink for inorganic nitrogen like observed in the Scheldt estuary. By consequence, differences for source and sink function between the Scheldt and Humber will be mainly explained by differences in estuarine processing.

Estuarine processing (2) of dissolved nitrogen within the estuary is mainly driven by organic matter mineralization, nitrification, denitrification and primary production. To identify underlying processes in dissolved inorganic nitrogen dynamics first ammonium and nitrate concentrations (a) are discussed. Next, gain and loss of dissolved inorganic nitrogen species is compared between estuaries (b) and finally, gain and loss of dissolved inorganic nitrogen species is discussed per estuary (c), related to hydrodynamics and morphology (see also '*3.1.1 Hydrodynamics*' & '*3.1.2 Morphology*').

Both nitrate and ammonium ***concentrations (a)*** are observed to be highest in the Scheldt estuary, while clearly lower in the Elbe estuary. The difference is most pronounced for ammonium concentrations, with ammonium concentrations being more than three times larger in the Scheldt than in the Elbe. Compared to the Elbe, the Scheldt is also characterized by very high organic matter concentrations (as approximated by biological oxygen demand, fig. 46). This is likely to be a source for ammonium input and explanation for the higher concentrations observed in the Scheldt estuary (Attachment 2). Compared to the TIDE estuaries, concentrations for nitrate and ammonium in the Humber are intermediate and lowest respectively. Also ammonium input in the Humber is observed to be lowest (fig. 35). Both the Trent and Ouse have been reported a sink for ammonium (Sanders et al. 1997), hence explaining this low estuary input. The Rupel on the contrary, is a source for ammonium to the Scheldt (input concentrations are about ten times higher than those observed for the Trent in the Humber, fig. 35). Concentrations in the Weser are in the same order of magnitude than those in the Elbe.

In both the Scheldt and Elbe ***gain and loss (b)*** of nitrogen mainly occur in the upstream part of the estuary, while in the Humber nitrogen dynamics are more spread along the estuarine gradient. Most ***nitrate*** is gained in the Elbe freshwater part of the estuary, while most nitrate is lost in the mesohaline zone of the Humber estuary. The Elbe is also characterized by the highest input from upstream. Furthermore an intense zone of nitrification can be observed in the deeper part of the freshwater zone, likely related to algal die off. The latter loss in the Humber seems contradictory to

the surfer plot where actually a major zone of nitrate gain can be observed in the oligo- and mesohaline zone. This is because only two sampling stations were averaged in the mesohaline zone and the second sampling station lies at the border with the polyhaline zone, where there is a sudden loss of nitrate observed, masking the increase in the first sampling station within the mesohaline zone. Thus, it is more accurate to state that nitrate loss is highest in the Humber polyhaline zone. This corresponds to what has been shown by Mortimer et al. (1998). Intertidal and subtidal areas generally increase towards the polyhaline zone so that in fact in total nitrate is mostly removed in the polyhaline zone. In the Scheldt nitrate gain and loss dynamics seem to alternate quickly along the estuarine gradient. This results in a limited gain of nitrate, mainly in the freshwater zone. Hence, in the Scheldt estuary nitrate dynamics appear to be more variable. Most ***ammonium*** is lost in the oligohaline zone of the Scheldt estuary, nearby the Rupel tributary. Previously, ammonium production was observed in the most upstream parts of the Scheldt estuary. However, from 2000 to 2002 ammonium removal was found almost everywhere along the estuarine gradient (Soetaert et al. 2006). With increasing oxygen levels most ammonium is almost immediately nitrified. Nitrate is subsequently found to be removed, nowadays mainly near the Rupel area, indicating a large area for denitrification (fig. 26). However, with increasing oxygen values also denitrification rates are lowered (Soetaert et al. 2006) and nitrification can be expected to gain in importance in the near future. In the Elbe gain and loss for ammonium are visible in the freshwater zone, but dynamics are limited in general. This is likely to be attributed to the high seasonal dynamics and much lower concentrations in the Elbe. In the Humber estuary most ammonium is gained in the oligo- and mesohaline zone. Peaks in ammonium concentration are found in the turbidity maximum zone, in agreement with earlier observations (Sanders et al. 1997) and could possibly be related to increased mineralization of particulate nitrogen, like observed previously in the Elbe estuary (Schlarbaum et al. 2010). However, considering input concentrations and the whole estuarine gradient, the impact of ammonium removal in the Scheldt is larger than ammonium gain in the Humber estuary. In general, considering the input ammonium concentrations, more ammonium is lost in summer (fig. 29), which can be related to more intense nitrification when temperatures are higher.

Overall, the ***Elbe (c)*** can be considered a major exporter of dissolved inorganic nitrogen, mostly attributed to nitrate dynamics. Previously the Elbe has been reported a nitrate sink, and it is only recently that the Elbe changed to a source for nitrate (Dähnke et al. 2008). This could be attributed to loss of sediments because of filling up of the shallow water zones and recent deepening of the Elbe freshwater zone near Hamburg (Kerner 2007, Dähnke et al. 2008). Gain of ammonium and nitrate seems to follow each other successively. Coinciding with peaks in biological oxygen demand and dissolved oxygen loss, it is likely that ammonium initially gained from organic matter mineralization is immediately further nitrified, explaining these consecutive peaks of ammonium and nitrate gain. Although, not an immediate link can be observed with chlorophyll *a*, the correlation of chlorophyll *a* with phaepigments and biological oxygen demand suggests chlorophyll *a* is in a degraded form. The peak in nitrate gain, together with the peak of dissolved oxygen loss both occur near TIDE kilometer 40. In this part of the freshwater zone of the Elbe, the estuary deepens with more than 10 meter. Alexander et al. (2000) found nitrogen to be less retained in deeper channels. Residence time increases, but euphotic depth decreases (fig. 14, fig. 15). By consequence algae might die off. Furthermore, the Elbe is characterized by the largest amount of organic nitrogen input. Accumulation of allochthonous and autochthonous organic matter within this deepened area (with increased residence time) most likely promotes intense nitrification. The study by BfG in TIDE (Schol et al. 2012) developed a model that simulated the effect of a lowered algal input at the boundary. This model demonstrated that a significant decrement of algae could enhance oxygen concentrations again along the estuarine gradient (see also Quiel et al. 2011). Thus, after mineralization, ammonium is gained, which is subsequently nitrified. Further in the estuary, ammonium is lost, while nitrate is still gained, probably since ammonium input has stopped while nitrification processes proceed further. Additional nitrate gain could also originate from input from of the Lühe river mouth, although discharge is likely to be too small to lead to a significant contribution. Near Pagensander Nebenelbe (80 TIDE km), a small peak of ammonium gain can be observed together with a peak of nitrate loss. This could indicate a small zone of denitrification, which could be attributed to the shallow water zones in this area. However, in general nitrification seems to be the major process. Together with high nitrogen input this makes

that the Elbe is a nitrogen source. However, it has to be noted that total dissolved inorganic nitrogen concentrations in the Elbe are the lowest of all estuaries studied in this report.

The ***Scheldt (c)*** is observed to be an overall sink for dissolved inorganic nitrogen. Most nitrogen loss occurs near the mouth of the Rupel tributary. Within this area peaks of ammonium gain and nitrate loss coincide with peaks of biological oxygen demand and dissolved oxygen loss. Hence, ammonium gained from organic matter mineralization is further nitrified to nitrate, which is probably immediately further denitrified, because of the low dissolved oxygen concentrations resulting from previous intense organic matter mineralization (fig. 36). Near the border between Belgium and the Netherlands two consecutive peaks of nitrate loss and gain can be observed, coinciding with a peak of dissolved oxygen gain. This could be attributed to the spiraling effect of nutrients and delivery of oxygen from the nearby 'Land van Saeftinghe' (Van Damme et al. 2009), first indicating an increased area of denitrification, followed by a peak of nitrification due to increased oxygen input. This intertidal area is however not represented in the graphs for intertidal and subtidal area as calculated in Vandenbruwaene et al. (2012). Chlorophyll *a* concentrations do not seem to explain any of the patterns observed in nitrogen dynamics. However, chlorophyll *a* concentrations seem to be higher in the Scheldt than those observed in the Elbe estuary. This can in part be related to differences in euphotic depth – mixing depth ratios (Underwood & Kromkamp 1999; see further, '*4.4 Primary production*'). However, in the most upstream part of the Elbe dissolved oxygen oversaturation is frequently noted and euphotic depth, mixing depth ratio is favorable. Thus, also grazing could be an important controlling factor explaining the lower chlorophyll *a* values in the Elbe (which is rather a proxy for biomass than for effective primary production). Although, dissolved inorganic nitrogen concentrations are highest in the Scheldt estuary compared to the other TIDE estuaries, lower nitrogen input and denitrification processes combined cause the Scheldt estuary to be a sink for total dissolved inorganic nitrogen. The sink function for dissolved inorganic nitrogen in the Scheldt estuary did not come very surprisingly, as this corresponds well to earlier results (Van Damme et al. 2005, Soetaert et al. 2006). However, with recent improvements of the oxygen state (fig. 43) and increasing importance of nitrification over denitrification near the Rupel, the Scheldt estuary might evolve towards a nitrogen source in the nearby future.

The ***Humber (c)*** was found an overall small source for dissolved inorganic nitrogen. Most gain of nitrate and ammonium and dissolved oxygen occurs at the border of the meso- and polyhaline zone. Nitrification appears to be more important than denitrification. As found earlier (in '*4.1 Estuarine patterns*') seasonal dynamics of chlorophyll concentrations are absent in the Humber estuary, attributed to very high concentrations of suspended particulate matter, thus low euphotic depths (see further, '*4.4 Primary production*') (Jickels et al. 2000). Furthermore, chlorophyll concentrations are very low and therefore not further discussed as explanatory factor in nitrogen dynamics. Despite similar nitrogen input in the Humber estuary and Scheldt estuary, the Humber is rather a source than a sink for dissolved inorganic nitrogen. This could be linked to a much smaller input of organic matter and higher dissolved oxygen concentrations as compared to the other TIDE estuaries (Attachment 2). Unfortunately no biological oxygen demand data were provided. However, the small nitrogen source function is not in correspondence to findings by Sanders et al. (1997) and Jickels et al. (2000), who found the Humber estuary to be a minor sink (4 % removal according to input). This small difference could well be in the range of errors for the method used. We averaged the gain and loss for every station sampled. However, a better approach is to integrate these expected gain and loss dynamics along the different sampling stations, since the number of sampling stations can strongly influence the outcome (Sanders et al. 1997). By consequence, it is better to interpret the overall surfer plot than using the averaged discrete fluxes per sampling station calculated. Indeed, when we consider the surfer plot for nitrate and ammonium in the Humber (fig. 26 & fig. 28), it could be that removal is slightly more intense than found from overall averaging (more intense red patches for both nitrate and ammonium). Hence, it can be concluded that either source or sink function for dissolved inorganic nitrogen of the Humber estuary is rather limited for the pelagic. Differences found with literature are likely attributed to the variability of these limited nitrogen dynamics and the error of the method.

In the ***Weser (c)*** not enough data was provided to find the sink or source function according to the conservative mixing plot methods used in this report (see table 1 & Attachment 1). Only limited studies have been performed in the Weser, mainly focusing on sediment dynamics (e.g. Müller et al. 1990, Grabemann & Krause 2001). However, some study reported also high oxygen consuming

processes within the upper reaches (nitrification can reach up 50 to 75% of the oxygen consumption observed) (in Cox et al. 2009: Schurchard et al. 1993).

In summary it can be concluded that in general chlorophyll *a* as indicator for nitrogen uptake by algae contributed only in a minor extent to nitrogen dynamics (in the Elbe estuary likely indirect as organic matter input). Organic matter mineralization, nitrification and more limited denitrification in function of organic matter and nitrogen input appear to be the main regulating processes for an estuary becoming a sink or source, with oxygen concentration as main indicator variable. However, when oxygen production caused by primary production increases it might also become a more important process to consider in nitrogen dynamics. Hence, in order to follow sink or source function for nitrogen in an estuary it is important to consider the most important processes influencing oxygen concentrations. Within both Elbe and Scheldt biological oxygen demand is an important indicator. Unfortunately, in the Weser and Humber this was not measured. Next, it is important to consider the hydro-morphological aspects such as residence time and freshwater discharge, bathymetrical depth, input from tributaries and upstream boundaries and the contribution of intertidal and subtidal area next to the estuary, and their implication oxygen concentrations along the estuarine gradient.

4.2.2 Phosphate

Overall, considering the whole estuarine gradient and all seasons, the Humber estuary can be considered a source, while the Scheldt can be considered a sink for phosphate (fig. 38). In the Humber most phosphate is gained along the oligo- and mesohaline stretch, coinciding with the turbidity maximum zone. In the Scheldt, most phosphate is lost in the oligohaline zone. In the Elbe gain and loss processes alternate each other in the freshwater part of the estuary, however concentrations are about four times lower and dynamics are rather limited. In the Weser phosphate concentrations are in the same order of magnitude than within the Elbe estuary. Considering the initial input concentrations, the Humber can be considered as a source of phosphate more important than the Scheldt can be considered a sink for phosphate for estuarine functioning. Comparing between seasons, in both the Elbe and Scheldt more phosphate is gained in summer than in winter. However in the Humber quite the opposite can be observed (more is lost in summer). Differences between winter and summer concentrations are less clear than for nitrogen. Most difference is observed in the Humber estuary, with clearly higher concentrations in summer. Within the other estuaries differences are very limited, but also for these estuaries concentrations are observed to be higher in summer. This can be attributed to the fact that phosphate sources are mostly point sources, and concentrations increase when discharge is lower in summer (Sanders et al. 1997). This corresponds to what can be expected for phosphate dynamics in the Scheldt and Elbe, with more gain in summer. On the contrary, in the Humber estuary an actual increase in loss in summer can be observed and this cannot be explained by the temporal pattern in phosphate concentrations. **Differences in sink source functions between estuaries can be explained by differences in (1) phosphorus input (both inorganic and organic) from the upper boundary and main tributaries and (2) estuarine processing.**

Considering differences in phosphorus ***input (1)***, it is clear that when solely input of phosphate is compared, most input is observed in the Humber estuary (fig. 39). However, when also the organic phosphorus fraction is considered, by comparing total phosphorus input, the Elbe is observed to have a larger phosphorus input. Nonetheless, total phosphorus is not measured within the Humber estuary and hence, it could be that the overall input is still largest within the Humber indeed. Furthermore, the Humber estuary over which the phosphate load is distributed, is about three times smaller than the Elbe estuary. Least input is observed in the Scheldt estuary, with slightly higher inputs near the Rupel tributary. Also in the Humber, input is clearly higher near the tributaries (Aire, Don and Trent). Hence, differences in input do in part explain differences in source and sink functions of the Humber and Scheldt respectively. Input from tributaries also explains the area of gain within the Humber, with increased phosphorus input from the Aire, Don and Trent along the oligo- and mesohaline stretch. In the Scheldt however, increased input near the Rupel is not reflected in the phosphate dynamics, since most phosphate is actually lost within the oligohaline zone of the Scheldt estuary. Considering seasonal differences, input is higher in winter than in summer except for the Humber, in which input is higher in summer. For none of the estuaries this corresponds to the observed seasonal patterns of gain and loss in winter and

summer. In the Scheldt and Elbe more is gained in summer, while in the Humber more is lost in summer. Although differences in phosphorus input appear to explain major difference in sink and source function between estuaries, it does not explain differences at a local scale within the estuary. From the difference in input and phosphate dynamics between winter and summer for Scheldt and Elbe as opposed to the Humber, it seems that estuarine dynamics in phosphate, both upstream and within the estuary, are regulated by different ecological processes. In the next paragraph estuarine differences in estuarine processing will be further discussed.

Estuarine processing (2) of phosphate within the estuary is mainly driven by suspended particulate matter dynamics, primary production and burial. To identify underlying processes in estuarine processing, gain and loss of phosphate is discussed, taking into account phosphate concentrations and hydro-geomorphology (see also '*3.1.1 Hydrodynamics*' & '*3.1.2 Morphology*'). Both in the Elbe and Scheldt phosphate is alternately gained and lost, with dynamics abruptly decreasing from the mid-mesohaline zone towards the sea. However, in the Elbe concentrations are very low and phosphate dynamics are limited (fig. 40).

In the ***Elbe*** no clear correlation could be found with neither dissolved oxygen dynamics, biological oxygen demand, suspended matter concentration, nor chlorophyll a concentrations. Then again, the Elbe is only a minor source for phosphate, dynamics are very limited and concentrations of phosphate are very low compared to the other estuaries examined. The low phosphate concentrations in the Elbe were in agreement with earlier studies (van Beusekom & Brockmann 1998). However, van Beusekom & Brockmann (1998) found the Elbe to be a sink, while in this report the Elbe is found to be a minor source for phosphate. Anyway, phosphate adsorption to suspended particulate matter concentrations is only considered a temporal sink (Jickels et al. 2000). When oxygen concentrations are low and iron-oxy-hydroxides are reduced, phosphate is again released. Furthermore, as the suspended matter concentration reaches the sea, other anions compete for adsorption and phosphate is desorbed again (cf. bell-shaped theory in Sanders et al. 1997, van Beusekom & Brockmann 1998, van der Zee et al. 2007 & Deborde et al. 2007).

In the ***Scheldt*** dynamics could be related to primary production (if you consider chlorophyll *a* here as a good proxy). Peaks of phosphate loss seem to decrease together with chlorophyll *a* concentrations from the freshwater towards the sea. It is observed that the Scheldt estuary shifted from a heterotrophic hyper-eutrophied system to a more autotrophic, eutrophied system (Cox et al. 2009). Hence, it could be that nowadays primary production is indeed the main regulating process in phosphate dynamics. Another explanation could be the gradual desorption of phosphate from suspended particulate matter, according to the bell-shaped theory. However, no clear correlation with suspended particulate matter is found (fig. 40). A small peak in phosphate gain near the Rupel could be associated with organic matter input and subsequent mineralization, as indicated by a peak in biological oxygen demand. Nevertheless, overall a loss of phosphate can be observed in the freshwater and oligohaline zone of the Scheldt estuary. A peak of gain followed again by phosphate loss near the border between Belgium and the Netherlands could be respectively attributed to the effects of release of phosphate in the high salinity zone and the spiraling effect with the 'Land van Saefthinge' serving as a major storage zone (uptake, burial). It has to be noted that the phosphate concentrations are highest in the Scheldt. However, the sink function for phosphate in the Scheldt is not in agreement with previous findings by Soetaert et al. (2006) who stated that the Scheldt estuary evolved from an overall sink to source for phosphate since 1995. At that time, this was also found to be rather unexpected. Oxygen concentrations increased and by consequence adsorptive removal by suspended particulate matter was expected to increase as well (Soetaert et al. 2006). Thus, contrary to earlier findings, it could be that the Scheldt did rather evolve to a more efficient sink and that corresponding to findings by Deborde et al. (2007) desorption is not increased by higher phosphate concentrations.

In the ***Humber*** phosphate dynamics can be related to a peak of oxygen gain and high suspended matter concentrations at the limit between the meso- and polyhaline zone. Again, dynamics in the Humber estuary seem to be mainly regulated by suspended matter dynamics. Here it could indicate that phosphate highly associated with suspended particulate matter being released as it comes in the high salinity zone. This is rather unexpected, since according to the bell-shaped theory phosphate would be removed by adsorption in the freshwater part of the estuary and desorbed again in the low salinity region (cf. fig.4, in the oligo- to mesohaline zone; van Beusekom

& Brockmann 1998, van der Zee et al. 2007 & Deborde et al. 2007). Indeed, phosphate dynamics observed in this report are not in agreement with previous results. In previous studies the Humber is actually considered a major sink associated with the adsorption to suspended matter particles in the turbidity maximum zone, as also observed in the very turbid Gironde estuary (Sanders et al. 1997, Jickels et al. 2000, Deborde et al. 2007). This could be due to the combined effect of increased adsorptive removal efficiency in the Humber, even in the lower salinity reaches, because of the very high suspended particulate matter concentrations and of a recent shift of the turbidity maximum zone towards the sea (fig. 13) giving rise to a major area of phosphate desorption (Sanders et al. 1997, Jickels et al. 2000, Deborde et al. 2007). It could also be consequence of less sampling stations within the low salinity reach in the Humber estuary, masking true dynamics. Chlorophyll concentrations are not considered in the Humber estuary, because of absence of seasonal dynamics and very low concentrations compared to the other two estuaries.

In summary, the Humber is a major source, both because of very high phosphorus input from upstream and likely because of desorption from the very high suspended matter concentrations in the high salinity reach. The Scheldt can be considered rather a sink for phosphate, likely related to increased oxygen state and primary production in the upper reaches of the estuary. Although, considering concentrations observed within the estuaries, the Scheldt being a sink affects the estuary less than the Humber does being a source. The Elbe is only a minor source and concentrations within this estuary are very low. Based on similarities of phosphate concentrations found in the Weser with concentrations observed in the Elbe, and input of phosphorus from the upper boundary being in the same range as input of phosphorus in the Scheldt, the Weser will also be characterized by low and rather variable and more unpredictable phosphate dynamics.

4.2.3 Dissolved silica

Dissolved silica concentrations are highest in the Scheldt estuary, next within the Elbe estuary (Attachment 2). In both the Humber and Weser dissolved silica is only rarely measured in time and space (Attachment 1). In the Weser very low concentrations are observed. However, measurements in the Weser were restricted to the polyhaline zone, in which dissolved silica concentrations are expected to be lower in general (cf. the other TIDE estuaries). In the Elbe dissolved silica concentrations were often limiting in the freshwater zone. In the Scheldt freshwater zone, dissolved silica limitation only occurred once in 2004. Next, dissolved silica limitations are regularly found in the polyhaline zone of both the Elbe and Scheldt estuary. However, in the Scheldt polyhaline zone limitations are less pronounced and even disappeared after 2007. In general, concentrations are higher in winter than in summer and despite limitations, dissolved silica concentrations are usually higher in the freshwater zone. Also primary production, and thus silica uptake by diatoms, is mainly observed in the upper part of the estuary and will be most intense during the warmer seasons (Carbonnel et al. 2009). Dissolved silica dynamics could only be considered in the Elbe and Scheldt estuary, due to sampling frequencies. For the Humber this is presumably not an issue, since seasonal dynamics in chlorophyll concentrations were absent anyway (see earlier analyses and discussions). However, in the Weser it would have been interesting to have a more clear view upon the spatial and temporal distribution of dissolved silica concentrations and dynamics.

Comparing dynamics between the Elbe and Scheldt, it shows that the Elbe is an overall source while the Scheldt is an overall sink for dissolved silica. In the Elbe, taking into account the input concentration within the estuary, most is gained along the oligo- to mesohaline stretch. In the Scheldt overall averaging seems to give an overall loss in the oligohaline zone. Most limitations for dissolved silica (< 0.3 mg/l) were observed in the Elbe estuary. Nevertheless, averaged over the whole gradient, dissolved silica removal (loss) seems to be larger in the Scheldt estuary. Considering gain and removal efficiency per zone, dissolved silica gain in the Elbe appears to have a larger impact upon estuarine functioning than loss has upon estuarine functioning in the Scheldt estuary. **Differences in sink and source function once again can be explained by (1) differences in dissolved silica input and (2) estuarine processing.**

Input (1) of dissolved silica is highest in the Elbe estuary, in part explaining source function of the Elbe estuary. In general input is largest in winter and lowest in summer corresponding with silica gain in winter and loss in summer. In the Scheldt an increased input of dissolved silica can be observed near the Rupel tributary. Although overall loss was observed when calculated as average

in the oligohaline zone, green patches of gain were indeed observed near the Rupel (fig. 33). Also at the tidal limit (kilometer 0) green patches of gain are observed in the Scheldt, reflecting gain by input from the upper boundary (Bovenschelde). Carbonnel et al. (2009) found the Scheldt to be a source between Gent (TIDE km 0) and Dendermonde (TIDE km 39) and an overall sink between Dendermonde and Hemiksem (TIDE km 60). On the contrary, our results suggest a sink in the upstream part and source near the Rupel tributary. This is likely corresponding to loss within the upper reaches related to primary production, and gain near the Rupel related to tributary input (see further). Nonetheless, considering the whole estuarine gradient, the Scheldt estuary is observed to be a sink for dissolved silica like also observed by Carbonnel et al. (2009). Also in the Elbe green patches appear to be located near the river mouths of the Lühe and Öste, however contrary to the Scheldt not near the tidal limit. In general it can be concluded that in both estuaries input from boundaries and tributaries are most contributing to gain of dissolved silica observed in the estuaries. Although there is more input from the upper boundary in the Elbe, this is not reflected at the tidal limit like it is in the Scheldt estuary. This could be due to differences in estuarine processing.

Estuarine processing (2) of dissolved silica is mainly regulated by diatom dissolved silica uptake and biogenic silica (diatom frustule) dissolution. The dissolved silica input at the upper boundary of the Elbe could by consequence be masked by an increase in primary production in the upper part of the estuary. However, since chlorophyll *a* concentrations are actually lower in the Elbe than in the Scheldt, this could not be the reason why input from the upper boundary is outbalanced. It might be because in the Elbe dissolved silica concentrations are less frequently measured in winter and by consequence the input from upstream which is mostly found in winter, is attenuated. In general there seems to be no clear relation of dissolved silica dynamics with neither chlorophyll *a*, nor suspended matter concentrations. It might be elucidating to also consider biogenic silica concentrations to interpret these dynamics. Unfortunately, this is not measured in either of the estuaries for the time period considered in TIDE.

In summary, it is clear that the Elbe is an overall source and the Scheldt is an overall sink for dissolved silica. From dynamics in dissolved silica it is shown that this difference in sink and source function is mainly regulated by differences in dissolved silica input from upper boundaries and tributaries. Furthermore, an area of dissolved silica loss in the upper part of the Scheldt estuary can be associated with diatom uptake. Diatom uptake was not very clear within the Elbe estuary, not even within the most upper more shallow part of the estuary. It seems diatom uptake in the Elbe is more limited, while absolute dissolved silica limitation is more quickly reached. Hence, also difference in estuarine processing, suggesting more algal activity within the Scheldt estuary, further promotes the sink function of the Scheldt versus the source function of the Elbe.

4.2.4 Nutrient ratios and expected effects of sink and source function

When considering six yearly average nutrient ratios (N/P, N/Si, P/Si), most ratios generally approach the Redfield ratio heading towards the sea, except for the phosphate dissolved silica ratio in the Elbe estuary (fig. 52, 53 & 54).

It is clear nitrogen is never limiting in any of the estuaries examined in TIDE. However, when compared between estuaries nitrogen is relatively most in excess in the Elbe estuary and least in excess, approaching the Redfield ratio in the Scheldt estuary. Nonetheless, absolute concentrations are highest in the Scheldt estuary for both dissolved inorganic nitrogen and phosphate.

Comparing silica limitation relative to nitrogen, dissolved silica is more limiting in the Scheldt than in the Elbe estuary. However, absolute dissolved silica limitations are almost never occurring in the Scheldt estuary, implicating other factors are limiting primary production here (see '*4.4 Primary production*'). In the Elbe however, dissolved silica limitation is frequently reached, although chlorophyll *a* values are clearly lower than in the Scheldt. Because of the positioning of the zones of dissolved silica limitation near the freshwater deeper part of the Elbe estuary, these limitations might be related to sinking of diatom frustules and subsequent limited recycling from the deeper parts in the estuary (the Elbe is known to be partially mixed).

When silica limitation relative to phosphorus is compared between estuaries, it can be found that in general silica is 10 times more limiting than in the Elbe estuary. However, dissolved silica is never

limiting in winter. In the Elbe mesohaline and most upstream freshwater zone phosphorus can become even limiting over dissolved silica concentration.

For the Humber these ratios are not considered relevant since no significant biological activity could be found (see '*4.1 Estuarine patterns*' and '*4.4 Primary production*'). In the Weser not enough data was provided for this discussion, although high oxygen values in the upper reaches and high gross primary production estimates (see further, '*4.4 Primary production*') indicate that it might be important to examine in this estuary.

Table 7 Source (+) and sink (-) function and six-yearly average estuarine concentrations (between brackets, in mg/l) for total dissolved inorganic nitrogen (TDIN), phosphate (PO4) and dissolved silica (DSi). In the Weser dissolved silica concentration is not given, since it is only measured in the polyhaline zone and therefore not representative as average for the whole estuarine gradient. In the Humber there is no significant biological activity and therefore not relevant (n.a. = not applicable).

	Elbe	Humber	Scheldt	Weser
TDIN	++ (2.96)	+ (3.8)	(-) (4.21)	? (3.33)
PO4	+ (0.06)	++ (0.18)	(-) (0.26)	? (0.07)
DSi	++ (2.26)	n.a. (2.09)	-. (3.43)	n.a.

Taking into account findings about the patterns observed for nitrogen, phosphorus and silica concentrations and the sink and source functions of the TIDE estuaries (table), the following trends might be expected:

- Excess in nitrogen relative to phosphorus will increase further in both the Elbe and Humber, while in the Scheldt it might still approach the Redfield ratio for a while. Nonetheless, it is expected to evolve to nitrogen excess in the Scheldt as well since the estuary is becoming more oxygenated.
- Patterns of silica limitation relative to nitrogen are expected to stay similar for the Elbe and Scheldt.
- Patterns of silica limitation relative to phosphorus are expected to decrease slightly for the Elbe and stay similar for the Scheldt estuary.

4.3 Oxygen deficiencies

Dissolved oxygen concentrations are observed to be highest in the Weser estuary. Because measurements in the Weser are restricted to the freshwater and oligohaline zones, this can be considered as truly high compared with the other estuaries, since mostly oxygen consuming processes have the tendency to be higher in the upstream part of an estuary (see also '*4.1 Estuarine patterns*'). Next, highest concentrations of dissolved oxygen are found in the oligohaline stretch of the Humber estuary. Main oxygen deficit problems are noted in the Elbe and Scheldt estuaries. Mainly in the Scheldt estuary, concentrations drop below 5 mg/l. This is the minimum amount of dissolved oxygen required to sustain a healthy ecological functioning system (Holzhauer et al. 2011). The zone of oxygen deficits in the Scheldt, extends over a large part of the freshwater zone and almost the entire oligohaline zone. In absolute values, most oxygen is lost in the freshwater part of the Elbe estuary. However, considering also the input concentration per zone, it seems that particularly the Scheldt oligohaline zone is affected by oxygen removal. This is in accordance with earlier findings (Van Damme et al. 2005, Soetaert et al. 2006). However, recently oxygen concentrations have improved in the Scheldt estuary and in 2009 oxygen concentrations did not drop below 5 mg/l anymore along the whole estuarine gradient. Nevertheless, a sag in the oligohaline persists and the Scheldt estuary still has the lowest dissolved oxygen concentrations compared to the other estuaries studied. In the Elbe freshwater zone, oxygen concentrations also regularly drop below this dissolved oxygen threshold concentration. Although the Elbe shows most oversaturation events in the most upstream part of the freshwater zone (the shallower part of the estuary), in the more downstream part of this freshwater zone an oxygen deficit zone can be observed, generated near TIDE kilometer 50. In 2006 this oxygen deficit zone temporarily disappeared. This temporary disappearance is likely to be related to the unusual high freshwater discharge during that summer (fig. 9). However, since 2007 the Elbe seems to re-experience oxygen deficits, with this zone apparently even extending over a longer stretch nowadays (a

stretch of up to 20 TIDE km). Although dissolved oxygen concentrations are markedly higher in the Elbe compared to the Scheldt estuary, the Elbe estuary appears to persistently experience these oxygen drops below 5 mg/l (see also Kerner 2007, Quiel et al. 2011). Hence, the question rises whether recent improvements observed in the Scheldt estuary will continue, or whether also the Scheldt will re-experience more severe oxygen deficiencies in the near future.

Oxygen dynamics in estuaries are controlled by several oxygen generating and oxygen consuming processes. In summary, the main processes are organic matter mineralization (respiration), nitrification and primary production (Statham et al. 2011). Therefore, biological oxygen demand concentrations, nitrate and ammonium dynamics and chlorophyll *a* concentrations are considered together with dissolved oxygen concentrations and dynamics (fig. 36). Lower dissolved oxygen concentrations in the Scheldt in general can be explained by the higher biological oxygen demand concentrations observed here compared to the Elbe estuary. Nevertheless, in the Scheldt biological oxygen demand concentrations have improved greatly, while in the Elbe biological oxygen demand concentrations did not change markedly (fig. 46). In the Scheldt input of ammonium strongly reduced. Furthermore, with an increasing water treatment effort since 2007 (Aquiris 2010) there is also less organic matter input in the Scheldt estuary coming from the Rupel tributary. Hence, in the Scheldt the improvement of water quality can be related to a decrease in oxygen consuming processes such as nitrification and mineralization. Also in the Elbe, oxygen deficiencies are likely related to an intense peak of nitrification and mineralization (fig. 36). Although, biological oxygen demand concentrations are much lower in the Elbe estuary, they did not change very much (fig. 46). Contrary to the other estuaries, in the Elbe estuary average depth abruptly increases near kilometer 40 in the freshwater zone, coinciding with a peak of oxygen loss and nitrate and ammonium gain. Increased depth also creates increased residence times and a decreased euphotic depth-mixing depth ratios within this area. As discussed earlier for nitrogen (see '*4.2.1 Different sink and source functions for nutrients: Dissolved inorganic nitrogen*'), it is likely that allochthonous (input from upstream) and autochthonous (from algae dying off) organic matter is piling up because of this sudden increase in depth, creating a large zone of intense nitrification and mineralization giving rise to oxygen deficiencies more downstream (Quiel et al. 2011). However, a coinciding peak of biological oxygen demand (like observed near the Rupel) is not observed in the Elbe. This could be explained by increased sinking of the organic matter within this zone, because of the abrupt increase in depth (sampling is performed at the surface). On the other hand, dissolubility for oxygen, nitrate and ammonium makes that these peaks in dynamics are still to be found within this area, contrary to the missing peak of biological oxygen demand.

Thus, ***in summary***, in the Scheldt severe oxygen deficiencies (<5 mg/l) have recently disappeared because of general water quality improvement. In the Elbe these oxygen deficiencies seem to persist due to intensified nitrification related to the particular morphometric characteristics of the freshwater zone. In conclusion, if water quality in the Scheldt does not deteriorate or the Scheldt is not suddenly deepened in a large extent within the freshwater zone, it can be carefully stated that problems of oxygen deficiencies are not expected in the nearby future. In the Elbe, biological oxygen demand concentrations are already much lower compared to the Scheldt estuary (fig. 47, Attachment 2) and much lower than what is considered as a healthy threshold (< 6 mg/l) for a good ecological functioning system according to Holzhauer et al. (2011). It might be unrealistic and even not very useful to further reduce the input of degradable organic matter (i.e. phytoplankton). A model has been run to test the effect of a strong reduced algal input at the upper boundary (0.1 µg/l). Severe oxygen deficiencies (<5 mg/l) indeed seem to disappear now in the Elbe freshwater zone. Nevertheless, concentrations still approach 5 mg/l, which is considered the minimum level needed for a good ecological status (Holzhauer et al. 2011). Model runs to test the oxygenation capacity from shallow water zones near the Hamburg port area, showed positive effects within these areas. However, positive effects from shallow water areas upon oxygen levels within the Elbe main stream were restricted (read also Schöl et al. 2012). Possibly the positioning of these shallow water zones near the freshwater part of increased depth makes exchange of oxygen with the deeper waters of the partially mixed Elbe very difficult.

4.4 Primary production

Chlorophyll a concentrations (fig. 49) are used as a proxy for algal biomass. However, this does not necessarily correspond to actual production (Underwood & Kromkamp 1999). Therefore, to see for difference in magnitude of primary production, also ***estimates of gross primary production*** based on continuous oxygen series were performed (fig. 51). Highest chlorophyll *a* concentrations are observed in the Scheldt estuary, next in the Elbe estuary (fig. 49, Attachment 2). Comparing gross primary production estimates between Scheldt and Elbe, production in the Elbe is slightly higher than in the Scheldt, contrarily to findings from the chlorophyll *a* concentrations. However, this rather seems to be an overestimation according to limitations of the method. The method is normally developed for macro-tidal well-mixed estuaries. The Elbe is in fact at the border between a meso- and macro-tidal estuary and is rather partially mixed (Kerner 2007). In the Weser no chlorophyll *a* measurements were done. Based on estimates for gross primary production from continuous oxygen series, it appears that production in the Weser could be highest of all estuaries studied. Hence, in the future it would be nice to also have an idea about the distribution of chlorophyll *a* in both time and space in the Weser. In the Humber, chlorophyll values measured were very low. Based on estimates from continuous dissolved oxygen series, in the Humber actually no primary production could be detected. Both findings correspond to earlier results from the multivariate analyses, in which the Humber was distinguished by its absence of seasonal chlorophyll dynamics. In addition the Humber could be distinguished from the other estuaries by its high suspended matter concentrations. Hence, primary production in the pelagic of the Humber estuary clearly seems to be impeded by light limitation.

In summary, primary production is absent in the ***Humber*** estuary and higher in the Scheldt than in the Elbe estuary. For both latter estuaries, highest concentrations of chlorophyll *a* are observed in the freshwater zone. Concentrations in the Scheldt freshwater zone are twice as high as those in the Elbe freshwater zone, despite the fact that in the most upstream part of the Elbe freshwater zone most dissolved oxygen oversaturation events occurred compared to the other estuaries. So, ***which parameters are limiting primary production in the Elbe and Scheldt and why is production twice as high in the Scheldt than in the Elbe? Light climate, nutrients and residence time are examined as possible factors limiting algal growth.***

In the Scheldt, euphotic depth in the freshwater decreases from 0.8 m to 0.4 m, while in the Elbe it decreases from 1.1 m to about 0.25 m. Despite euphotic depth decreasing more in the Elbe, these differences do not seem large enough to explain differences in primary production. However, when also bathymetrical depth (as proxy for mixing depth in macro-tidal estuaries) is considered, it is clear that in the Elbe from TIDE kilometer 40 the increase in depth causes a decrease in the euphotic depth-mixing depth ratio, detrimental to algal growth. Hence, light climate does seem to be an important factor contributing to a lower algal growth in the Elbe estuary.

Residence time when summed over the length for each zone, appears to be higher in the freshwater zone of the Elbe than in the freshwater zone of the Scheldt. Even when corrected for distance per zone (in days/km), residence times is higher in the Elbe than in the Scheldt estuary. Hence, residence time does not provide any clear explanation.

Limitation by nutrients is examined by comparing nutrient ratios with the 'ideal' Redfield ratio, along the estuarine gradient. Nitrogen is clearly not limited in any of the estuaries studied within this report (fig. 51, fig. 52 & fig. 53). When nitrogen silica and phosphorus silica ratios are considered, it is clear that most limitation for silica occurs in the freshwater zone of both Scheldt and Elbe estuaries. However, in the Elbe estuary this is most pronounced in the most downstream part of the freshwater zone, after the area of increased depth observed in this estuary. Although relative ratios might be limiting according to the Redfield ratio, it are the absolute concentrations that will effectively prevent algal growth. Most dissolved silica concentrations lower than 0.3 mg/l, are clearly observed in the freshwater zone of the Elbe estuary (fig. 32). This might be attributed to sinking of diatoms to the deeper layers within the freshwater part of the Elbe estuary and more limited recycling to the upper layers of the water column. In the Scheldt, basically no absolute dissolved silica limitations are observed.

Since chlorophyll *a* is mainly a proxy for algal biomass, grazing (by zooplankton) is another factor that might explain the discrepancy of the lower chlorophyll *a* values in the shallower, most

upstream part of the Elbe and the regular observed oversaturation events in the most upstream part of the Elbe estuary indicating primary production. Unfortunately no data were provided on this. However, grazing is also reported to be an important controlling factor in the Elbe by Quiel et al. (2011).

In summary, it can be concluded primary production is limited by light climate in the Humber estuary, and by a combined effect of dissolved silica limitation, light climate and possibly grazing within the Elbe estuary. Primary production in the Scheldt has been considered to be limited by light. However, recently chlorophyll *a* values seem to increase again in the freshwater zone, indicating another limitation must have played previously. Hypotheses suggest ammonium and oxygen could have had inhibitory effects upon algal growth, when oxygen deficits were more prevalent in the Scheldt estuary (Cox et al. 2009).

5. Conclusion

5.1 What are the important factors controlling ecosystem functioning within the TIDE estuaries?

Chlorinity is the most structuring element in all estuaries, next temperature (winter-summer opposition). Dissolved constituents decrease towards the sea while pH and dissolved oxygen increase. Chlorinity (zonality) is more important in the ***Scheldt*** estuary explaining 66.5 % of the variation than in the Elbe explaining only 32.5 % of the variation. In the Elbe estuary seasonality plays a much greater role compared to the Scheldt and Humber estuaries. Patterns are least conspicuous in the Elbe, because of the very high freshwater discharge continuously disrupting the salinity gradient. Nitrate constitutes the major part of total dissolved inorganic nitrogen in all estuaries, indicating nitrification and mineralization's relevance over denitrification and primary production. Physical correlations, like between temperature and dissolved oxygen are to be found in all estuaries. However, the latter least pronounced in the Scheldt together with highest dissolved inorganic nitrogen, phosphate and biological oxygen demand concentrations, reflect the importance of other biological oxygen influencing processes within this estuary. Within the ***Elbe*** the correlation found between phaeopigments, chlorophyll *a* and biological oxygen demand might well indicate the importance of autochthonous organic matter input of the algae in the freshwater zone, as also found by the contributions of BfG in TIDE (Schöl et al. 2012). Concentrations of nutrients are much lower in the Elbe. This is likely the combined effect of the largest river drainage basin, highest freshwater discharge and earlier water treatment since the 80ies. Primary production peaks earlier in spring in the Elbe, while in summer in the Scheldt. In the ***Humber*** primary production can be considered insignificant and estuarine functioning is mostly regulated by the suspended matter dynamics. For the ***Weser*** no typical patterns could be found, since too few data was available for a more detailed analysis. However, likely, as seen from gross primary production estimates and high dissolved oxygen concentrations, the Weser might give some interesting estuarine patterns different from those observed in the Scheldt, Elbe and Humber.

5.2 How do TIDE estuaries function as a filter for nutrients?

Dissolved inorganic nitrogen: The Elbe can be considered a major source, while the Scheldt can be considered a minor sink. This sink or source function is defined by both input and estuarine processing. The input is highest in the Elbe, while lowest in the Scheldt. It is only since recent the Elbe evaluated to a source of dissolved inorganic nitrogen (Dähnke et al. 2008). This is thought to be related to loss of shallow water zones and/or recent deepening (Kerner 2007). Dissolved inorganic nitrogen removal decreased in the Scheldt estuary. This is believed to be associated with increased oxygen concentrations and decreased ammonium input (Van Damme et al. 2005, Soetaert et al. 2006). Hence, finally the Scheldt could also evolve to a source of dissolved inorganic nitrogen. Nevertheless, compared to the Elbe the Scheldt is still a sink today. Ammonium and nitrate concentrations, as indirect and direct substrate for denitrification respectively, are both higher in the Scheldt than in the Elbe estuary. The Humber can be considered a source in which intermediate dissolved inorganic nitrogen concentrations are observed. While in the Scheldt and Elbe nitrogen dynamics are mainly concentrated in the upstream part, nitrogen dynamics in the the Humber are found along the oligo- and mesohaline stretch. In the Elbe and Scheldt nitrogen dynamics are mainly regulated by organic matter dynamics (as indicated by biological oxygen demand), morphology and dissolved inorganic nitrogen input. In the Humber more particularly, the interaction with suspended particulate matter is of utmost importance. Unfortunately in the Humber biological oxygen demand as proxy for organic matter was not measured. For the Weser insufficient data were provided along the estuarine gradient to see any patterns and find the eventual sink or source function.

Phosphorus: The Humber can be considered a source, while the Scheldt can be considered a sink for phosphate. The effect of phosphate delivery is higher in the Humber estuary than removal is in the Scheldt estuary, since concentrations are about two times lower in the Humber. In the Elbe very low phosphate concentrations and limited phosphate dynamics are observed. Phosphate concentrations in the Weser are in the same range of the Elbe. Unfortunately, not enough data were available to calculate gain and loss along the estuarine gradient. Difference in phosphate

dynamics can be explained by differences in input and estuarine processing. Input of phosphate in the Humber is larger than in the Scheldt. However, input in winter and summer do not explain different source or sink function in neither the Humber, nor the Scheldt estuary. Hence, a closer look at estuarine processing is required. The observation of a phosphate sink is not in agreement with earlier findings of the Scheldt evolving to a phosphate source since 1995 (Soetaert et al. 2006). However, at that time this change was also found to be rather unexpected. With increasing oxygen concentrations, also adsorption of phosphate to suspended particulate matter is expected to increase. Thus, it could be that the estuary is rather a phosphate sink and that high phosphate concentrations do not increase desorption. Or it could be that primary production is nowadays a more regulating factor in phosphate dynamics, as the estuary evolved from a heterotrophic, hyper-eutrophied to a more autotrophic, eutrophied system (Cox et al. 2009). Phosphate dynamics in the Humber are again coupled to suspended matter dynamics. However, rather than a sink because of phosphate adsorption in the turbidity maximum, here a major source could be detected. This could be attributed to a downstream shift of the turbidity maximum zone. When the phosphate-enriched suspended particulate matter arrives in the high salinity zones, phosphate is released again because of competition with stronger anions, such as sulfate. The effect of initial phosphate loss in the upstream part of the estuary could have been overlooked, because of less sampling stations in this area. Or it could be that the particulate suspended matter associated with organic phosphorus is a source of phosphate by mineralization.

Dissolved silica: The Elbe is a source, while the Scheldt is a sink for dissolved silica. The concentrations are slightly higher in the Scheldt estuary. Most absolute limitations (DSI < 0.3 mg/l, Holzhauer et al. 2011) are observed in the freshwater zone of the Elbe estuary. Concentrations are only limitedly measured in the Humber and Weser estuaries. Therefore, only dynamics in the Elbe and Scheldt could be considered. For the Humber this is likely to be not important, since dissolved silica is mainly biologically regulated and primary production appeared to be insignificant in this estuary. In the Elbe most is gained along the oligo- to mesohaline stretch, suggesting large biogenic silica dissolution and/or tributary input. In the Scheldt estuary many patches of loss are observed in the freshwater zone, while patches of gain can be observed near upper boundary and the mouth of the Rupel tributary. Dissolved silica input is higher in the Elbe than in the Scheldt. Gain is mostly observed near the tidal limit and tributaries, except at the boundary for the Elbe estuary. Likely this difference can be attributed to different sampling campaigns. In the Elbe dissolved silica is less frequently measured in winter, masking the input from upstream and thus gain in calculation of dissolved silica dynamics. No clear relation could be found with chlorophyll or suspended particulate matter. In conclusion, dynamics are possibly most affected by boundary and tributary input, rather than by differences in estuarine processing.

Effect for nutrient ratios: nitrogen is never limiting in any of the estuaries examined. Taking into account different sink and source functions found, nitrogen excess relative to phosphorus and silica will further increase in both the Elbe and Humber estuaries. In the Scheldt nitrogen availability relative to phosphorus and silica stays more or less similar, approaching the Redfield ratio. In the Humber silica ratios are not relevant, since no significant biological activity was found. Also in the Weser silica ratios are not considered, since only limited measurements in the polyhaline zone are available. Comparing the Scheldt and Elbe, silica is relatively more limiting in the Scheldt estuary. Phosphorus limitation can be found in the most upstream and in the mesohaline part of the Elbe estuary. However, absolute dissolved silica limitation (<0.3 mg/l) mostly occurs in the Elbe freshwater zone. Taking into account sink and source functions, patterns for relative silica and phosphorus limitation do not change in any of the estuaries examined.

5.3 How can we avoid oxygen deficiency situations in the TIDE estuaries?

Main problems of oxygen deficiency are observed in the Elbe and Scheldt estuary. Although, overall dissolved oxygen concentrations are lowest in the Scheldt estuary, since 2009 oxygen drops below 5 mg/l are no longer observed along the estuarine gradient. In the Elbe a zone of oxygen deficiency nearby the freshwater deeper part of the estuary appears to persist. When oxygen dynamics are compared, it can be concluded that in the Scheldt estuary the oxygen deficiencies are mainly related to water quality, while in the Elbe oxygen sags are related to the particular morphometric characteristics of the estuary. With water quality improvements, oxygen in

the nearby future is not likely to drop below 5 mg/l again. In the Elbe the effect of the installation of shallow water zones and reduction of algal input upon estuarine oxygen concentrations has been examined (Schöl et al. 2012). None of these measures seem to be sufficient to restore good ecological functioning.

5.4 Which variables limit primary production in the TIDE estuaries?

From chlorophyll *a* concentrations, gross primary production estimates and multivariate analysis combined, it can be concluded that primary production in the Humber is impeded by light limitation, due to the very high suspended particluate matter concentrations. In the Weser estimates for gross primary production from continuous oxygen data series suggest that primary production is highest within this estuary. However, in the Weser too few data is available to come to further conclusions. Chlorophyll *a* values seem to show higher primary production in the Scheldt estuary. However, in the most upstream part of the Elbe estuary dissolved oxygen oversaturation (>100%) is frequently observed. When light climate, residence time and absolute dissolved silica limitation are considered, it could be that primary production is higher in the Scheldt because of more beneficial light climate and less absolute dissolved silica limitation. Another explanation could be that primary production is effectively higher within the Elbe estuary, but not found by difference in chlorophyll *a* concentration. Indeed, chlorophyll *a* is a proxy for algal biomass and not for effective primary production. Unfortunately no data for grazing were available for any of the estuaries examined. In the Scheldt it is generally accepted that primary production is further limited by light. However, recently observed increase in chlorophyll *a* values suggest other limitations might have been important previously.

5.5 Lessons learnt from TIDE: towards ecosystem services and measures, recommendations for further estuarine management

Water quality management is a measure that seems to pay off in all estuaries (read also Saathoff et al. 2012 for other type of measures). Although highest nitrogen and phosphorus concentrations are observed in the Scheldt estuary, water quality improvement has been observed most recently in this estuary for the time period studied in TIDE. It seems organic matter input is the largest driver in general, but that freshwater discharge, residence time, light climate and bathymetry can be important constraints for further improvement of ecological functioning and ecosystem services following from it (read also Sanders et al. 2012). Within the Humber estuary, pelagic primary productivity most likely will always be very limited or insignificant because of high suspended matter concentrations, which implies the estuary is more susceptible to organic matter pollution. Hence, monitoring of biological oxygen demand in the Humber estuary would be interesting. However, the Humber comprises most shallow subtidal area compared with the other TIDE estuaries in which microphytobenthos can contribute up to 50 % of primary production (Underwood & Kromkamp 1999 and refs herein). Nevertheless, more managed-realignment sites could increase sedimentation and decrease turbidity again. In the Elbe it will be very difficult to restore ecological functioning because of local deepening in the upper reaches of the estuary. In this instance the best measure is prevention. Installation of shallow water zones will not contribute sufficiently to restore oxygen deficiencies. Further reduction of chlorophyll *a* input in the Elbe is questionable, since biological oxygen demand is already very low compared to the Scheldt estuary. The Scheldt and Weser are more similar to the Elbe estuary, while the Humber is really type specific. As the Scheldt water quality is recently improving, it is important to keep in mind the effect of deepening as observed within the Elbe in future estuarine management. Otherwise recent improvements of water management might be reset. For the Weser it is suggested to increase monitoring effort, since data in only the upper reaches is too limited to see any pattern or trend.

6. References

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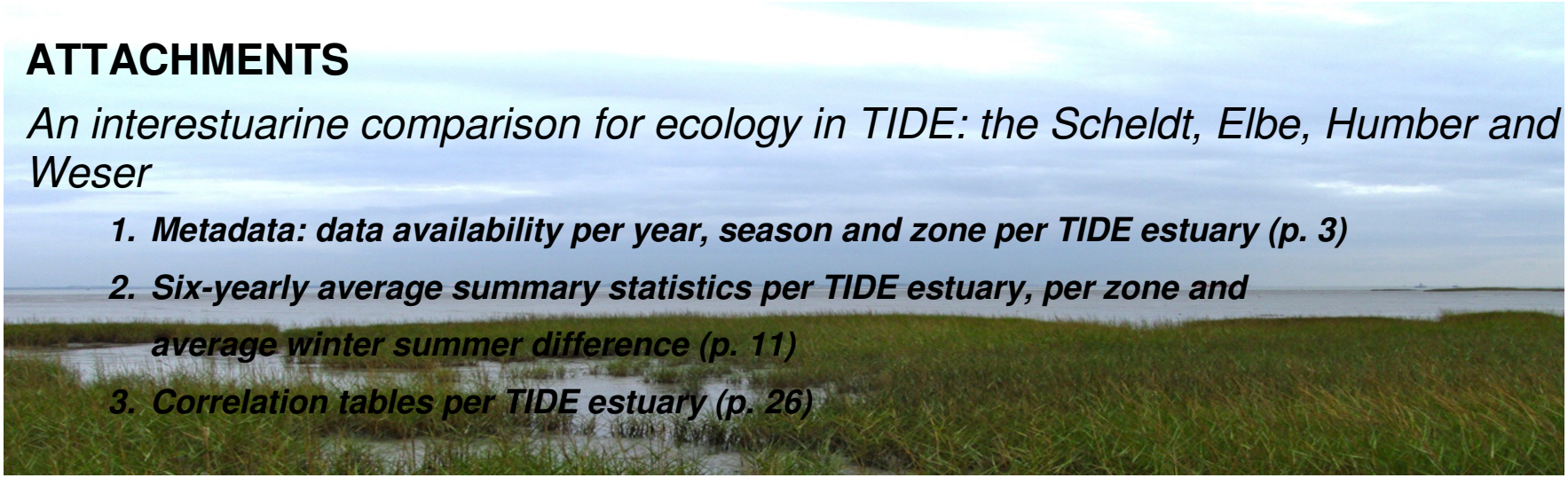

ATTACHMENTS

An interestuarine comparison for ecology in TIDE: the Scheldt, Elbe, Humber and Weser

1. ***Metadata: data availability per year, season and zone per TIDE estuary (p. 3)***
2. ***Six-yearly average summary statistics per TIDE estuary, per zone and average winter summer difference (p. 11)***
3. ***Correlation tables per TIDE estuary (p. 26)***

Geerts L, Maris T, Meire P

With contributions of Beauchard O, Schöl A, Vandenbruwaene W., Van Damme S, Wolfstein K, Manson S, Saathoff S, Soetaert K, Cox T, Meire A, (February 2013)

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Attachment 1:

Metadata: data availability per year, season (1 winter; 2 spring; 3 summer, 4 autumn) and zone per TIDE estuary

The Elbe estuary

ELBE

	CL	T	pH	COND	DO	Dosat	NH4	NO3	NO2	TN	ORG_N	SPM	CHL_A	CHL_extract	PO4	TP	Dsi	BOD5	PHAE	DOC	POC	TOC
2004	*168*	*168*	*168*	*168*	*168*	*168*	*107*	*168*	*98*	*168*	*72*	*166*	*36*		*155*	*168*	*76*	*168*	*36*	*168*	*168*	*168*
FW1	24	24	24	24	24	24	11	24	16	24	8	24	12		16	24	5	24	12	24	24	24
1	4	4	4	4	4	4	4	4	4	4	4	4	2		4	4	2	4	2	4	4	4
2	4	4	4	4	4	4	3	4		4		4	2			4	1	4	2	4	4	4
3	12	12	12	12	12	12	4	12	12	12	4	12	6		8	12		12	6	12	12	12
4	4	4	4	4	4	4		4		4		4	2		4	4	2	4	2	4	4	4
FW2	24	24	24	24	24	24	18	24	22	24	17	24	6		20	24	11	24	6	24	24	24
1	4	4	4	4	4	4	4	4	4	4	4	4	1		4	4	2	4	1	4	4	4
2	4	4	4	4	4	4	2	4	3	4	2	4	1		2	4	2	4	1	4	4	4
3	12	12	12	12	12	12	9	12	12	12	9	12	3		10	12	5	12	3	12	12	12
4	4	4	4	4	4	4	3	4	3	4	2	4	1		4	4	2	4	1	4	4	4
FW3	66	66	66	66	66	66	30	66	36	66	26	64	6		66	66	30	66	6	66	66	66
1	11	11	11	11	11	11	11	11	11	11	11	11	1		11	11	5	11	1	11	11	11
2	11	11	11	11	11	11	6	11	6	11	4	11	1		11	11	5	11	1	11	11	11
3	33	33	33	33	33	33	10	33	13	33	8	33	3		33	33	15	33	3	33	33	33
4	11	11	11	11	11	11	3	11	6	11	3	9	1		11	11	5	11	1	11	11	11
OLIGO	24	24	24	24	24	24	18	24	4	24	4	24			24	24	12	24		24	24	24
1	4	4	4	4	4	4	4	4	4	4	4	4			4	4	2	4		4	4	4
2	4	4	4	4	4	4	4	4		4		4			4	4	2	4		4	4	4
3	12	12	12	12	12	12	7	12		12		12			12	12	6	12		12	12	12
4	4	4	4	4	4	4	3	4		4		4			4	4	2	4		4	4	4
MESO	18	18	18	18	18	18	18	18	12	18	11	18	6		18	18	6	18	6	18	18	18
1	3	3	3	3	3	3	3	3	3	3	3	3	1		3	3	1	3	1	3	3	3
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3	9	9	9	9	9	9	9	9	7	9	6	9	3		9	9	3	9	3	9	9	9
4	3	3	3	3	3	3	3	3	2	3	2	3	1		3	3	1	3	1	3	3	3
POLY	12	12	12	12	12	12	12	12	8	12	6	12	6		11	12	12	12	6	12	12	12
1	2	2	2	2	2	2	2	2	2	2	2	2	1		2	2	2	2	1	2	2	2
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3	6	6	6	6	6	6	6	6	4	6	2	6	3		6	6	6	6	3	6	6	6
4	2	2	2	2	2	2	2	2	2	2	2	2	1		2	2	2	2	1	2	2	2

	CL	T	pH	COND	DO	Dosat	NH4	NO3	NO2	TN	ORG_N	SPM	CHL_A	CHL_extract	PO4	TP	Dsi	BOD5	PHAE	DOC	POC	TOC
2007	*155*	*156*	*156*	*156*	*153*	*153*	*85*	*156*	*93*	*156*	*76*	*156*			*137*	*156*	*68*	*156*		*155*	*155*	*155*
FW1	24	24	24	24	23	23	15	24	20	24	15	24			13	24	10	24		24	24	24
1	4	4	4	4	4	4	4	4	4	4	4	4			4	4	2	4		4	4	4
2	4	4	4	4	4	4		4	3	4		4			1	4		4		4	4	4
3	12	12	12	12	12	12	7	12	9	12	7	12			4	12	6	12		12	12	12
4	4	4	4	4	3	4	4	4	4	4	4	4			4	4	2	4		4	4	4
FW2	24	24	24	24	24	24	22	24	23	24	22	24			16	24	11	24		24	24	24
1	4	4	4	4	4	4	4	4	4	4	4	4			4	4	2	4		4	4	4
2	4	4	4	4	4	4	4	4	4	4	3	4				4	1	4		4	4	4
3	12	12	12	12	12	12	11	12	11	12	11	12			8	12	6	12		12	12	12
4	4	4	4	4	4	4	4	4	4	4	4	4			4	4	2	4		4	4	4
FW3	65	66	66	66	65	65	34	66	38	66	31	66			66	66	29	66		65	65	65
1	11	11	11	11	11	11	9	11	11	11	9	11			11	11	5	11		11	11	11
2	11	11	11	11	10	10	3	11	4	11	3	11			11	11	5	11		11	11	11
3	33	33	33	33	33	33	11	33	14	33	10	33			33	33	14	33		33	33	33
4	10	11	11	11	11	11	11	11	9	11	9	11			11	11	5	11		10	10	10
OLIGO	24	24	24	24	24	24	5	24	2	24		24			24	24	12	24		24	24	24
1	4	4	4	4	4	4		4	2	4		4			4	4	2	4		4	4	4
2	4	4	4	4	4	4		4		4		4			4	4	2	4		4	4	4
3	12	12	12	12	12	12	3	12		12		12			12	12	6	12		12	12	12
4	4	4	4	4	4	4	2	4		4		4			4	4	2	4		4	4	4
MESO	18	18	18	18	17	17	9	18	10	18	8	18			18	18	6	18		18	18	18
1	3	3	3	3	2	2		3	2	3		3			3	3	1	3		3	3	3
2	3	3	3	3	3	3		3		3		3			3	3	1	3		3	3	3
3	9	9	9	9	9	9	7	9	6	9	6	9			9	9	3	9		9	9	9
4	3	3	3	3	3	3	2	3	2	3	2	3			3	3	1	3		3	3	3
POLY																						
1																						
2																						
3																						
4																						

	CL	T	pH	COND	DO	Dosat	NH4	NO3	NO2	TN	ORG_N	SPM	CHL_A	CHL_extract	PO4	TP	Dsi	BOD5	PHAE	DOC	POC	TOC
2005	*166*	*168*	*168*	*168*	*168*	*168*	*96*	*168*	*97*	*160*	*72*	*168*	*36*		*147*	*168*	*81*	*166*	*36*	*166*	*164*	*164*
FW1	23	24	24	24	24	24	6	24	12	24	6	24	12		13	24	10	24	12	23	23	23
1	4	4	4	4	4	4	4	4	4	4	4	4	2		4	4	2	4	2	4	4	4
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FW2	24	24	24	24	24	24	19	24	22	24	19	24	6		19	24	11	24	6	24	24	24
1	4	4	4	4	4	4	4	4	4	4	4	4	1		4	4	2	4	1	4	4	4
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4	4	4	4	4	4	4	3	4	3	4	3	4	1		4	4	2	4	1	4	4	4
FW3	65	66	66	66	66	66	38	66	40	66	32	66	6		65	66	30	64	6	65	64	64
1	11	11	11	11	11	11	11	11	11	11	11	11	1		11	11	5	11	1	11	11	11
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4	4	4	4	4	4	4	2	4		4		4			4	4	2	4		4	4	4
MESO	18	18	18	18	18	18	10	18	14	18	8	18	6		18	18	6	18	6	18	18	18
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4	3	3	3	3	3	3	3	3	2	3	2	3	1		3	3	1	3	1	3	3	3
POLY	12	12	12	12	12	12	11	12	5	4	3	12	6		8	12	12	12	6	12	11	11
1	2	2	2	2	2	2	2	2	2	2	2	2	1		2	2	2	2	1	2	2	2
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3	6	6	6	6	6	6	6	6	2			6	3		4	6	6	6	3	6	6	6
4	2	2	2	2	2	2	2	2	1	1	1	2	1		2	2	2	2	1	2	1	1

	CL	T	pH	COND	DO	Dosat	NH4	NO3	NO2	TN	ORG_N	SPM	CHL_A	CHL_extract	PO4	TP	Dsi	BOD5	PHAE	DOC	POC	TOC
2008	*133*	*165*	*165*	*165*	*164*	*164*	*100*	*165*	*104*	*164*	*78*	*139*	*37*		*144*	*139*	*69*	*165*	*37*	*133*	*133*	*133*
FW1	20	24	24	24	24	24	13	24	19	24	10	20	10		8	20	10	24	10	20	20	20
1	4	4	4	4	4	4	4	4	4	4	4				4			4				
2	4	4	4	4	4	4		4	2	4		4	2			4	2	4	2	4	4	4
3	12	12	12	12	12	12	5	12	12	12	5	12	6			12	6	12	6	12	12	12
4	4	4	4	4	4	4	4	4	1	4	1	4	2		4	4	2	4	2	4	4	4
FW2	20	24	24	24	23	23	22	24	24	24	22	20	4		19	20	10	24	4	20	20	20
1	4	4	4	4	4	4	4	4	4	4	4				4			4				
2	4	4	4	4	4	4	3	4	4	4	3	4			2	4	2	4		4	4	4
3	12	12	12	12	11	11	11	12	12	12	11	12	3		9	12	6	12	3	12	12	12
4	4	4	4	4	4	4	4	4	4	4	4	4	1		4	4	2	4	1	4	4	4
FW3	55	66	66	66	66	66	31	66	33	65	27	55	5		66	55	25	66	5	55	55	55
1		11	11	11	11	11	11	11	11	10	10				11			11				
2	11	11	11	11	11	11	4	11	8	11	4	11	1		11	11	5	11	1	11	11	11
3	33	33	33	33	33	33	8	33	8	33	7	33	3		33	33	15	33	3	33	33	33
4	11	11	11	11	11	11	8	11	6	11	6	11	1		11	11	5	11	1	11	11	11
OLIGO	19	23	23	23	23	23	15	23	7	23	5	19			23	19	9	23		19	19	19
1		4	4	4	4	4	2	4	4	4	2				4			4				
2	4	4	4	4	4	4		4		4		4			4	4	2	4		4	4	4
3	11	11	11	11	11	11	10	11	3	11	3	11			11	11	5	11		11	11	11
4	4	4	4	4	4	4	3	4		4		4			4	4	2	4		4	4	4
MESO	15	18	18	18	18	18	14	18	12	18	9	15	8		18	15	5	18	8	15	15	15
1		3	3	3	3	3	1	3	3	3	1				3			3				
2	3	3	3	3	3	3	1	3	1	3		3	1		3	3	1	3	1	3	3	3
3	9	9	9	9	9	9	7	9	5	9	7	9	5		9	9	3	9	5	9	9	9
4	3	3	3	3	3	3	1	3	1	3	1	3	2		3	3	1	3	2	3	3	3
POLY	4	10	10	10	10	10	5	10	9	10	5	10	10		10	10	10	10	10	4	4	4
1																						
2		2	2	2	2	2		2	2	2		2	2		2	2	2	2	2			
3	3	6	6	6	6	6	3	6	5	6	3	6	6		6	6	6	6	6	2	2	2
4	2	2	2	2	2	2	2	2	2	2	2	2	2		2	2	2	2	2	2	2	2

The Elbe estuary (2)

ELBE

	2006	167	167	167	167	166	166	71	166	105	165	61	167	36	163	167	83	167	36	167	167	167
FW1		24	24	24	24	24	24	7	24	11	24	4	24	12	24	24	12	24	12	24	24	24
	1	4	4	4	4	4	4	4	4	4	4	4	4	2	4	4	2	4	2	4	4	4
	2	4	4	4	4	4	4		4	4	4		4	2	4	4	2	4	2	4	4	4
	3	12	12	12	12	12	12		12	3	12		12	6	12	12	6	12	6	12	12	12
	4	4	4	4	4	4	4	3	4		4		4	2	4	4	2	4	2	4	4	4
FW2		24	24	24	24	24	24	15	24	21	24	14	24	6	24	24	12	24	6	24	24	24
	1	4	4	4	4	4	4	4	4	4	4	4	4	1	4	4	2	4	1	4	4	4
	2	4	4	4	4	4	4		4	4	4		4	1	4	4	2	4	1	4	4	4
	3	12	12	12	12	12	12	7	12	10	12	7	12	3	12	12	6	12	3	12	12	12
	4	4	4	4	4	4	4	4	4	3	4	3	4	1	4	4	2	4	1	4	4	4
FW3		65	65	65	65	64	64	30	65	49	65	29	65	6	65	65	29	65	6	65	65	65
	1	10	10	10	10	9	9	10	10	10	10	10	10	1	10	10	5	10	1	10	10	10
	2	11	11	11	11	11	11	6	11	11	11	6	11	1	11	11	5	11	1	11	11	11
	3	33	33	33	33	33	33	10	33	22	33	9	33	3	33	33	14	33	3	33	33	33
	4	11	11	11	11	11	11	4	11	6	11	4	11	1	11	11	5	11	1	11	11	11
OLIGO		24	24	24	24	24	24	5	24	8	24	3	24		24	24	12	24		24	24	24
	1	4	4	4	4	4	4	3	4	4	4	3	4		4	4	2	4		4	4	4
	2	4	4	4	4	4	4		4	4	4		4		4	4	2	4		4	4	4
	3	12	12	12	12	12	12	1	12		12		12		12	12	6	12		12	12	12
	4	4	4	4	4	4	4	1	4		4		4		4	4	2	4		4	4	4
MESO		18	18	18	18	18	18	8	18	10	18	7	18	6	17	18	6	18	6	18	18	18
	1	3	3	3	3	3	3	3	3	3	3	3	3	1	3	3	1	3	1	3	3	3
	2	3	3	3	3	3	3		3	3	3		3	1	2	3	1	3	1	3	3	3
	3	9	9	9	9	9	9	2	9	2	9	2	9	3	9	9	3	9	3	9	9	9
	4	3	3	3	3	3	3	3	3	2	3	2	3	1	3	3	1	3	1	3	3	3
POLY		12	12	12	12	12	12	6	11	6	10	4	12	6	9	12	12	12	6	12	12	12
	1	2	2	2	2	2	2	2	2	2	2	2	2	1	2	2	2	2	1	2	2	2
	2	2	2	2	2	2	2		2	2	2		2	1	1	2	2	2	1	2	2	2
	3	6	6	6	6	6	6	2	5		4		6	3	4	6	6	6	3	6	6	6
	4	2	2	2	2	2	2	2	2	2	2	2	2	1	2	2	2	2	1	2	2	2

	2009	167	161	167	167	167	161	74	166	75	166	49	167	42	149	167	78	167	42	167	165	165
FW1		24	21	24	24	24	21	11	24	6	24	2	24	12	12	24	9	24	12	24	24	24
	1																					
	2	8	8	8	8	8	8	4	8	4	8	2	8	4	4	8	2	8	4	8	8	8
	3	12	9	12	12	12	9	3	12	2	12		12	6	4	12	5	12	6	12	12	12
	4	4	4	4	4	4	4	4	4		4		4	2	4	4	2	4	2	4	4	4
FW2		23	20	23	23	23	20	18	23	16	23	12	23	6	17	23	10	23	6	23	23	23
	1																					
	2	8	8	8	8	8	8	6	8	7	8	4	8	2	6	8	3	8	2	8	8	8
	3	12	9	12	12	12	9	9	12	7	12	6	12	3	8	12	6	12	3	12	12	12
	4	3	3	3	3	3	3	3	3	2	3	2	3	1	3	3	1	3	1	3	3	3
FW3		66	66	66	66	66	66	31	65	39	66	28	66	6	66	66	30	66	6	66	66	66
	1																					
	2	22	22	22	22	22	22	13	22	16	22	12	22	2	22	22	10	22	2	22	22	22
	3	33	33	33	33	33	33	11	32	15	33	10	33	3	33	33	15	33	3	33	33	33
	4	11	11	11	11	11	11	7	11	8	11	6	11	1	11	11	5	11	1	11	11	11
OLIGO		24	24	24	24	24	24	1	24	1	24		24		24	24	11	24		24	24	24
	1																					
	2	8	8	8	8	8	8		8	1	8		8		8	8	4	8		8	8	8
	3	12	12	12	12	12	12		12		12		12		12	12	6	12		12	12	12
	4	4	4	4	4	4	4	1	4		4		4		4	4	1	4		4	4	4
MESO		18	18	18	18	18	18	9	18	9	18	3	18	6	18	18	6	18	6	18	18	18
	1																					
	2	6	6	6	6	6	6	3	6	3	6	1	6	2	6	6	2	6	2	6	6	6
	3	9	9	9	9	9	9	3	9	4	9		9	3	9	9	3	9	3	9	9	9
	4	3	3	3	3	3	3	3	3	2	3	2	3	1	3	3	1	3	1	3	3	3
POLY		12	12	12	12	12	12	4	12	4	11	4	12	12	12	12	12	12	12	12	10	10
	1																					
	2	4	4	4	4	4	4	2	4	2	4	2	4	4	4	4	4	4	4	4	4	4
	3	6	6	6	6	6	6		6		5		6	6	6	6	6	6	6	6	5	5
	4	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	1	1
	2004 - 2009	956	985	991	991	986	980	533	989	572	979	408	963	187	895	965	455	989	187	956	952	952

The Scheldt estuary

SCHELDE

	CL	T	pH	COND	DO	Dosat	NH4	NO3	NO2	TN	ORG_N	SPM	CHL_A	CHL_extract	PO4	TP	Dsi	BOD5	PHAE	DOC	POC	TOC
2004	*321*	*322*	*322*	*192*	*335*	*335*	*335*	*333*	*334*	*189*	*192*	*323*	*304*		*335*	*186*	*335*	*190*	*140*	*323*	*192*	*151*
FW1	36	36	36	36	36	36	36	34	35	33	36	33	27		36		36	34	24	33	36	25
1	9	9	9	9	9	9	9	9	9	9	9	6	9		9		9	8		9	9	9
2	9	9	9	9	9	9	9	9	9	9	9	9	6		9		9	9	9	6	9	4
3	9	9	9	9	9	9	9	9	8	8	9	9	9		9		9	8	9	9	9	6
4	9	9	9	9	9	9	9	7	9	7	9	9	3		9		9	9	6	9	9	6
FW2	60	60	60	60	60	60	60	60	60	60	60	55	45		60		60	60	44	55	60	55
1	15	15	15	15	15	15	15	15	15	15	15	10	14		15		15	15		15	15	15
2	15	15	15	15	15	15	15	15	15	15	15	15	10		15		15	15	15	10	15	10
3	15	15	15	15	15	15	15	15	15	15	15	15	15		15		15	15	15	15	15	15
4	15	15	15	15	15	15	15	15	15	15	15	15	6		15		15	15	14	15	15	15
OLIGO	81	82	82	72	83	83	83	83	83	72	72	81	83		83	54	83	72	54	81	72	57
1	19	20	20	18	21	21	21	21	21	18	18	19	22		21	14	21	18		21	18	15
2	21	21	21	18	21	21	21	21	21	18	18	21	21		21	15	21	18	18	19	18	12
3	20	20	20	18	20	20	20	20	20	18	18	20	22		20	10	20	18	18	20	18	15
4	21	21	21	18	21	21	21	21	21	18	18	21	18		21	15	21	18	18	21	18	15
MESO	84	84	84	24	90	90	90	90	90	24	24	88	83		90	66	90	24	18	88	24	14
1	18	18	18	6	24	24	24	24	24	6	6	22	23		24	18	24	6		24	6	6
2	24	24	24	6	24	24	24	24	24	6	6	24	21		24	18	24	6	6	22	6	2
3	18	18	18	6	18	18	18	18	18	6	6	18	18		18	12	18	6	6	18	6	3
4	24	24	24	6	24	24	24	24	24	6	6	24	21		24	18	24	6	6	24	6	3
POLY	60	60	60		66	66	66	66	66			66	66		66	66	66			66		
1	12	12	12		18	18	18	18	18			18	18		18	18	18			18		
2	18	18	18		18	18	18	18	18			18	18		18	18	18			18		
3	12	12	12		12	12	12	12	12			12	12		12	12	12			12		
4	18	18	18		18	18	18	18	18			18	18		18	18	18			18		
2005	*330*	*332*	*338*	*181*	*338*	*338*	*337*	*337*	*337*	*179*	*181*	*295*	*350*		*333*	*204*	*337*	*180*	*93*	*327*	*92*	*66*
FW1	36	36	36	36	36	36	36	35	36	35	36	24	36		33		35	35	18	33	18	10
1	9	9	9	9	9	9	9	9	9	9	9		9		9		9	9		9	6	4
2	9	9	9	9	9	9	9	9	9	9	9	6	9		9		9	8	6	9	3	2
3	9	9	9	9	9	9	9	8	9	8	9	9	9		6		8	9	6	9	6	4
4	9	9	9	9	9	9	9	9	9	9	9	9	9		9		9	9	6	6	3	
FW2	60	60	60	60	60	60	60	60	59	59	60	41	61		58		60	60	31	55	28	23
1	15	15	15	15	15	15	15	15	15	15	15		15		15		15	15		15	8	8
2	16	16	16	16	16	16	16	16	15	15	16	11	16		16		16	16	11	16	5	5
3	15	15	15	15	15	15	15	15	15	15	15	15	15		13		15	15	10	15	10	10
4	14	14	14	14	14	14	14	14	14	14	14	15	15		14		14	14	10	9	5	
OLIGO	74	74	75	62	75	75	75	75	75	62	62	70	87		75	60	75	62	32	74	36	27
1	20	20	20	17	20	20	20	20	20	17	17	15	23		20	15	20	17		20	12	10
2	19	19	19	15	19	19	19	19	19	15	15	19	22		19	15	19	15	12	19	9	6
3	18	18	18	15	18	18	18	18	18	15	15	18	21		18	15	18	15	10	18	10	8
4	17	17	18	15	18	18	18	18	18	15	15	18	21		18	15	18	15	10	17	5	3
MESO	89	90	95	23	95	95	94	95	95	23	23	88	95		95	72	95	23	12	93	10	6
1	24	24	24	6	24	24	24	24	24	6	6	18	24		24	18	24	6		24	2	1
2	23	23	23	5	23	23	23	23	23	5	5	22	23		23	18	23	5	4	23	2	1
3	24	24	24	6	24	24	24	24	24	6	6	24	24		24	18	24	6	4	24	4	4
4	18	19	24	6	24	24	23	24	24	6	6	24	24		24	18	24	6	4	22	2	
POLY	71	72	72		72	72	72	72	72			72	71		72	72	72			72		
1	18	18	18		18	18	18	18	18			18	18		18	18	18			18		
2	18	18	18		18	18	18	18	18			18	18		18	18	18			18		
3	18	18	18		18	18	18	18	18			18	18		18	18	18			18		
4	17	18	18		18	18	18	18	18			18	17		18	18	18			18		

	CL	T	pH	COND	DO	Dosat	NH4	NO3	NO2	TN	ORG_N	SPM	CHL_A	CHL_extract	PO4	TP	Dsi	BOD5	PHAE	DOC	POC	TOC
2007	*296*	*296*	*296*	*179*	*307*	*308*	*309*	*309*	*309*	*179*	*179*	*256*	*305*		*309*	*307*	*309*	*179*	*109*	*306*	*134*	*109*
FW1	36	36	36	36	36	36	36	36	36	36	36	24	33		36	36	36	36	24	36	27	22
1	9	9	9	9	9	9	9	9	9	9	9		6		9	9	9	9		9	3	3
2	9	9	9	9	9	9	9	9	9	9	9	6	9		9	9	9	9	6	9	9	6
3	9	9	9	9	9	9	9	9	9	9	9	9	9		9	9	9	9	9	9	6	4
4	9	9	9	9	9	9	9	9	9	9	9	9	9		9	9	9	9	9	9	9	9
FW2	59	59	59	59	59	59	59	59	59	59	59	37	53		59	58	59	59	36	58	43	43
1	15	15	15	15	15	15	15	15	15	15	15		10		15	15	15	15		14	5	5
2	15	15	15	15	15	15	15	15	15	15	15	9	15		15	15	15	15	9	15	14	14
3	14	14	14	14	14	14	14	14	14	14	14	14	13		14	14	14	14	13	14	9	9
4	15	15	15	15	15	15	15	15	15	15	14	14	15		15	14	15	15	14	15	15	15
OLIGO	69	69	69	60	70	70	70	70	70	60	60	61	77		70	69	70	60	35	70	46	36
1	16	16	16	15	17	17	17	17	17	15	15	10	17		17	16	17	15		17	6	4
2	18	18	18	15	18	18	18	18	18	15	15	17	21		18	18	18	15	10	18	15	12
3	18	18	18	15	18	18	18	18	18	15	15	18	21		18	18	18	15	15	18	10	8
4	17	17	17	15	17	17	17	17	17	15	15	16	18		17	17	17	15	10	17	15	12
MESO	78	78	78	24	83	83	84	84	84	24	24	74	82		84	84	84	24	14	82	18	8
1	12	12	12	6	17	17	18	18	18	6	6	12	16		18	18	18	6		16	2	
2	24	24	24	6	24	24	24	24	24	6	6	22	24		24	24	24	6	4	24	6	3
3	24	24	24	6	24	24	24	24	24	6	6	24	24		24	24	24	6	6	24	4	2
4	18	18	18	6	18	18	18	18	18	6	6	16	18		18	18	18	6	4	18	6	3
POLY	54	54	54		59	60	60	60	60			60	60		60	60	60			60		
1	6	6	6		11	12	12	12	12			12	12		12	12	12			12		
2	18	18	18		18	18	18	18	18			18	18		18	18	18			18		
3	18	18	18		18	18	18	18	18			18	18		18	18	18			18		
2008	*317*	*317*	*316*	*173*	*316*	*317*	*316*	*317*	*316*	*173*	*174*	*279*	*322*		*317*	*315*	*317*	*173*	*120*	*317*	*148*	*121*
FW1	33	33	32	32	33	33	33	33	33	33	33	24	30		33	32	33	32	24	33	30	22
1	6	6	6	6	6	6	6	6	6	6	6		6		6	6	6	6		6	6	6
2	9	9	9	9	9	9	9	9	9	9	9	6	9		9	9	9	9	6	9	6	4
3	9	9	8	9	9	9	9	9	9	9	9	9	7		9	8	9	8	9	9	9	6
4	9	9	9	8	9	9	9	9	9	9	9	9	8		9	9	9	9	9	9	9	6
FW2	57	57	57	57	57	57	57	57	56	56	57	40	57		57	56	57	57	40	57	50	50
1	12	12	12	12	12	12	12	12	12	12	12		12		12	12	12	12		12	10	10
2	15	15	15	15	15	15	15	15	15	15	10	15	15		15	15	15	15	10	15	11	11
3	15	15	15	15	15	15	14	14	15	15	15	15	15		15	15	15	15	15	15	14	14
4	15	15	15	15	15	15	15	15	15	15	15	15	15		15	14	15	15	15	15	15	15
OLIGO	71	71	71	60	70	71	71	71	71	60	60	67	81		71	71	71	60	40	71	49	39
1	18	18	18	15	18	18	18	18	18	15	15	15	21		18	18	18	15		18	10	8
2	17	17	17	15	17	17	17	17	17	15	15	16	18		17	17	17	15	10	17	15	12
3	18	18	18	15	17	18	18	18	18	15	15	18	21		18	18	18	15	15	18	9	7
4	18	18	18	15	18	18	18	18	18	15	15	18	21		18	18	18	15	15	18	15	12
MESO	90	90	90	24	90	90	90	90	90	24	24	82	88		90	90	90	24	16	90	19	10
1	24	24	24	6	24	24	24	24	24	6	6	18	24		24	24	24	6		24	4	2
2	18	18	18	6	18	18	18	18	18	6	6	16	17		18	18	18	6	4	18	6	3
3	24	24	24	6	24	24	24	24	24	6	6	24	24		24	24	24	6	6	24	3	2
4	24	24	24	6	24	24	24	24	24	6	6	24	23		24	24	24	6	6	24	6	3
POLY	66	66	66		66	66	65	66	66			66	66		66	66	66			66		
1	18	18	18		18	18	18	18	18			18	18		18	18	18			18		
2	12	12	12		12	12	12	12	12			12	12		12	12	12			12		
3	18	18	18		18	18	18	18	18			18	18		18	18	18			18		
4	18	18	17	18	18							18	18		18	18	18			18		

The Scheldt estuary (2)

SCHELDE

	2006	333	331	332	177	331	331	333	332	331	160	162	282	316	333	204	333	176	108	322	143	109	2009	336	325	324	165	325	325	334	336	336	177	178	276	343	335	328	336	120	45	324	120	95
FW1		34	34	34	34	34	34	34	34	33	30	31	18	29	34		34	34	17	31	25	17	FW1		36	33	33	33	33	33	36	36	36	34	34	21	31	36	33	36	24	9	33	24	16
	1	9	9	9	9	9	9	9	9	9	9	9		6	9		9	9		9	6	4		1	9	6	6	6	6	6	9	9	9	9	9	3	9	9	9	9	6		9	9	6
	2	7	7	7	7	7	7	7	7	7	7	7	3	6	7		7	7	3	7	7	7		2	9	9	9	9	9	9	9	9	9	9	9	6	9	9	8	9	9	6	9	6	4
	3	9	9	9	9	9	9	9	9	9	6	6	6	8	9		9	9	6	6	9	4		3	9	9	9	9	9	9	9	9	9	7	7	3	4	9	7	9	9	3	6		
	4	9	9	9	9	9	9	9	9	8	8	9	9	9	9		9	9	8	9	3	2		4	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9			9	9	6
FW2		59	57	59	59	57	57	59	59	58	53	54	36	48	59		59	58	35	54	47	41	FW2		60	55	55	55	55	55	60	60	60	59	60	31	60	59	55	60	40	15	54	40	39
	1	14	12	14	14	12	12	14	14	14	14	14		9	14		14	13		14	13	12		1	15	10	10	10	10	10	15	15	15	15	15	5	15	15	15	15	10		14	15	14
	2	15	15	15	15	15	15	15	15	14	14	15	10	10	15		15	15	10	14	14	13		2	15	15	15	15	15	15	15	15	15	15	15	10	15	14	14	15	15	10	15	10	10
	3	15	15	15	15	15	15	15	15	15	10	10	11	15	15		15	15	11	11	15	11		3	15	15	15	15	15	15	15	15	15	14	15	5	15	15	14	15	15	5	10		
	4	15	15	15	15	15	15	15	15	15	15	15	15	14	15		15	15	14	15	5	5		4	15	15	15	15	15	15	15	15	15	15	15	11	15	15	12	15			15	15	15
OLIGO		72	72	72	60	72	72	72	72	72	55	55	68	80	72	60	72	60	40	71	51	42	OLIGO		72	71	71	55	71	71	72	72	72	60	60	66	84	72	72	72	40	15	71	40	32
	1	18	18	18	15	18	18	18	18	18	15	15	15	19	18	15	18	15		18	16	12		1	18	17	17	10	17	17	18	18	18	15	15	16	21	18	18	18	10		18	15	12
	2	18	18	18	15	18	18	18	18	18	15	15	17	19	18	15	18	15	10	18	15	15		2	18	18	18	15	18	18	18	18	18	15	15	17	21	18	18	18	15	10	18	10	8
	3	18	18	18	15	18	18	18	18	18	10	10	18	21	18	15	18	15	15	17	15	11		3	18	18	18	15	18	18	18	18	18	15	15	16	21	18	18	18	15	5	17		
	4	18	18	18	15	18	18	18	18	18	15	15	18	21	18	15	18	15	15	18	5	4		4	18	18	18	15	18	18	18	18	18	15	15	17	21	18	18	18			18	15	12
MESO		96	96	96	24	96	96	96	96	96	22	22	88	91	96	72	96	24	16	94	20	9	MESO		96	94	93	22	94	94	94	96	96	24	24	86	96	96	96	96	16	6	94	16	8
	1	24	24	24	6	24	24	24	24	24	6	6	18	22	24	18	24	6		24	6	3		1	24	22	21	4	22	22	24	24	24	6	6	20	24	24	24	24	4		24	6	3
	2	24	24	24	6	24	24	24	24	24	6	6	22	22	24	18	24	6	4	24	6	3		2	24	24	24	6	24	24	24	24	24	6	6	22	24	24	24	24	6	4	24	4	2
	3	24	24	24	6	24	24	24	24	24	4	4	24	23	24	18	24	6	6	22	6	2		3	24	24	24	6	24	24	22	24	24	6	6	20	24	24	24	24	6	2	22		
	4	24	24	24	6	24	24	24	24	24	6	6	24	24	24	18	24	6	6	24	2	1		4	24	24	24	6	24	24	24	24	24	6	6	24	24	24	24	24			24	6	3
POLY		72	72	71		72	72	72	71	72			72	68	72	72	72			72			POLY		72	72	72		72	72	72	72	72			72	72	72	72	72			72		
	1	18	18	17		18	18	18	17	18			18	18	18	18	18			18				1	18	18	18		18	18	18	18	18			18	18	18	18	18			18		
	2	18	18	18		18	18	18	18	18			18	18	18	18	18			18				2	18	18	18		18	18	18	18	18			18	18	18	18	18			18		
	3	18	18	18		18	18	18	18	18			18	14	18	18	18			18				3	18	18	18		18	18	18	18	18			18	18	18	18	18			18		
	4	18	18	18		18	18	18	18	18			18	18	18	18	18			18				4	18	18	18		18	18	18	18	18			18	18	18	18	18			18		
																							2004 - 2009		1933	1923	1928	1067	1952	1954	1964	1964	1963	1057	1066	1711	1940	1962	1544	1967	1018	615	1919	829	651

The Humber estuary

HUMBER

	CL	T	pH	COND	DO	Dosat	NH4	NO3	NO2	TN	ORG_N	SPM	CHL_A	CHL_extract	PO4	TP	Dsi	BOD5	PHAE	DOC	POC	TOC
2004	*144*	*174*	*173*		*170*	*173*	*156*	*98*	*98*	*152*	*13*	*131*		*119*	*155*	*12*	*116*					
FW		24	48	48		48	48	48	48	48	8	24		12	48	12	45					
	1	5	10	10		10	10	10	10	10	1	5		2	10	2	10					
	2	5	10	10		10	10	10	10	10	1	5		3	10	3	9					
	3	8	16	16		16	16	16	16	16	5	8		4	16	4	14					
	4	6	12	12		12	12	12	12	12	1	6		3	12	3	12					
MESO		47	46	46		45	46	45	15	15	43		46		47	44		27				
	1	13	13	13		13	13	13	3	3	13		12		13	13		7				
	2	13	12	12		12	12	13	4	4	11		13		13	12		8				
	3	14	14	14		14	14	12	5	5	12		14		14	12		8				
	4	7	7	7		6	7	7	3	3	7		7		7	7		4				
OLIGO		28	33	32		33	33	32	27	27	32	5	16		28	32		29				
	1	8	9	9		9	9	9	5	5	9	2	6		8	9		5				
	2	8	9	9		9	9	9	9	9	9	1	4		8	9		9				
	3	8	9	8		9	9	8	7	7	8	1	4		8	8		9				
	4	4	6	6		6	6	6	6	6	6	1	2		4	6		6				
POLY		45	47	47		44	46	31	8	8	29		45		32	31		15				
	1	9	10	10		9	10	9	2	2	9		9		9	9		5				
	2	13	13	13		12	13	9	2	2	7		13		9	9		4				
	3	14	15	15		14	14	8	2	2	8		14		9	8		4				
	4	9	9	9		9	9	5	2	2	5		9		5	5		2				
2005	*142*	*177*	*177*		*172*	*177*	*152*	*112*	*119*	*153*	*12*	*155*		*119*	*153*	*12*	*117*					
FW		24	48	48		48	48	48	48	48	8	47		12	48	11	47					
	1	6	12	12		12	12	12	12	12	3	11		3	12	2	12					
	2	6	12	12		12	12	12	12	12	2	12		3	12	3	11					
	3	6	12	12		12	12	12	12	12		12		3	12	3	12					
	4	6	12	12		12	12	12	12	12	3	12		3	12	3	12					
MESO		47	48	48		47	48	46	25	25	46	1	47		47	46		26				
	1	12	12	12		12	12	12	7	7	12		12		12	12		8				
	2	14	14	14		14	14	14	8	8	14		14		14	14		6				
	3	14	14	14		14	14	13	7	7	13		14		14	13		8				
	4	7	8	8		7	8	7	3	3	7	1	7		7	7		4				
OLIGO		28	33	33		33	33	26	26	33	27	3	17		28	27		32				
	1	8	9	9		9	9	8	7	9	8	1	6		8	8		9				
	2	8	8	8		8	8	5	6	8	6		4		8	6		7				
	3	8	10	10		10	10	8	8	10	8	1	3		8	8		10				
	4	4	6	6		6	6	5	5	6	5	1	4		4	5		6				
POLY		43	48	48		44	48	32	13	13	32		44		32	32	1	12				
	1	7	10	10		8	10	8	4	4	8		8		8	8		4				
	2	12	12	12		12	12	8	2	2	8		12		8	8		1				
	3	14	14	14		14	14	10	4	4	10		14		10	10		4				
	4	10	12	12		10	12	6	3	3	6		10		6	6	1	3				
2006	*141*	*174*	*174*		*170*	*174*	*156*	*116*	*117*	*157*	*23*	*154*		*113*	*156*	*13*	*104*					
FW		23	51	51		47	51	46	47	47	47	12	47		11	47	11	47					
	1	4	10	10		9	10	9	9	9	9	5	9		2	9	2	9					
	2	5	11	11		11	11	11	11	11	11	2	11		2	11	2	11					
	3	6	15	15		12	15	11	12	12	12		12		3	12	3	12					
	4	8	15	15		15	15	15	15	15	15	5	15		4	15	4	15					
MESO		45	45	45		45	45	45	23	23	45	6	45		44	45		19					
	1	7	7	7		7	7	7	4	4	7		7		7	7							
	2	13	13	13		13	13	13	7	7	13	1	13		13	13		8					
	3	6	6	6		6	6	6	1	1	6	1	6		6	6		2					
	4	19	19	19		19	19	19	11	11	19	4	19		18	19		9					
OLIGO		28	33	33		33	33	32	32	33	32	4	17		25	31		28					
	1	4	5	5		5	5	5	4	5	4		2		4	5		1					
	2	8	9	9		9	9	9	9	9	9	2	4		8	7		9					
	3	4	5	5		5	5	5	5	5	5		2		4	5		5					
	4	12	14	14		14	14	13	14	14	14	2	9		9	14		13					
POLY		45	45	45		45	45	33	14	14	33	1	45		33	33	2	10					
	1	9	9	9		9	9	5	2	2	5		9		5	5							
	2	13	13	13		13	13	9	4	4	9		13		9	9	2	4					
	3	10	10	10		10	10	6	2	2	6		10		6	6		2					
	4	13	13	13		13	13	13	6	6	13	1	13		13	13		4					

	CL	T	pH	COND	DO	Dosat	NH4	NO3	NO2	TN	ORG_N	SPM	CHL_A	CHL_extract	PO4	TP	Dsi	BOD5	PHAE	DOC	POC	TOC
2007	*135*	*189*	*167*	*41*	*183*	*189*	*139*	*102*	*104*	*140*	*29*	*183*		*101*	*140*	*14*	*107*					
FW		32	48	48	38	48	48	48	46	48	46	13	49		21	46	12	49				
	1	6	11	11	7	11	11	11	11	11	11	2	11		3	11	2	11				
	2	5	9	9	9	9	9	9	7	9	7	1	9		4	7	3	9				
	3	8	10	10	8	10	10	10	10	10	10	3	11		6	10	3	11				
	4	13	18	18	14	18	18	18	18	18	18	7	18		8	18	4	18				
MESO		42	51	50		49	51	41	22	22	42	7	51		31	42		24				
	1	8	9	8		9	9	8	4	4	8	2	9		9	8		4				
	2	8	10	10		9	10	8	4	4	8	2	9		5	8		4				
	3	13	16	16		15	16	13	7	7	13	2	16		8	13		8				
	4	13	16	16		16	16	12	7	7	13	1	17		9	13		8				
OLIGO		23	34	31	1	34	34	24	26	26	26	8	33		13	26		26				
	1	5	6	5		6	6	5	5	5	5	1	6		5	5		5				
	2	4	5	5		5	5	2	4	4	4	1	5		1	4		4				
	3	6	11	11	1	11	11	8	8	8	8	3	10		3	8		8				
	4	8	12	10		12	12	9	9	9	9	3	12		4	9		9				
POLY		38	56	38	2	52	56	26	8	8	26	1	50		36	26	2	8				
	1	14	18	14		16	18	6	2	2	6		16		8	6		2				
	2	4	8	4		6	8	4			4		6		6	4						
	3	13	19	13	2	19	19	9	4	4	9	1	19		13	9	2	4				
	4	7	11	7		11	11	7	2	2	7		9		9	7		2				
2008	*103*	*185*	*134*	*44*	*184*	*183*	*116*	*107*	*108*	*124*	*33*	*176*		*135*	*123*	*12*	*72*					
FW		29	49	49	44	48	48	49	48	49	48	18	48		23	48	12	13				
	1	7	9	9	9	9	9	9	9	9	9	2	9		5	9	3	4				
	2	8	11	11	9	11	11	11	11	11	11	5	11		5	11	3	3				
	3	7	10	10	9	10	10	10	10	10	10	3	10		4	10	3	3				
	4	7	19	19	17	18	18	19	18	19	18	8	18		9	18	3	3				
MESO		25	44	28		48	44	24	20	20	32	6	41		41	32		22				
	1	8	13	10		11	13	7	5	5	8	1	11		10	8		6				
	2	5	7	5		10	7	5	4	4	5	1	7		7	5		4				
	3	8	10	9		13	10	8	8	8	9	3	10		11	9		8				
	4	4	14	4		14	14	4	3	3	10	1	13		13	10		4				
OLIGO		21	38	28		36	38	27	27	27	27	5	34		29	26		25				
	1	6	11	9		9	11	7	7	7	7	1	8		8	7		7				
	2	4	7	5		7	7	5	5	5	5	2	6		5	5		4				
	3	8	11	10		11	11	10	10	10	10	1	11		8	10		10				
	4	3	9	4		9	9	5	5	5	5	1	9		8	4		4				
POLY		28	54	29		52	53	16	12	12	17	4	53		42	17		12				
	1	6	12	6		12	12	6	4	4	6		12		12	6		4				
	2	8	14	8		14	14	4	2	2	4		14		10	4		2				
	3	8	15	9		13	14	4	4	4	4	2	14		11	4		4				
	4	6	13	6		13	13	2	2	2	3	2	13		9	3		2				
2009	*36*	*121*	*61*	*52*	*121*	*121*	*49*	*49*	*49*	*72*	*17*	*122*		*79*	*72*	*12*	*13*					
FW		24	48	48	48	48	48	48	48	48	48	16	48		22	48	12	12				
	1	5	9	9	9	9	9	9	9	9	9	4	9		4	9	3	3				
	2	6	9	9	9	9	9	9	9	9	9		9		3	9	3	3				
	3	6	13	13	13	13	13	13	13	13	13	4	13		6	13	3	3				
	4	7	17	17	17	17	17	17	17	17	17	8	17		9	17	3	3				
MESO			24		2	24	24				22		24		23	22						
	1		5			5	5				5		5		5	5						
	2		2		2	2	2				1		2		2	1						
	3		8			8	8				7		8		7	7						
	4		9			9	9				9		9		9	9						
OLIGO			12	1	2	12	12	1	1	1	1	1	13		10	1		1				
	1		3	1	1	3	3	1	1	1	1	1	3		1	1		1				
	2		1		1	1	1						1		1							
	3		3			3	3						4		3							
	4		5			5	5						5		5							
POLY			37	12		37	37				1		37		24	1						
	1		6			6	6						6		6							
	2	4	11	4		11	11				1		11		6	1						
	3	4	10	4		10	10						10		6							
	4	4	10	4		10	10						10		6							
2004 - 2009	*701*	*1020*	*886*	*137*	*1000*	*1017*	*768*	*584*	*595*	*798*	*127*	*921*		*666*	*799*	*75*	*529*					

The Weser estuary

WESER

	CL	T	pH	COND	DO	Dosat	NH4	NO3	NO2	TN	ORG_N	SPM	CHL_A	CHL_extract	PO4	TP	Dsi	BOD5	PHAE	DOC	POC	TOC
2004	*38*	*38*	*38*	*38*	*38*	*26*	*38*	*38*	*38*	*38*	*35*	*14*			*38*	*38*		*26*		*38*	*25*	*25*
FW1	12	12	12	12	12		12	12	12	12	11	12			12	12				12		
1	3	3	3	3	3		3	3	3	3	3	3			3	3				3		
2	3	3	3	3	3		3	3	3	3	3	3			3	3				3		
3	3	3	3	3	3		3	3	3	3	3	3			3	3				3		
4	3	3	3	3	3		3	3	3	3	2	3			3	3				3		
FW2	13	13	13	13	13	13	13	13	13	13	12	1			13	13		13		13	12	12
1	3	3	3	3	3	3	3	3	3	3	2				3	3		3		3	2	2
2	4	4	4	4	4	4	4	4	4	4	4	1			4	4		4		4	4	4
3	3	3	3	3	3	3	3	3	3	3	3				3	3		3		3	3	3
4	3	3	3	3	3	3	3	3	3	3	3				3	3		3		3	3	3
OLIGO	13	13	13	13	13	13	13	13	13	13	12	1			13	13		13		13	13	13
1	3	3	3	3	3	3	3	3	3	3	3				3	3		3		3	3	3
2	4	4	4	4	4	4	4	4	4	4	4	1			4	4		4		4	4	4
3	3	3	3	3	3	3	3	3	3	3	2				3	3		3		3	3	3
4	3	3	3	3	3	3	3	3	3	3	3				3	3		3		3	3	3
MESO																						
1																						
2																						
3																						
4																						
POLY																						
1																						
2																						
3																						
4																						

	CL	T	pH	COND	DO	Dosat	NH4	NO3	NO2	TN	ORG_N	SPM	CHL_A	CHL_extract	PO4	TP	Dsi	BOD5	PHAE	DOC	POC	TOC
2005	*38*	*38*	*38*	*25*	*38*	*26*	*38*	*38*	*38*	*37*	*37*	*14*			*38*	*38*	*23*			*38*	*26*	*26*
FW1	12	12	12	12	12		12	12	12	12	12	12			12	12				12		
1	3	3	3	3	3		3	3	3	3	3	3			3	3				3		
2	3	3	3	3	3		3	3	3	3	3	3			3	3				3		
3	3	3	3	3	3		3	3	3	3	3	3			3	3				3		
4	3	3	3	3	3		3	3	3	3	3	3			3	3				3		
FW2	13	13	13	13	13	13	13	13	13	13	13	1			13	13	11			13	13	13
1	3	3	3	3	3	3	3	3	3	3	3				3	3	3			3	3	3
2	4	4	4	4	4	4	4	4	4	4	4				4	4	3			4	4	4
3	3	3	3	3	3	3	3	3	3	3	3	1			3	3	3			3	3	3
4	3	3	3	3	3	3	3	3	3	3	3				3	3	2			3	3	3
OLIGO	13	13	13		13	13	13	13	13	12	12	1			13	13	12			13	13	13
1	3	3	3		3	3	3	3	3	3	3				3	3	3			3	3	3
2	4	4	4		4	4	4	4	4	3	3				4	4	3			4	4	4
3	3	3	3		3	3	3	3	3	3	3	1			3	3	3			3	3	3
4	3	3	3		3	3	3	3	3	3	3				3	3	3			3	3	3
MESO																						
1																						
2																						
3																						
4																						
POLY															50	49	38			50	38	38
1															12	12				12		
2															3	3				3		
3															3	3				3		
4															3	3				3		

	CL	T	pH	COND	DO	Dosat	NH4	NO3	NO2	TN	ORG_N	SPM	CHL_A	CHL_extract	PO4	TP	Dsi	BOD5	PHAE	DOC	POC	TOC
2007	*45*	*44*	*44*	*22*	*33*	*33*	*45*	*45*	*45*	*45*	*44*	*27*			*45*	*45*		*17*		*45*	*45*	*45*
FW1	12	11	11	10			12	12	12	12	12	12			12	12				12	12	12
1	3	3	3	3			3	3	3	3	3	3			3	3				3	3	3
2	3	3	3	3			3	3	3	3	3	3			3	3				3	3	3
3	3	3	3	3			3	3	3	3	3	3			3	3				3	3	3
4	3	2	2	1			3	3	3	3	3	3			3	3				3	3	3
FW2	12	12	12	12	12	12	12	12	12	12	12	4			12	12	5			12	12	12
1	3	3	3	3	3	3	3	3	3	3	3	1			3	3	2			3	3	3
2	3	3	3	3	3	3	3	3	3	3	3				3	3	3			3	3	3
3	3	3	3	3	3	3	3	3	3	3	3	1			3	3				3	3	3
4	3	3	3	3	3	3	3	3	3	3	3	2			3	3				3	3	3
OLIGO	21	21	21		21	21	21	21	21	21	20	11			21	21	12			21	21	21
1	4	4	4		4	4	4	4	4	4	3	3			4	4	3			4	4	4
2	5	5	5		5	5	5	5	5	5	5	3			5	5	5			5	5	5
3	6	6	6		6	6	6	6	6	6	6	3			6	6	2			6	6	6
4	6	6	6		6	6	6	6	6	6	6	2			6	6	2			6	6	6
MESO																						
1																						
2																						
3																						
4																						
POLY																						
1																						
2																						
3																						
4																						

	CL	T	pH	COND	DO	Dosat	NH4	NO3	NO2	TN	ORG_N	SPM	CHL_A	CHL_extract	PO4	TP	Dsi	BOD5	PHAE	DOC	POC	TOC
2008	*36*	*36*	*36*	*24*	*36*	*36*	*36*	*36*	*37*	*35*	*32*	*26*	*8*		*36*	*37*	*8*	*36*	*34*	*35*		
FW1	12	12	12	12	12	12	12	12	12	11	8	12			12	12		11	10	11		
1	3	3	3	3	3	3	3	3	3	3	1	3			3	3		3	3	3		
2	3	3	3	3	3	3	3	3	3	3	2	3			3	3		3	3	3		
3	3	3	3	3	3	3	3	3	2	2	2	3			3	3		2	2	2		
4	3	3	3	3	3	3	3	3	3	3	3	3			3	3		3	2	3		
FW2	12	12	12	12	12	12	12	12	12	12	12	7			12	12		12	12	12		
1	3	3	3	3	3	3	3	3	3	3	3	2			3	3		3	3	3		
2	3	3	3	3	3	3	3	3	3	3	3	1			3	3		3	3	3		
3	3	3	3	3	3	3	3	3	3	3	3	2			3	3		3	3	3		
4	3	3	3	3	3	3	3	3	3	3	3	2			3	3		3	3	3		
OLIGO	12	12	12		12	12	12	12	12	12	12	7			12	12		12	12	12		
1	3	3	3		3	3	3	3	3	3	3	2			3	3		3	3	3		
2	3	3	3		3	3	3	3	3	3	3	1			3	3		3	3	3		
3	3	3	3		3	3	3	3	3	3	3	2			3	3		3	3	3		
4	3	3	3		3	3	3	3	3	3	3	2			3	3		3	3	3		
MESO																						
1																						
2																						
3																						
4																						
POLY									1				8			1		8	1			
1																						
2													3					3				
3									1				3			1		3	1			
4													2					2				

The Weser estuary (2)

| WESER | | |

Attachment 2:

Six-yearly average summary statistics per TIDE estuary, per zone and average winter summer difference

Six-yearly average per estuary as a whole

	Elbe						Scheldt					
	n	mean	median	se	min	max	n	mean	median	se	min	max
CL (mg/l)	603	1690,66	156,00	151,39	63,00	17800,00	566	4868,52	1000,81	247,90	55,30	17929,34
T (°C)	630	12,99	13,50	0,24	0,60	23,90	566	13,19	13,62	0,23	2,36	23,67
PH	629	8,00	7,90	0,01	7,50	9,23	566	7,81	7,78	0,01	7,42	8,30
COND (µSm/cm)	632	531,67	95,00	41,50	57,00	4940,00	370	3554,87	1041,83	264,30	757,00	23383,33
DO (mg/l)	625	9,35	9,50	0,10	3,80	15,50	565	6,94	7,31	0,10	0,83	11,20
Dosat (%)	624	87,56	89,00	0,73	42,00	170,67	565	68,84	72,00	1,01	7,50	110,61
ORG_N (mg/l)	310	0,79	0,68	0,03	0,01	3,68	74	0,55	0,53	0,02	0,22	0,78
NH4 (mg/l)	397	0,13	0,09	0,01	0,01	0,47	565	0,44	0,12	0,03	0,01	3,00
NO3 (mg/l)	627	2,60	2,60	0,05	0,04	6,20	566	3,67	4,21	0,07	0,29	6,20
NO2 (mg/l)	407	0,03	0,02	0,001	0,003	0,11	565	0,10	0,05	0,004	0,01	0,59
TDIN (mg/l)	315	2,96	2,86	0,08	0,06	6,55	564	4,21	4,52	0,09	0,36	7,83
TN (mg/l)	622	3,53	3,40	0,06	0,27	8,30						
SPM (mg/l)	599	84,71	50,80	3,89	5,40	714,00	502	65,28	52,35	2,03	8,62	393,00
CHL_A (µg/l)	115	38,08	11,00	4,86	3,00	210,00	520	52,07	22,75	3,09	2,97	467,75
PO4 (mg/l)	580	0,06	0,06	0,00	0,01	0,12	566	0,26	0,20	0,01	0,03	1,32
TP (mg/l)	600	0,18	0,15	0,00	0,02	0,80	519	0,43	0,37	0,01	0,06	1,83
DSI (mg/l)	286	2,26	1,45	0,12	0,02	5,69	565	3,43	3,13	0,10	0,05	8,15
N/P	290	157,69	122,62	6,71	9,62	811,28	557	43,51	38,85	0,81	8,09	123,03
N/DSi	132	11,56	1,90	2,75	0,63	235,59	554	10,69	2,53	2,20	1,33	1060,94
P/DSi	269	0,10	0,03	0,01	0,01	0,91	565	0,31	0,08	0,05	0,02	9,88
BOD5 (mg/l)	626	2,47	1,80	0,07	0,60	9,43	355	6,81	6,40	0,16	1,40	17,00
DIC (mg/l)							133	55,12	56,22	0,79	37,45	77,68
PHAE	115	21,72	14,00	1,93	3,00	99,33	260	31,71	28,00	1,35	4,10	123,67
DOC (mg/l)	602	5,90	6,00	0,03	2,20	7,70	566	4,63	5,11	0,07	1,39	7,20
PN (mg/l)							151	0,68	0,55	0,04	0,10	2,34
POC (mg/l)	594	3,68	2,53	0,15	0,10	28,80	306	5,40	4,76	0,18	0,87	16,82
TOC (mg/l)												
TIC (mg/l)	600	23,22	23,00	0,13	14,67	35,00						

Six-yearly average per estuary as a whole (2)

	Humber						Weser					
	n	mean	median	se	min	max	n	mean	median	se	min	max
CL (mg/l)	221	6526,51	6091,41	426,76	17,55	21319,93	69	1097,70	270,95	184,87	148,12	6171,30
T (°C)	294	10,92	10,72	0,26	3,35	20,82	70	12,85	12,90	0,65	3,60	21,71
PH	269	7,78	7,81	0,01	6,60	8,57	70	7,80	7,80	0,02	7,30	8,33
COND (µSm/cm)	50	2497,26	490,08	1166,96	302,50	47700,00	52	2090,77	1308,33	354,93	940,00	13233,33
DO (mg/l)	293	9,44	9,40	0,10	4,74	13,63	66	9,51	9,49	0,23	6,37	13,83
Dosat (%)	295	89,18	90,60	0,60	50,83	121,90	54	87,56	86,50	1,27	73,33	130,00
ORG_N (mg/l)	86	0,002	0,002	0,0001	0,00	0,00	69	2,25	1,01	1,23	0,23	85,94
NH4 (mg/l)	230	0,09	0,07	0,01	0,01	0,56	69	0,12	0,11	0,01	0,04	0,28
NO3 (mg/l)	192	3,67	3,73	0,10	0,25	7,13	69	3,19	3,04	0,11	1,40	4,95
NO2 (mg/l)	194	0,03	0,02	0,002	0,004	0,15	73	0,03	0,02	0,00	0,01	0,06
TDIN (mg/l)	192	3,80	3,89	0,10	0,41	7,15	69	3,33	3,18	0,11	1,56	5,17
TN (mg/l)	239	3,65	3,70	0,09	0,25	7,13	69	5,50	4,37	1,25	2,25	90,36
SPM (mg/l)	277	268,13	171,50	18,14	2,75	2082,00	53	94,46	46,00	13,19	14,14	423,00
CHL_A (µg/l)	204	4,69	4,18	0,22	0,50	19,35	6	18,31	17,75	2,41	10,00	25,80
PO4 (mg/l)	239	0,18	0,18	0,01	0,04	0,51	69	0,07	0,07	0,002	0,02	0,09
TP (mg/l)							73	0,35	0,25	0,03	0,10	1,20
DSI (mg/l)	27	2,09	2,18	0,14	0,22	3,14	3	0,49	0,42	0,08	0,40	0,66
N/P	190	52,88	46,41	1,73	10,78	139,19	69	134,85	120,84	8,72	42,22	487,67
N/DSi	26	4,36	3,34	0,47	2,16	9,75						
P/DSi	27	0,10	0,06	0,02	0,03	0,31						
BOD5 (mg/l)												
DIC (mg/l)												
PHAE							6	8,20	6,55	3,14	1,70	23,17
DOC (mg/l)							73	6,44	6,13	0,19	2,55	10,57
PN (mg/l)												
POC (mg/l)												
TOC (mg/l)							58	13,27	12,62	0,70	4,30	28,00
TIC (mg/l)												

Six-yearly winter average per estuary as a whole

	Elbe						Scheldt					
	n	mean	median	se	min	max	n	mean	median	se	min	max
CL (mg/l)	109	1266,23	129,00	301,25	83,00	16100,00	142	4329,99	367,63	471,63	55,30	16681,84
T (°C)	135	4,62	5,00	0,15	0,60	7,80	142	6,16	6,36	0,13	2,36	9,20
PH	134	7,90	7,90	0,01	7,70	8,10	142	7,78	7,72	0,02	7,42	8,20
COND (µSm/cm)	135	374,13	89,00	70,32	70,00	4450,00	94	2650,93	995,00	374,16	803,33	16116,67
DO (mg/l)	133	12,21	12,20	0,07	10,30	15,50	141	8,51	9,10	0,15	3,80	11,20
Dosat (%)	133	95,26	95,00	0,37	85,00	121,00	141	72,56	74,50	1,51	30,33	96,78
ORG_N (mg/l)	118	1,07	0,94	0,06	0,01	3,68	12	0,47	0,43	0,04	0,27	0,74
NH4 (mg/l)	120	0,20	0,16	0,01	0,04	0,47	142	0,77	0,64	0,06	0,03	2,80
NO3 (mg/l)	134	4,11	4,00	0,08	0,69	6,20	142	4,14	4,83	0,13	0,88	6,20
NO2 (mg/l)	131	0,03	0,02	0,002	0,01	0,11	142	0,09	0,08	0,00	0,01	0,24
TDIN (mg/l)	119	4,37	4,28	0,10	0,81	6,55	142	5,00	5,85	0,18	0,93	7,83
TN (mg/l)	133	5,45	5,30	0,12	0,96	8,30						
SPM (mg/l)	108	135,24	85,20	12,44	16,60	578,00	79	84,43	61,00	7,64	20,48	393,00
CHL_A (µg/l)	18	10,44	10,00	1,28	4,00	24,00	130	15,88	13,94	0,90	2,97	48,75
PO4 (mg/l)	134	0,05	0,05	0,001	0,01	0,10	142	0,27	0,21	0,01	0,06	0,66
TP (mg/l)	106	0,25	0,20	0,01	0,05	0,80	130	0,44	0,43	0,02	0,09	0,99
DSI (mg/l)	54	4,84	5,29	0,15	1,30	5,69	142	5,26	6,76	0,20	0,88	8,15
N/P	119	241,29	224,00	10,01	88,42	811,28	142	46,94	43,70	1,27	22,63	96,52
N/DSi	48	1,79	1,76	0,05	1,25	2,75	142	1,97	1,92	0,02	1,58	2,61
P/DSi	53	0,01	0,01	0,0004	0,01	0,02	142	0,05	0,05	0,001	0,02	0,08
BOD5 (mg/l)	134	2,66	2,20	0,10	1,17	6,13	94	7,40	7,45	0,28	1,40	13,27
DIC (mg/l)												
PHAE	18	17,17	12,00	2,95	5,00	43,00						
DOC (mg/l)	108	6,02	6,00	0,08	2,40	7,70	142	4,85	5,60	0,14	1,39	7,10
PN (mg/l)							46	0,44	0,43	0,03	0,10	0,80
POC (mg/l)	107	5,65	3,40	0,51	0,30	27,80	94	4,45	4,01	0,23	0,87	12,58
TOC (mg/l)												
TIC (mg/l)	108	24,67	24,00	0,27	20,00	33,00						

Six-yearly winter average per estuary as a whole (2)

	Humber						Weser					
	n	mean	median	se	min	max	n	mean	median	se	min	max
CL (mg/l)	53	4968,51	3180,51	815,83	22,27	21319,93	18	895,45	225,85	276,18	148,12	3989,37
T (°C)	72	5,44	5,42	0,10	3,35	7,12	18	5,60	5,40	0,30	3,60	8,73
PH	64	7,80	7,84	0,03	6,60	8,57	18	7,73	7,77	0,04	7,30	7,93
COND (µSm/cm)	13	440,27	451,50	28,43	302,50	669,00	13	1491,69	1120,00	352,97	975,00	5710,00
DO (mg/l)	73	11,36	11,40	0,13	9,46	13,63	17	11,60	11,80	0,24	9,90	13,83
Dosat (%)	73	94,50	94,75	0,79	78,30	114,50	14	92,89	92,50	1,32	85,67	106,67
ORG_N (mg/l)	19	0,002	0,002	0,0003	0,0002	0,004	18	6,02	1,24	4,70	0,67	85,94
NH4 (mg/l)	60	0,14	0,10	0,01	0,02	0,56	18	0,17	0,17	0,01	0,10	0,28
NO3 (mg/l)	50	3,90	3,95	0,18	0,95	5,98	18	4,16	4,20	0,14	2,93	4,95
NO2 (mg/l)	50	0,03	0,02	0,00	0,00	0,10	18	0,03	0,03	0,002	0,02	0,06
TDIN (mg/l)	50	4,08	4,24	0,18	1,00	6,13	18	4,37	4,38	0,14	3,13	5,17
TN (mg/l)	62	3,94	3,99	0,15	0,97	6,03	18	10,21	5,53	4,72	4,73	90,36
SPM (mg/l)	70	226,62	130,23	27,21	5,50	1143,50	13	113,40	47,50	37,55	14,14	423,00
CHL_A (µg/l)	55	3,26	2,90	0,30	0,50	9,50						
PO4 (mg/l)	62	0,16	0,16	0,01	0,04	0,44	18	0,06	0,06	0,003	0,04	0,08
TP (mg/l)							18	0,47	0,31	0,08	0,17	1,20
DSI (mg/l)	6	2,73	2,66	0,09	2,49	3,06						
N/P	49	67,03	66,92	3,73	27,58	139,19	18	169,70	172,43	7,44	120,84	233,44
N/DSi	6	3,24	3,09	0,21	2,76	3,94						
P/DSi	6	0,04	0,03	0,003	0,03	0,05						
BOD5 (mg/l)												
DIC (mg/l)												
PHAE												
DOC (mg/l)							18	8,15	8,40	0,34	5,25	10,57
PN (mg/l)												
POC (mg/l)												
TOC (mg/l)							15	17,45	17,67	1,61	7,03	28,00
TIC (mg/l)												

Six-yearly summer average per estuary as a whole

	Elbe						Scheldt					
	n	mean	median	se	min	max	n	mean	median	se	min	max
CL (mg/l)	166	1902,93	185,33	304,75	75,67	16700,00	143	5339,57	1929,50	506,96	57,33	17856,92
T (°C)	166	20,08	20,10	0,11	16,93	23,90	143	20,23	20,13	0,11	17,60	23,67
PH	166	8,01	7,87	0,03	7,60	9,23	143	7,86	7,87	0,02	7,43	8,30
COND (µSm/cm)	166	589,42	104,00	85,15	57,00	4656,67	92	4248,36	1000,67	608,68	757,00	19746,67
DO (mg/l)	166	7,23	7,17	0,15	3,80	14,37	143	6,08	6,54	0,16	1,03	8,95
Dosat (%)	166	80,19	79,17	1,78	42,00	170,67	143	70,94	76,35	2,05	11,67	102,70
ORG_N (mg/l)	81	0,67	0,62	0,03	0,22	1,44	28	0,50	0,51	0,03	0,22	0,78
NH4 (mg/l)	112	0,10	0,08	0,01	0,01	0,29	142	0,17	0,08	0,02	0,02	1,51
NO3 (mg/l)	166	1,72	1,78	0,05	0,04	2,97	143	3,20	3,80	0,13	0,29	5,17
NO2 (mg/l)	107	0,03	0,02	0,002	0,004	0,08	143	0,10	0,04	0,01	0,01	0,59
TDIN (mg/l)	88	1,64	1,72	0,06	0,06	2,65	142	3,46	4,03	0,14	0,36	6,33
TN (mg/l)	164	2,51	2,53	0,05	0,27	3,90						
SPM (mg/l)	166	59,36	43,93	3,46	5,70	217,33	142	56,08	52,18	2,79	8,62	170,00
CHL_A (µg/l)	33	59,38	19,00	11,36	5,00	210,00	134	90,81	41,71	8,70	5,21	467,75
PO4 (mg/l)	159	0,06	0,06	0,002	0,02	0,11	143	0,25	0,19	0,02	0,03	1,32
TP (mg/l)	166	0,15	0,14	0,004	0,04	0,35	133	0,46	0,34	0,03	0,06	1,83
DSI (mg/l)	80	0,66	0,43	0,08	0,04	3,00	142	1,27	1,03	0,10	0,05	4,94
N/P	71	80,02	71,05	5,43	9,62	212,58	136	35,10	34,21	0,97	8,09	66,12
N/DSi	36	19,97	7,28	4,26	1,28	114,90	134	33,45	7,20	8,80	1,87	1060,94
P/DSi	77	0,22	0,15	0,02	0,01	0,91	142	1,00	0,24	0,17	0,05	9,88
BOD5 (mg/l)	166	2,54	1,61	0,15	0,60	7,59	92	6,37	6,35	0,27	1,60	13,00
DIC (mg/l)							47	52,87	54,74	1,20	38,62	69,34
PHAE	33	31,03	14,67	5,14	3,33	99,33	91	34,21	30,05	2,49	4,10	123,67
DOC (mg/l)	166	5,95	6,08	0,06	3,17	7,33	143	4,49	4,83	0,13	1,58	7,10
PN (mg/l)							30	1,01	0,95	0,11	0,12	2,34
POC (mg/l)	166	3,03	2,67	0,13	0,20	8,43	61	7,04	6,58	0,46	1,19	16,79
TOC (mg/l)												
TIC (mg/l)	166	21,27	21,00	0,21	14,67	27,33						

Six-yearly summer average per estuary as a whole (2)

	Humber						Weser					
	n	mean	median	se	min	max	n	mean	median	se	min	max
CL (mg/l)	57	7272,90	6900,27	889,57	22,93	19048,13	17	1417,24	348,51	450,00	192,06	5329,15
T (°C)	74	17,33	17,38	0,18	13,80	20,82	17	20,04	19,90	0,19	18,25	21,71
PH	70	7,78	7,80	0,02	7,15	8,25	17	7,77	7,80	0,03	7,47	8,00
COND (µSm/cm)	13	4250,51	528,67	3622,29	433,67	47700,00	13	2361,18	1396,67	908,91	1119,00	13233,33
DO (mg/l)	73	7,36	7,42	0,13	4,74	11,68	16	7,29	7,27	0,12	6,37	8,18
Dosat (%)	74	81,85	82,82	1,50	50,83	120,00	13	78,74	76,67	1,21	73,33	86,00
ORG_N (mg/l)	22	0,002	0,0020	0,0002	0,0001	0,005	17	0,97	0,83	0,09	0,51	1,77
NH4 (mg/l)	56	0,06	0,04	0,01	0,01	0,28	17	0,09	0,10	0,01	0,04	0,18
NO3 (mg/l)	48	3,42	3,26	0,21	0,25	6,89	17	2,23	2,13	0,10	1,40	3,10
NO2 (mg/l)	48	0,04	0,03	0,01	0,00	0,15	19	0,03	0,02	0,00	0,01	0,06
TDIN (mg/l)	48	3,53	3,31	0,21	0,41	6,90	17	2,35	2,28	0,10	1,56	3,22
TN (mg/l)	59	3,35	3,24	0,18	0,25	6,89	17	3,23	3,20	0,15	2,25	4,93
SPM (mg/l)	68	250,45	139,73	40,96	2,75	1886,67	15	81,51	46,00	16,38	14,14	216,67
CHL_A (µg/l)	49	5,99	5,75	0,49	0,63	19,35	2	16,25	16,25	1,75	14,50	18,00
PO4 (mg/l)	59	0,23	0,21	0,01	0,05	0,51	17	0,07	0,07	0,003	0,04	0,09
TP (mg/l)							19	0,26	0,19	0,03	0,12	0,54
DSI (mg/l)	7	1,85	2,02	0,30	0,22	2,58	1	0,42	0,42		0,42	0,42
N/P	47	36,60	34,39	1,43	10,78	64,95	17	88,67	81,54	7,48	42,22	178,32
N/DSi	7	4,73	3,48	1,16	2,16	9,32						
P/DSi	7	0,14	0,11	0,04	0,05	0,31						
BOD5 (mg/l)												
DIC (mg/l)												
PHAE							2	4,50	4,50	2,80	1,70	7,30
DOC (mg/l)							19	5,42	5,67	0,19	3,17	6,93
PN (mg/l)												
POC (mg/l)												
TOC (mg/l)							14	10,59	10,37	0,78	5,65	16,17
TIC (mg/l)												

Six-yearly average for the freshwater zone per estuary

	Elbe						Scheldt					
	n	mean	median	se	min	max	n	mean	median	se	min	max
CL (mg/l)	415	141,71	130,00	2,42	63,00	479,33	196	86,17	76,49	2,52	55,30	326,31
T (°C)	433	13,23	14,20	0,31	0,60	23,90	196	13,92	13,98	0,39	3,60	23,67
PH	434	7,99	7,90	0,02	7,50	9,23	196	7,73	7,70	0,01	7,45	8,30
COND (µSm/cm)	435	89,95	87,00	0,85	57,00	203,33	196	939,19	912,17	7,88	757,00	1548,33
DO (mg/l)	429	9,32	9,90	0,13	3,80	15,50	195	6,35	6,43	0,14	0,85	10,55
Dosat (%)	428	86,41	88,00	1,03	42,00	170,67	195	60,13	60,67	1,27	7,50	100,00
ORG_N (mg/l)	242	0,79	0,73	0,03	0,01	2,32	2	0,64	0,64	0,14	0,50	0,78
NH4 (mg/l)	279	0,14	0,11	0,01	0,04	0,47	195	0,82	0,63	0,05	0,08	3,00
NO3 (mg/l)	431	2,77	2,70	0,05	0,62	6,20	196	4,96	5,07	0,05	1,62	6,20
NO2 (mg/l)	311	0,03	0,02	0,001	0,01	0,09	195	0,16	0,14	0,01	0,01	0,59
TDIN (mg/l)	244	3,19	3,04	0,09	0,70	6,55	194	5,95	5,86	0,07	3,66	7,83
TN (mg/l)	432	3,69	3,40	0,06	1,73	7,70						
SPM (mg/l)	411	65,89	42,20	3,42	9,00	527,00	161	84,07	75,28	3,08	17,00	227,50
CHL_A (µg/l)	71	55,98	25,00	7,05	5,00	210,00	195	101,06	73,50	6,64	10,00	467,75
PO4 (mg/l)	392	0,05	0,06	0,001	0,01	0,10	196	0,43	0,39	0,01	0,15	1,32
TP (mg/l)	413	0,17	0,15	0,004	0,05	0,79	195	0,72	0,66	0,02	0,31	1,83
DSI (mg/l)	185	2,55	2,65	0,15	0,02	5,69	195	4,97	5,12	0,16	0,05	8,15
N/P	220	180,98	162,48	7,80	60,57	811,28	187	37,52	35,76	1,15	8,09	76,73
N/DSi	91	15,82	2,07	3,91	1,19	235,59	184	21,09	2,19	6,50	1,33	1060,94
P/DSi	174	0,11	0,02	0,01	0,01	0,91	195	0,64	0,08	0,13	0,02	9,88
BOD5 (mg/l)	431	2,92	2,17	0,09	0,73	9,43	188	8,19	7,72	0,21	3,63	17,00
DIC (mg/l)							74	61,49	61,39	0,59	51,15	77,68
PHAE	71	30,27	26,00	2,62	5,00	99,33	137	45,60	44,00	1,70	14,00	123,67
DOC (mg/l)	414	6,15	6,20	0,02	4,90	7,33	196	5,79	5,93	0,05	3,76	7,20
PN (mg/l)							80	0,87	0,71	0,05	0,26	2,34
POC (mg/l)	411	3,28	2,40	0,14	0,10	23,00	161	6,71	5,93	0,25	1,88	16,82
TOC (mg/l)												
TIC (mg/l)	412	22,65	23,00	0,16	14,67	32,00						

Six-yearly average for the freshwater zone per estuary (2)

	Humber						Weser					
	n	mean	median	se	min	max	n	mean	median	se	min	max
CL (mg/l)	54	31,04	30,21	1,09	17,55	66,93	48	257,74	244,16	13,89	148,12	718,99
T (°C)	95	11,15	10,70	0,48	4,17	20,82	48	12,80	12,90	0,78	3,70	21,43
PH	95	7,82	7,85	0,02	7,21	8,57	48	7,81	7,83	0,03	7,30	8,33
COND (µSm/cm)	44	470,96	480,50	11,97	302,50	725,00	48	1506,44	1285,00	178,82	940,00	9700,00
DO (mg/l)	95	9,95	10,24	0,21	5,19	13,63	44	9,51	9,48	0,27	6,37	13,83
Dosat (%)	95	88,82	91,76	1,19	57,67	121,90	32	88,48	89,04	1,30	76,00	106,67
ORG_N (mg/l)	47	0,002	0,002	0,0002	0,0001	0,004	48	0,90	0,91	0,05	0,23	1,67
NH4 (mg/l)	95	0,10	0,09	0,01	0,03	0,27	48	0,12	0,10	0,01	0,04	0,28
NO3 (mg/l)	94	3,60	3,54	0,09	1,70	5,99	48	3,28	3,08	0,12	1,95	4,83
NO2 (mg/l)	95	0,03	0,02	0,002	0,01	0,09	48	0,03	0,03	0,001	0,01	0,06
TDIN (mg/l)	94	3,74	3,62	0,10	1,79	6,09	48	3,43	3,20	0,13	2,11	5,09
TN (mg/l)	94	3,64	3,57	0,09	1,71	6,04	48	4,29	4,33	0,14	2,70	6,10
SPM (mg/l)	87	163,02	37,90	27,12	4,50	1603,33	38	44,87	29,69	6,20	14,14	171,67
CHL_A (µg/l)	35	3,55	2,07	0,54	0,50	11,15						
PO4 (mg/l)	94	0,17	0,15	0,01	0,07	0,51	48	0,06	0,07	0,002	0,02	0,09
TP (mg/l)							48	0,24	0,20	0,02	0,12	0,63
DSI (mg/l)	24	2,29	2,38	0,10	1,39	3,14						
N/P	94	63,26	60,28	2,82	22,65	139,19	48	141,58	129,09	11,00	68,87	487,67
N/DSi	24	4,16	3,16	0,46	2,16	9,75						
P/DSi	24	0,09	0,06	0,02	0,03	0,29						
BOD5 (mg/l)												
DIC (mg/l)												
PHAE												
DOC (mg/l)							48	6,46	6,19	0,23	4,20	10,57
PN (mg/l)												
POC (mg/l)												
TOC (mg/l)							36	10,78	10,43	0,60	5,53	19,00
TIC (mg/l)												

Six-yearly average for the oligohaline zone per estuary

	Elbe						Scheldt					
	n	mean	median	se	min	max	n	mean	median	se	min	max
CL (mg/l)	88	1027,41	566,00	115,54	86,00	5120,00	126	909,35	378,80	99,71	61,81	5332,88
T (°C)	92	12,74	13,50	0,60	0,90	20,57	126	13,38	13,78	0,48	2,55	22,37
PH	91	7,93	7,90	0,01	7,60	8,20	126	7,61	7,61	0,01	7,42	7,92
COND (µSm/cm)	92	356,17	211,17	34,32	65,00	1600,00	126	3432,02	1757,33	304,82	830,67	16230,00
DO (mg/l)	92	9,41	8,75	0,18	6,93	13,00	126	4,65	4,75	0,19	0,83	10,45
Dosat (%)	92	87,43	89,00	0,57	75,00	97,00	126	42,90	44,00	1,62	8,33	77,50
ORG_N (mg/l)	16	1,76	1,75	0,22	0,43	3,68	33	0,55	0,52	0,02	0,22	0,78
NH4 (mg/l)	44	0,08	0,07	0,01	0,04	0,19	126	0,52	0,34	0,05	0,08	2,20
NO3 (mg/l)	92	2,93	2,65	0,10	1,60	5,00	126	4,55	4,63	0,05	3,04	5,80
NO2 (mg/l)	25	0,04	0,03	0,01	0,01	0,11	126	0,11	0,08	0,01	0,01	0,41
TDIN (mg/l)	16	4,17	4,60	0,29	1,70	5,20	126	5,18	5,01	0,08	3,16	7,12
TN (mg/l)	90	4,09	3,60	0,16	1,90	8,30						
SPM (mg/l)	88	192,50	142,75	15,08	15,20	714,00	105	83,60	67,80	5,67	24,39	393,00
CHL_A (µg/l)							104	33,99	19,88	2,94	9,59	137,25
PO4 (mg/l)	91	0,07	0,07	0,002	0,03	0,11	126	0,25	0,23	0,01	0,12	0,52
TP (mg/l)	87	0,29	0,25	0,02	0,10	0,80	103	0,41	0,39	0,01	0,18	1,01
DSI (mg/l)	43	2,47	1,80	0,27	0,42	5,69	126	4,41	4,73	0,18	0,28	7,59
N/P	16	167,39	182,19	20,57	29,54	295,48	126	52,89	50,65	1,66	20,63	106,94
N/DSi	7	2,09	1,79	0,24	1,59	3,41	126	5,53	2,51	1,12	1,58	116,84
P/DSi	43	0,05	0,04	0,01	0,01	0,23	126	0,14	0,05	0,03	0,02	2,31
BOD5 (mg/l)	90	1,48	1,30	0,07	0,68	4,09	121	5,90	5,80	0,22	1,40	11,13
DIC (mg/l)							42	49,75	49,62	0,82	40,85	64,02
PHAE							89	19,56	16,07	1,03	5,40	48,33
DOC (mg/l)	88	6,01	5,98	0,06	4,40	7,20	126	5,64	5,58	0,06	4,10	7,10
PN (mg/l)							51	0,54	0,51	0,04	0,10	1,20
POC (mg/l)	87	7,04	5,40	0,58	0,73	28,80	105	4,51	4,29	0,22	0,87	12,58
TOC (mg/l)												
TIC (mg/l)	88	24,52	24,00	0,37	19,00	35,00						

Six-yearly average for the oligohaline zone per estuary (2)

	Humber						Weser					
	n	mean	median	se	min	max	n	mean	median	se	min	max
CL (mg/l)	40	642,68	130,78	142,91	30,26	3804,13	21	3017,61	2833,80	340,36	419,08	6171,30
T (°C)	44	10,99	11,24	0,70	3,45	20,20	21	12,85	12,73	1,25	3,60	21,71
PH	41	7,56	7,62	0,04	6,60	7,93	21	7,77	7,77	0,02	7,43	7,97
COND (µSm/cm)	3	1549,67	1850,00	447,69	669,00	2130,00	4	9102,71	8805,00	2018,56	5567,50	13233,33
DO (mg/l)	45	9,13	9,01	0,31	4,74	12,70	21	9,32	9,45	0,39	6,77	12,00
Dosat (%)	45	81,30	81,67	1,63	50,83	100,33	21	84,14	84,50	1,43	73,33	93,67
ORG_N (mg/l)	21	0,002	0,002	0,0002	0,001	0,005	21	5,34	1,29	4,03	0,56	85,94
NH4 (mg/l)	41	0,14	0,10	0,02	0,01	0,56	21	0,12	0,12	0,01	0,05	0,18
NO3 (mg/l)	41	5,03	4,98	0,15	2,99	7,13	21	2,98	3,00	0,24	1,40	4,95
NO2 (mg/l)	41	0,05	0,05	0,01	0,00	0,15	21	0,02	0,01	0,003	0,01	0,06
TDIN (mg/l)	41	5,23	5,10	0,14	3,20	7,15	21	3,12	3,15	0,24	1,56	5,17
TN (mg/l)	41	5,08	5,04	0,15	3,03	7,13	21	8,26	4,44	4,11	2,25	90,36
SPM (mg/l)	37	480,73	473,93	67,19	42,50	1886,67	15	220,09	200,00	21,34	100,00	423,00
CHL_A (µg/l)	41	5,60	5,25	0,59	0,71	19,35						
PO4 (mg/l)	41	0,28	0,27	0,01	0,13	0,44	21	0,07	0,06	0,004	0,04	0,09
TP (mg/l)							21	0,64	0,61	0,04	0,32	1,20
DSI (mg/l)												
N/P	41	45,70	41,18	2,31	27,58	101,35	21	119,48	118,87	13,49	42,22	233,44
N/DSi												
P/DSi												
BOD5 (mg/l)												
DIC (mg/l)												
PHAE												
DOC (mg/l)							21	6,85	6,35	0,30	4,63	9,27
PN (mg/l)												
POC (mg/l)												
TOC (mg/l)							21	17,99	17,00	0,99	9,73	28,00
TIC (mg/l)												

Six-yearly average for the mesohaline zone per estuary

	Elbe						Scheldt					
	n	mean	median	se	min	max	n	mean	median	se	min	max
CL (mg/l)	66	5708,52	6055,00	313,14	422,00	10616,67	100	6545,28	6198,06	279,97	1810,51	13482,65
T (°C)	69	12,26	13,30	0,65	1,80	20,17	100	13,28	13,00	0,53	2,38	22,23
PH	68	8,02	8,00	0,02	7,87	8,70	100	7,88	7,88	0,01	7,63	8,11
COND (µSm/cm)	69	1700,60	1780,00	87,38	177,00	3110,00	48	14558,02	14836,67	637,73	6576,67	23383,33
DO (mg/l)	68	9,46	9,20	0,20	7,00	13,00	100	8,18	7,92	0,13	5,67	11,20
Dosat (%)	68	90,44	91,00	0,80	78,00	116,00	100	80,91	81,64	0,88	57,67	100,74
ORG_N (mg/l)	33	0,62	0,43	0,09	0,17	2,72	39	0,54	0,54	0,02	0,22	0,78
NH4 (mg/l)	47	0,09	0,08	0,01	0,04	0,23	100	0,14	0,08	0,01	0,01	0,72
NO3 (mg/l)	68	2,19	1,98	0,12	0,47	4,50	100	3,23	3,13	0,10	1,42	5,12
NO2 (mg/l)	46	0,02	0,02	0,002	0,01	0,07	100	0,05	0,05	0,00	0,01	0,12
TDIN (mg/l)	34	2,05	1,63	0,18	0,53	4,61	100	3,42	3,28	0,11	1,45	5,78
TN (mg/l)	68	2,94	2,45	0,17	0,83	7,00						
SPM (mg/l)	64	92,85	70,50	9,80	21,00	443,00	92	55,84	41,66	4,63	15,42	237,00
CHL_A (µg/l)	20	8,95	6,00	1,91	3,00	41,00	77	16,00	12,19	1,25	3,43	56,87
PO4 (mg/l)	65	0,07	0,07	0,003	0,01	0,12	100	0,17	0,16	0,005	0,09	0,33
TP (mg/l)	64	0,16	0,14	0,01	0,06	0,47	77	0,26	0,24	0,01	0,14	0,58
DSI (mg/l)	22	1,88	1,35	0,32	0,30	4,69	100	2,52	2,55	0,14	0,45	5,84
N/P	33	69,48	46,24	8,54	17,97	175,74	100	47,65	41,28	1,86	21,10	97,34
N/DSi	13	2,14	1,88	0,22	1,35	3,58	100	4,22	3,04	0,30	1,66	20,47
P/DSi	20	0,05	0,04	0,01	0,01	0,13	100	0,11	0,08	0,01	0,02	0,33
BOD5 (mg/l)	69	1,38	1,25	0,06	0,60	2,85	46	3,56	3,18	0,21	1,55	8,43
DIC (mg/l)							17	40,67	39,99	0,59	37,45	47,21
PHAE	20	10,49	8,33	1,50	4,00	34,00	34	7,53	6,42	0,58	4,10	19,10
DOC (mg/l)	66	5,42	5,28	0,10	3,60	7,70	100	4,37	4,33	0,10	2,25	6,73
PN (mg/l)							20	0,31	0,26	0,04	0,10	0,94
POC (mg/l)	64	3,09	2,10	0,35	0,50	14,50	40	2,44	2,26	0,22	0,94	8,87
TOC (mg/l)												
TIC (mg/l)	66	24,40	24,00	0,33	19,00	30,00						

Six-yearly average for the mesohaline zone per estuary (2)

	Humber					
	n	mean	median	se	min	max
CL (mg/l)	56	7229,68	7011,36	321,23	1758,77	12831,90
T (°C)	75	10,98	10,85	0,53	3,35	20,75
PH	62	7,73	7,76	0,02	7,15	8,05
COND (µSm/cm)	2	25896,00	25896,00	2575,00	23321,00	28471,00
DO (mg/l)	73	9,37	9,25	0,19	6,69	13,45
Dosat (%)	75	88,95	87,67	0,98	74,00	114,50
ORG_N (mg/l)	14	0,002	0,001	0,0003	0,0001	0,004
NH4 (mg/l)	57	0,07	0,03	0,01	0,01	0,47
NO3 (mg/l)	38	3,70	3,73	0,14	1,99	5,69
NO2 (mg/l)	39	0,02	0,01	0,003	0,004	0,07
TDIN (mg/l)	38	3,81	3,83	0,14	2,09	5,77
TN (mg/l)	66	3,95	3,88	0,09	2,77	5,72
SPM (mg/l)	73	402,27	319,00	38,14	21,50	2082,00
CHL_A (µg/l)	67	5,53	5,64	0,38	0,50	14,34
PO4 (mg/l)	66	0,20	0,19	0,01	0,07	0,33
TP (mg/l)						
DSI (mg/l)						
N/P	37	43,27	40,97	1,86	25,68	80,46
N/DSi						
P/DSi						
BOD5 (mg/l)						
DIC (mg/l)						
PHAE						
DOC (mg/l)						
PN (mg/l)						
POC (mg/l)						
TOC (mg/l)						
TIC (mg/l)						

Six-yearly average for the polyhaline zone per estuary

	Elbe						Scheldt					
	n	mean	median	se	min	max	n	mean	median	se	min	max
CL (mg/l)	34	14514,31	14900,00	304,95	10500,00	17800,00	144	13677,68	14013,03	197,90	6751,73	17929,34
T (°C)	36	12,22	12,40	0,79	2,30	19,43	144	11,98	11,61	0,43	2,36	20,06
PH	36	8,18	8,10	0,03	8,00	8,80	144	8,06	8,05	0,01	7,80	8,24
COND (µSm/cm)	36	4077,22	4125,00	72,39	3050,00	4940,00						
DO (mg/l)	36	9,37	9,20	0,23	6,50	12,50	144	8,89	9,09	0,09	7,11	10,77
Dosat (%)	36	96,12	94,00	2,00	75,00	138,00	144	94,93	93,98	0,38	85,69	110,61
ORG_N (mg/l)	19	0,33	0,30	0,07	0,03	1,29						
NH4 (mg/l)	27	0,10	0,09	0,01	0,01	0,25	144	0,07	0,06	0,004	0,01	0,34
NO3 (mg/l)	36	0,59	0,41	0,08	0,04	1,90	144	1,44	1,31	0,06	0,29	3,62
NO2 (mg/l)	25	0,02	0,02	0,003	0,003	0,06	144	0,03	0,03	0,002	0,01	0,12
TDIN (mg/l)	21	0,75	0,51	0,13	0,06	2,11	144	1,54	1,40	0,06	0,36	3,79
TN (mg/l)	32	1,05	0,86	0,12	0,27	3,30						
SPM (mg/l)	36	21,62	14,78	3,31	5,40	106,00	144	36,94	32,46	1,47	8,62	111,86
CHL_A (µg/l)	24	9,37	8,50	1,82	3,00	47,00	144	18,06	13,95	1,35	2,97	79,08
PO4 (mg/l)	32	0,03	0,03	0,002	0,01	0,06	144	0,09	0,09	0,00	0,03	0,15
TP (mg/l)	36	0,06	0,06	0,005	0,02	0,17	144	0,15	0,16	0,00	0,06	0,24
DSI (mg/l)	36	0,70	0,39	0,12	0,03	2,70	144	1,12	0,96	0,06	0,08	3,40
N/P	21	44,89	27,08	7,82	9,62	117,90	144	40,22	35,85	1,67	15,99	123,03
N/DSi	21	2,09	1,49	0,33	0,63	7,35	144	6,42	2,77	0,63	1,67	51,53
P/DSi	32	0,10	0,05	0,03	0,01	0,79	144	0,17	0,11	0,01	0,03	1,08
BOD5 (mg/l)	36	1,71	1,44	0,14	0,73	4,36						
DIC (mg/l)												
PHAE	24	5,79	4,50	0,59	3,00	14,00						
DOC (mg/l)	34	3,42	3,52	0,11	2,20	4,70	144	2,35	2,22	0,05	1,39	4,31
PN (mg/l)												
POC (mg/l)	32	0,87	0,60	0,14	0,10	3,30						
TOC (mg/l)												
TIC (mg/l)	34	24,36	24,33	0,35	19,00	28,00						

Six-yearly average for the polyhaline zone per estuary (2)

	Humber						Weser					
	n	mean	median	se	min	max	n	mean	median	se	min	max
CL (mg/l)	71	14226,93	14529,51	348,76	5721,93	21319,93						
T (°C)	80	10,56	9,74	0,49	3,65	18,30	1	15,00	15,00		15,00	15,00
PH	71	7,92	7,92	0,01	7,60	8,25	1	8,00	8,00		8,00	8,00
COND (µSm/cm)	1	47700,00	47700,00		47700,00	47700,00						
DO (mg/l)	80	9,07	9,20	0,13	6,87	11,68	1	13,50	13,50		13,50	13,50
Dosat (%)	80	94,24	93,53	0,76	81,60	120,00	1	130,00	130,00		130,00	130,00
ORG_N (mg/l)	4	0,003	0,003	0,001	0,0002	0,005						
NH4 (mg/l)	37	0,05	0,03	0,01	0,01	0,27						
NO3 (mg/l)	19	0,97	0,99	0,08	0,25	1,69						
NO2 (mg/l)	19	0,01	0,01	0,00	0,00	0,05	4	0,01	0,01	0,001	0,01	0,01
TDIN (mg/l)	19	1,05	1,05	0,09	0,41	2,02						
TN (mg/l)	38	1,62	1,51	0,13	0,25	3,72						
SPM (mg/l)	80	161,69	118,84	13,42	2,75	528,25						
CHL_A (µg/l)	61	3,80	3,35	0,27	0,96	9,13	6	18,31	17,75	2,41	10,00	25,80
PO4 (mg/l)	38	0,10	0,09	0,01	0,04	0,19						
TP (mg/l)							4	0,12	0,12	0,01	0,10	0,13
DSI (mg/l)	3	0,46	0,41	0,16	0,22	0,77	3	0,49	0,42	0,08	0,40	0,66
N/P	18	34,72	32,78	2,84	10,78	55,04						
N/DSi	2	6,81	6,81	2,51	4,30	9,32						
P/DSi	3	0,18	0,15	0,07	0,07	0,31						
BOD5 (mg/l)												
DIC (mg/l)												
PHAE							6	8,20	6,55	3,14	1,70	23,17
DOC (mg/l)							4	3,96	3,65	0,75	2,55	6,00
PN (mg/l)												
POC (mg/l)												
TOC (mg/l)							1	4,30	4,30		4,30	4,30
TIC (mg/l)												

Attachment 3:

Correlation tables per TIDE estuary

Correlations (r> 0.5) per parameter found in all estuaries

	Elbe		**Scheldt**		**Weser**		**Humber**	
Temperature (T)	DO	*-0,54*	P_Si	*0,53*	DO	*-0,71*	DO	*-0,64*
	DSI	*-0,50*			DOsat	*-0,51*		
	NO3	*-0,52*			NO3	*-0,55*		
	P_Si	*0,50*			TDIN	*-0,56*		
	TDIN	*-0,58*			TN	*-0,58*		
Chlorid (CL)	COND	*0,91*	COND	*0,80*	CHL_A	*-0,52*	COND	*0,70*
			DIC	*-0,51*	COND	*0,78*		
			DOC	*-0,69*				
			NO3	*-0,71*				
			PO4	*-0,58*				
			TDIN	*-0,72*				
			TP	*-0,66*				
Conductivity (COND)	CL	*0,91*	CL	*0,80*	CL	*0,78*	CL	*0,70*
	PHAE	*-0,55*					NO3	*0,52*
							TDIN	*0,51*
							TN	*0,52*
Dissolved oxygen (DO)	DOsat	*0,75*	DOsat	*0,66*	DOsat	*0,75*	DOsat	*0,59*
	P_Si	*-0,63*			NO3	*0,56*	T	*-0,64*
	T	*-0,54*			T	*-0,71*		
					TDIN	*0,56*		
					TN	*0,54*		

Correlations (r> 0.5) per parameter found in all estuaries (2)

	Elbe		**Scheldt**		**Weser**		**Humber**	
Dissolved oxygen saturation (DOsat)	DO	*0,75*	DO	*0,66*	DO	*0,75*	DO	*0,59*
	P_Si	*-0,51*	DOC	*-0,50*	T	*-0,51*		
	pH	*0,58*	pH	*0,70*				
			TP	*-0,54*				
Total dissolved inorganic nitrogen (TDIN)	DSi	*0,57*	CL	*-0,72*	DO	*0,56*	COND	*0,51*
	N_P	*0,58*	DOC	*0,66*	N_P	*0,60*	NO3	*0,96*
	NO3	*0,96*	NH4	*0,55*	NO3	*0,97*	TN	*0,96*
	P_Si	*-0,54*	NO3	*0,86*	T	*-0,56*		
	T	*-0,58*	pH	*-0,51*	TN	*0,70*		
	TN	*0,84*	TN	*0,72*				
			TP	*0,58*				
Nitrate (NO3)	DSi	*0,54*	DOC	*0,61*	DO	*0,56*	COND	*0,52*
	NO3	*-0,71*	DSi	*0,55*	N_P	*0,59*	TDIN	*0,96*
	N_P	*0,56*	TDIN	*0,86*	T	*-0,55*	TN	*0,99*
	T	*-0,52*	TN	*0,56*	TDIN	*0,97*		
	TDIN	*0,96*	TP	*0,59*	TN	*0,70*		
	TN	*0,81*						
Phosphate (PO4)	BOD5	*-0,51*	CL	*-0,58*	N_P	*-0,66*	P_Si	*0,50*
			DOC	*0,54*				
			TP	*0,59*				

Correlations (r> 0.5) per parameter found in 3 out of 4 estuaries studied

	Elbe		**Scheldt**		**Weser**		**Humber**	
Suspended matter concentration (SPM)	POC	*0,61*	EUPH_D	*-0,56*	TOC	*0,68*		
	TP	*0,66*	TP	*0,56*	TP	*0,68*		
			Kd	*0,54*				
N/Si ratio (N_Si)	DSi	*-0,56*	DSi	*-0,58*			CL	*0,51*
			P_Si	*0,53*				
P/Si ratio (P_Si)	DO	*-0,63*	DSi	*-0,56*			PO4	*0,50*
	DOsat	*-0,51*	N_Si	*0,53*			N_P	*-0,56*
	DSi	*-0,78*	T	*0,53*				
	T	*0,50*						
	TDIN	*-0,54*						
N/P ratio (N_P)	NO3	*0,56*			NO3	*0,59*	P_Si	*-0,56*
	TDIN	*0,58*			PO4	*-0,66*		
	TN	*0,56*			TDIN	*0,59*		
Chlorophyll a (CHL_A)	BOD5	*0,59*	PHAE	*0,60*	CL	*-0,52*		
	PHAE	*0,62*	PN	*0,52*				
Total phosphorous (TP)	SPM	*0,66*	ORG_N	*0,51*	TOC	*0,71*		
			DOC	*0,56*	SPM	*0,68*		
			PN	*0,52*				
			TDIN	*0,58*				
			PO4	*0,59*				
			SPM	*0,56*				
			NO3	*0,59*				
			DOsat	*-0,54*				
			CL	*-0,66*				

Correlations (r> 0.5) per parameter found in 2 out of 4 estuaries studied

	Elbe		**Scheldt**			**Elbe**		**Scheldt**	
pH	DOsat	*0,58*	DOC	*-0,54*	**Particulate Organic Carbon (POC)**	PHAE	*0,57*	EUPH_D	*-0,65*
			DOsat	*0,68*		SPM	*0,62*	Kd	*0,62*
			TDIN	*-0,51*				ORG_N	*0,53*
Organic nitrogen (ORG_N)	PHAE	*0,55*	PN	*0,64*				PHAE	*0,61*
			POC	*0,53*				PN	*0,87*
			TP	*0,51*					
Dissolved silica (DSi)	N_Si	*-0,55*	N_Si	*-0,58*	**Dissolved organic carbon (DOC)**	PHAE	*0,57*	CL	*-0,69*
	NO3	*0,54*	NO3	*0,55*				DOsat	*-0,50*
	P_Si	*-0,78*	P_Si	*-0,56*				NO3	*0,61*
	T	*-0,50*						pH	*-0,54*
	TDIN	*0,57*						PO4	*0,54*
Phaeopigments (PHAE)	BOD5	*0,51*	CHL_A	*0,60*				TDIN	*0,66*
	CHL_A	*0,62*	PN	*0,63*				TP	*0,56*
	COND	*-0,55*	POC	*0,61*					
	DOC	*0,57*							
	ORG_N	*0,55*							
	POC	*0,57*							

Correlations (r> 0.5) per parameter found specific for 1 estuary

	Elbe		**Scheldt**		**Weser**		**Humber**	
Biological oxygen demand (BOD5)	CHL_A	*0,59*						
	PHAE	*0,51*						
	PO4	*-0,51*						
Euphotic depth (EUPH_D)			Kd	*-0,99*				
			POC	*-0,65*				
			SPM	*-0,56*				
Ammonium (NH4)			TDIN	*0,55*				
Dissolved inorganic carbon (DIC)			CL	*-0,51*				
Total organic carbon (TOC)					SPM	*0,68*		
					TP	*0,71*		