UMEÅ UNIVERSITET

SPATIOTEMPORAL VARIATIONS OF NUTRIENTS AND WATER COLOUR IN ÖRE RIVER AND RECIPIENT COASTAL WATERS

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Abstract

Inputs of nitrogen, phosphorus and organic carbon can lead to the deterioration of the coastal ecosystems, through the disturbance of food web efficiency, eutrophication of waters or promotion of toxic cyanobacteria 'blooms'. Climate warming may worsen such effects. The aim of this study was to assess changes in carbon, nitrogen and phosphorous concentrations and water colour in the Öre River (north Sweden), and the adjacent coastal area during the 1991-2020 period. Time series analyses showed that organic carbon increased in both the river and the coast during the study period, while the water colour did not. In contrast, brown-coloured humic substances decreased in coastal waters. The inorganic nitrogen showed decreasing concentrations in both the river and coastal waters, while phosphorus increased at the coast. The ratio between inorganic nitrogen and phosphorus indicates a general phosphorus limitation in the river. In contrast, a change from phosphorus limitation in the 90's to nitrogen limitation during the last 10 years was observed at the coast. The increasing organic carbon concentrations might be due to changed land use or climate warming, since the river inflow did not show any increasing or decreasing trend. Decreasing nitrogen concentrations in the river during the 90's might be coupled to reduced forest fertilization. Increased phosphorus concentrations in the coast may be linked to eutrophication and inflows from the Baltic Proper. Taken together, this study showed that key factors have changed during the past 30 years, potentially influencing the ecosystem services in rivers and coasts of the northern Baltic Sea.

Key words: nutrients inputs, water colour , coastal waters, freshwater, river.

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1. Introduction

River ecosystems comprise some of the most biodiverse spots on Earth and carry out numerous biophysical processes essential to life. They enable the transport of nutrients, dissolved substances, suspended organic and inorganic particles and act as ecological corridors, allowing the movement of fauna through different habitats, and transporting seeds from upper land to seas and oceans contributing the dispersion of the flora (Sabater and Elosegi, 2009).

Rivers are also essential to human development: they sustain many ecosystem services such as water for agriculture or household consumption; provide habitat for fish; generate hydropower electricity; and breakdown of wastewater (Allan and Castillo, 2007). Adequate river water management is essential to protect rivers from anthropogenic impacts, as almost every river in the world has already lost their natural condition as a consequence of human activities taking place around them (Malmqvist and Rundle, 2002).

Sweden is no difference and rivers are also under significant pressure by human activity. This pressure is also transferred to the receiving coastal waters, as rivers transport great amounts of nutrients and other substances from inland into the sea. This is the case of the national river mouths that lead to the Baltic Sea, except those within the Skagerrak and Kattegat Water District, e.g., Lagan, Ätran, Viskan or Göta älv, which currently experience a number of water quality issues (SwAM, 2021). Coastal areas are transition zones, or ecotones, which means they are sensitive zones susceptible to a great degree of physio-chemical change, where even small changes on the environmental conditions can have a greater impact on the local aquatic communities they host (Attrill and Rundle, 2002). Much of the nutrients and substances that reach coastal waters are sourced through freshwater outputs from rivers.

The load of nutrients and its sources (natural or anthropogenic) into waterbodies include nitrates and nitrites, which are the most abundant, as well as phosphates and organic matter, which include a number of carbon-based compounds and humic substances originating from organic fractions of nearby soils (Shrestha et al., 2008). Nitrates are usually sourced from nitrogen-based fertilizers (e.g., potassium nitrate), animal or human waste that is not adequately treated in wastewater treatment plants. Nitrites can easily be oxidized to nitrates, and therefore are found in lower concentrations than nitrates, which generally predominate in ground and surface waters (Shrestha et al., 2008).

Phosphates, also come from overfertilized soils and urban wastewater (with a significant proportion coming from laundry and cleaning products), industrial effluents or natural sources (i.e., phosphorus-rich bedrock) (Shrestha et al., 2008). Indeed, the Öre River estuary is dominated by basic and intermediate rocks (e.g., basic metavolcanics and granodiorites), composed by rich-phosphate minerals (Forsgren and Jansson, 1993), which might act as a contributor to phosphate concentrations in the river. With regards to sources of organic matter, two major natural inputs can be distinguished, coniferous forests and peatlands, while human induced sources include wastewater, deforestation, or events like wildfires which can introduce great amounts of particulate organic matter in a very short timeframe (Finstad et al. 2016).

There is scientific consensus on the effect of nutrient loading into aquatic ecosystems, especially nitrogen and phosphorus, as these are drivers of the increase of eutrophication events. This is mainly due to the fact that algal growth in aquatic ecosystems is frequently limited by either of these nutrients (Shrestha et al., 2008; Paerl and Huisman, 2009; Lefébure et al., 2013; Andersson et al., 2015). The Redfield ratio is an indicator of optimal conditions for phytoplankton to grow (Redfield, 1934; Danish Environmental Protection Agency and National Environmental Research Institute, 2021). The disturbance in this ratio can lead to negative impacts on the river ecosystem, such as algal or cyanobacteria blooms (and the resulting cyanotoxins released). The aftereffect of this process is a deterioration of the water quality and it is often dangerous for animal and human health, as well as a main cause of economic loss (Paerl and Huisman, 2009).

The use of chemical indicators to measure river water quality as a proxy to evaluate ecosystem health is a common procedure. Water quality monitoring uses a number of parameters to do so (biological and hydro-morphological). However, this project will focus on chemical water quality indicators -and observance- to elucidate how these might be determined by the geomorphology and human activity taking place in the Öre River catchment area.

In Sweden, river water quality is regulated by the Water Framework Directive (WFD). The Directive was developed in late 1990s, in response to a general increasing concern over the deterioration of freshwaters, including rivers, lakes, transitional waters and coastal waters out to one nautical mile (12 nautical miles for chemical status, i.e., for territorial waters) (DG Environment, 2021). The WFD is the base legislation in freshwater matters and is a guideline of actions to be taken to protect waterbodies from human polluting activities and climate change. One way of protecting rivers is through monitoring and keeping track of any environmental disturbances that these can experience (Collins et al., 2012).

The main objective of this study is to assess the spatial variation of different concentrations of nutrients and the water colour between the Öre River (northern Sweden), and two coastal stations, situated in the first 10 kilometres stretching from the coastal margin into the sea, within the Öre estuary. The analysis will aim to identify positive or negative trends of nutrient concentrations and water colour, in both, river and coastal water locations. These objectives were approached through analysis of long-term data series for several environmental parameters during the period 1991-2020.

Previous investigations have been carried out in the Öre River and estuary (Forsgren and Jansson, 1993; Ivarsson and Jansson, 1994; Laudon, et al., 2004; Malmgren and Brydsten, 1992; Ågren et al., 2007; Ågren, 2007). This analysis aims to develop new information that can add to this wealth of evidence as it is important to keep track of the water quality status of the Öre River and the corresponding estuary, as well as to continue monitoring the fluctuations of nutrients and water colour taking place to enable the prediction of the river ecosystem responses to future environmental change.

Specifically, this study will focus on the following research questions:

- Identify significantly representative differences on the concentrations of selected parameters: nitrate, phosphate, total nitrogen, and total phosphorus between river and coastal waters.
- Characterise the difference of the concentration of organic carbon (DOC and TOC) and colour (humic substances and absorbance 420) between river and coastal waters between river and coastal waters.
- Establish whether these parameters show positive or negative trends over time.

2. Materials and methods

2.1. Study area description

The study area comprises the Öre River catchment area and the recipient coastal area, more specifically, the first 10 kilometres stretching from the coastal margin into the sea (Fig. 1a and 1b). The estuary formed by the river is circa 50 km^2 with a mean depth of 16 m, semi-closed and with low salinity levels (Malmgren and Brydsten, 1992). The elevation in the basin ranges from 0 to 713 meters above sea level. The Öre River catchment area is located in the north of Sweden and it follows a NW-SE trajectory, it covers 2970 km^2, and the length of the main river is 225 km. The river mouth leads to the Baltic Sea, specifically to the Bothnian Sea (Forsgren and Jansson, 1993).

According to Köppen and Geiger (1930), the corresponding climate classification is Dfc, characterised by precipitation in the form of snow (D), it is fully humid (f), and it has cool summers (c). The annual average temperature is 4.3 ºC, and the average volume of precipitation is 790 mm year^{-1} (2004-2020). The evapotranspiration, however, is relatively low with a mean of 378 mm year $^{-1}$ (1981-2010) compared with the mean precipitation in the same period (775 mm year $^{-1}$) (Ivarsson and Jansson, 1994).

The adjacent land to the river basin is composed by different topographies and land uses, where the forest predominates with a 79% of land coverage, followed by a 16% of marshes and other wetlands, 2% of land coverage by lakes and watercourses, 1% of farming land, 1 % of moorlands, 0.2% coverage of urban land, and 0.02 % of bedrock (SMHI, 2021).

Podzols with a humus layer of ca. 7 cm thick predominate in the area (Ivarsson and Jansson, 1994). These are usually characteristic soils of cold and humid climates, and very common in Scandinavia (Schad, 2016).

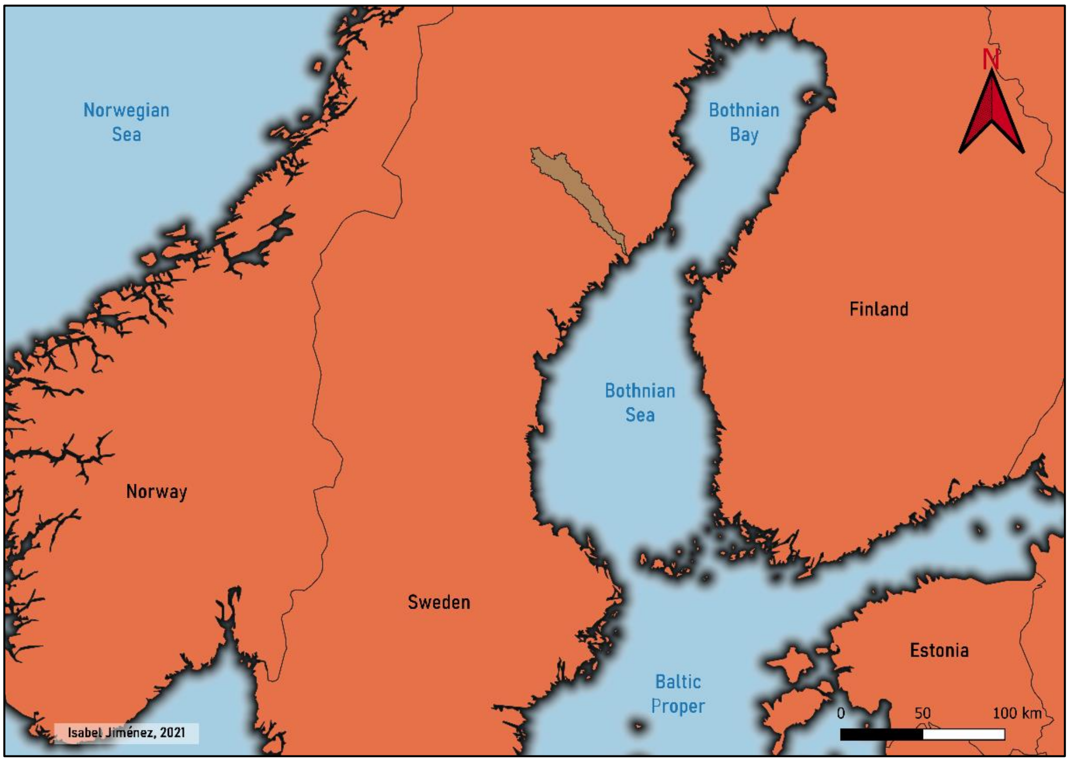


Figure 1a. Study area map. Grey delimited zone: Öre River watershed.

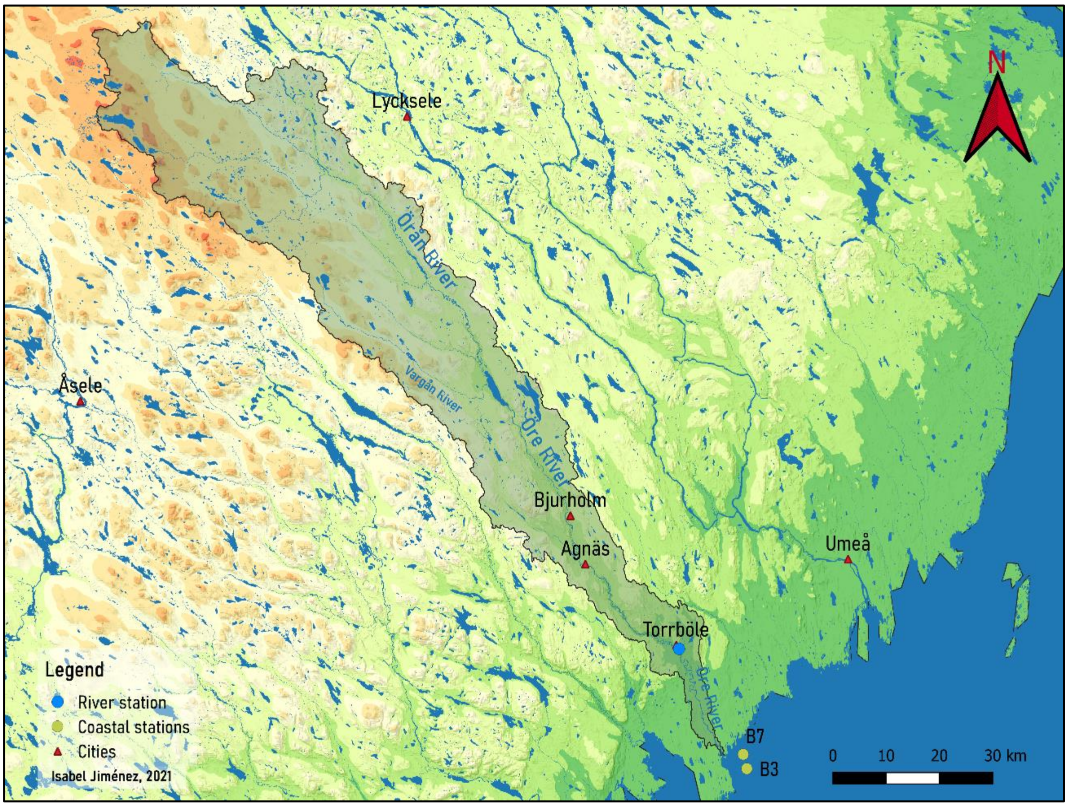


Figure 1b. Sample stations map. Torrböle (blue dot): river station at Torrböle. B3 and B7 (green dots): coastal stations. Grey delimited zone: Öre River watershed.

2.2. Data collection

The river data were collected from SLU (https://miljodata.slu.se/MVM/Search), while the coastal waters data was retrieved from SMHI (https://www.smhi.se/en/services/open-data/national-archive-for-oceanographic-data/download-data-1.153150). The selection of parameters was constrained by their availability in databases, to enable a robust comparison between the overall status of river and coastal waters. All the chosen data samples were water column samples taken at the surface (0-1 meters).

Selected parameters included: river flow; nitrate and nitrite concentration (NO2 + NO3, from now on only nitrates to simplify); phosphate (PO4); total nitrogen (TN); total phosphorus (TP); total organic carbon (TOC); and absorbance 420 (filtered), for the river, and nitrates and nitrites (NO2 + NO3, from now on nitrates); phosphate (PO4); total nitrogen; total phosphorus; dissolved organic carbon (DOC); and humic substances (HS) for the coastal stations.

These parameters were chosen due to their optimal characteristics to be able to determine chemical changes in the water column, both at river and marine stations, throughout the period 1991-2020, except for humic substances, for which data availability was limited to the period 1998 to 2020. DOC in the sea is almost the same as TOC in the Öre River, since the particulate fraction is never higher than 5% of TOC (Ågren et al. 2007). For river data, one sample was taken every month in the monitoring station of Torrböle (Fig. 1b), generally, there are between 10-12 samples per year. On the contrary, for the coastal data, one or two samples, were taken every month at two sampling stations (B3: 63°29'58.9"N 19°49'08.4"E and B7: 63°31'30.0"N 19°48'29.5"E; Fig. 1b). The year 2021 was not included in this analysis, since the dataset was incomplete for that year.

2.3. Data processing and statistical analysis

Raw data was processed in Excel, first to filter out the time series years (data were available from the 1960s for most parameters, except for the humic substances for which the measurements started in 1998), and secondly to calculate the annual means of each parameter. The annual mean was chosen because the different variables showed different seasonal patterns which would make the comparison too complex.

The values were then represented in combined plots (bars for annual mean, and lines for moving average over 3 years), to observe the trend and smoothen the inter-annual variability visually (Fig. 2). This was made with Grapher v.12, a graphing tool application software, to make the plots.

Additionally, the DIN:DIP ratio was calculated and represented in a bar plot (Fig. 3), in order to observe when the water was in a nitrogen limited or phosphorus limited state. As well, the Humic substances:DOC ratio and the Absorbance 420:TOC ratio (Fig. 4) were calculated and represented in plots to establish the changes in the colour of the water.

The independence of the variables over time was checked using autocorrelation test. As well, cross correlation tests were run to exclude the similarity and lag of series between pairs of variables. Thereafter, trend analyses (Mann-Kendall test) for all the parameters were run in PAST v.4.07 (statistical analysis software) to observe if there was any significant positive or negative trend (Table 1).

Lastly, linear regressions were made to compare each pair of parameters. Only absorbance 420 and TOC; humic substances in the sea and DOC in the sea; and TOC and DOC in the sea (Fig. 5), were presented, since the other results were not significant or relevant for this case study.

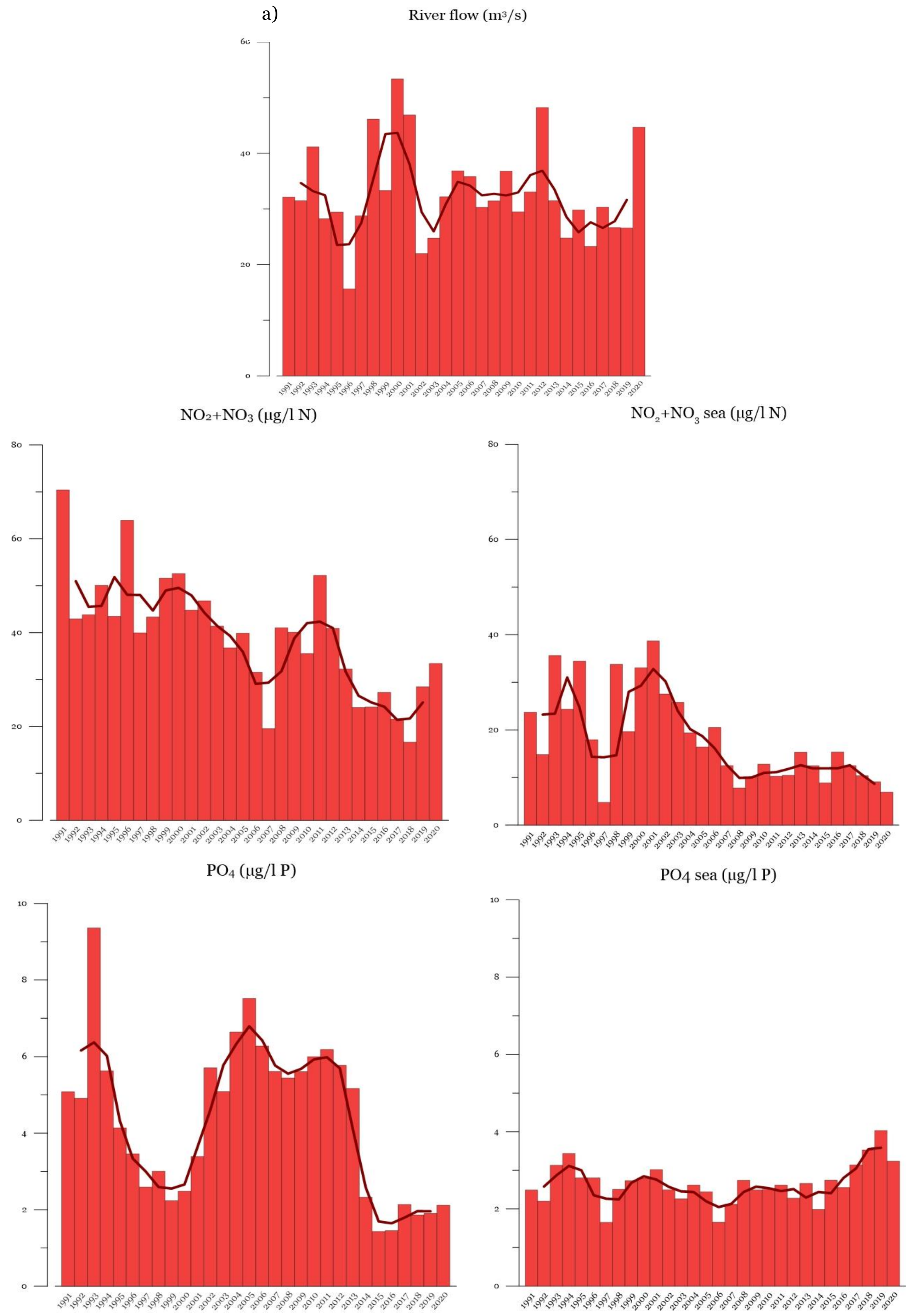
3. Results

3.1. Environmental variables

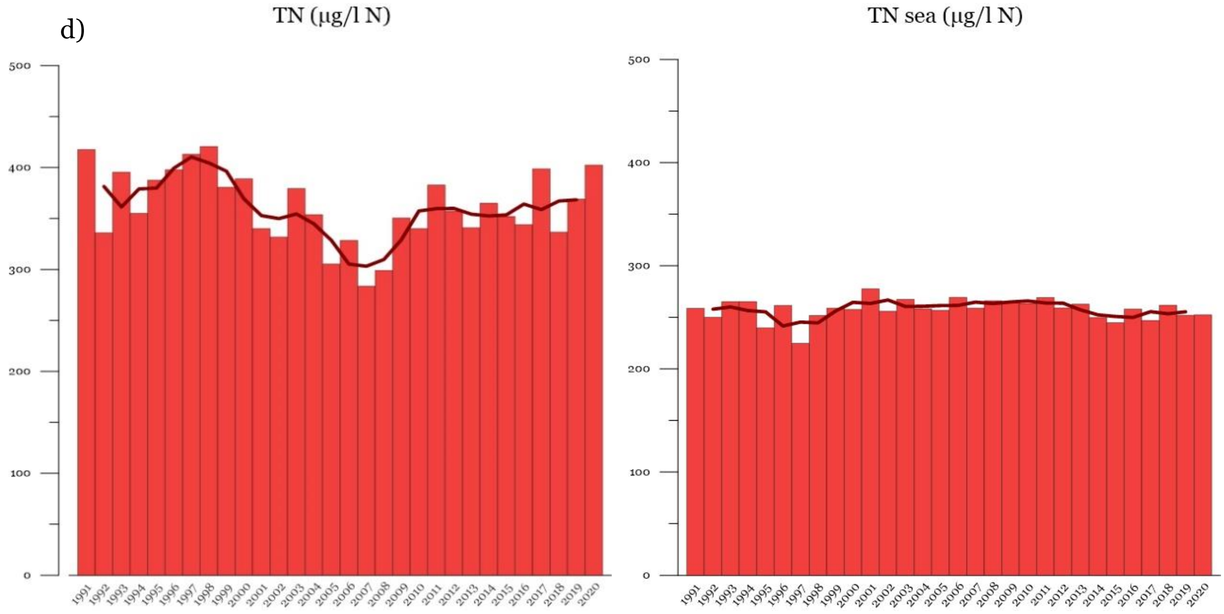
The river flow has been fairly stable through time, and most of the annual means were circa 30 $m^3 s^{-1}$ excluding some years where the mean flow was higher, for example in 1993 (41 $m^3 s^{-1}$), 1998 (46 $m^3 s^{-1}$), 2000 (53 $m^3 s^{-1}$), 2001 (47 $m^3 s^{-1}$), 2012 (48 $m^3 s^{-1}$), and 2020 (45 $m^3 s^{-1}$). Unusually low flows took place in 1996 (16 $m^3 s^{-1}$), 2002 (22 $m^3 s^{-1}$), and 2016 (23 $m^3 s^{-1}$) (Fig. 2a).

The annual means for nitrates were higher in the years 1990s and early 2000s but, with time, they have tailed off. In the river, nitrates have two periods of significant decreasing concentration: from 2000 to 2007, and from 2011 to 2015. In the sea, there is a higher variability, but there are two clear high peaks in 1993 and 2001. In the last 14 years the nitrates concentration has remained low and stable with some oscillations (Fig. 2b).

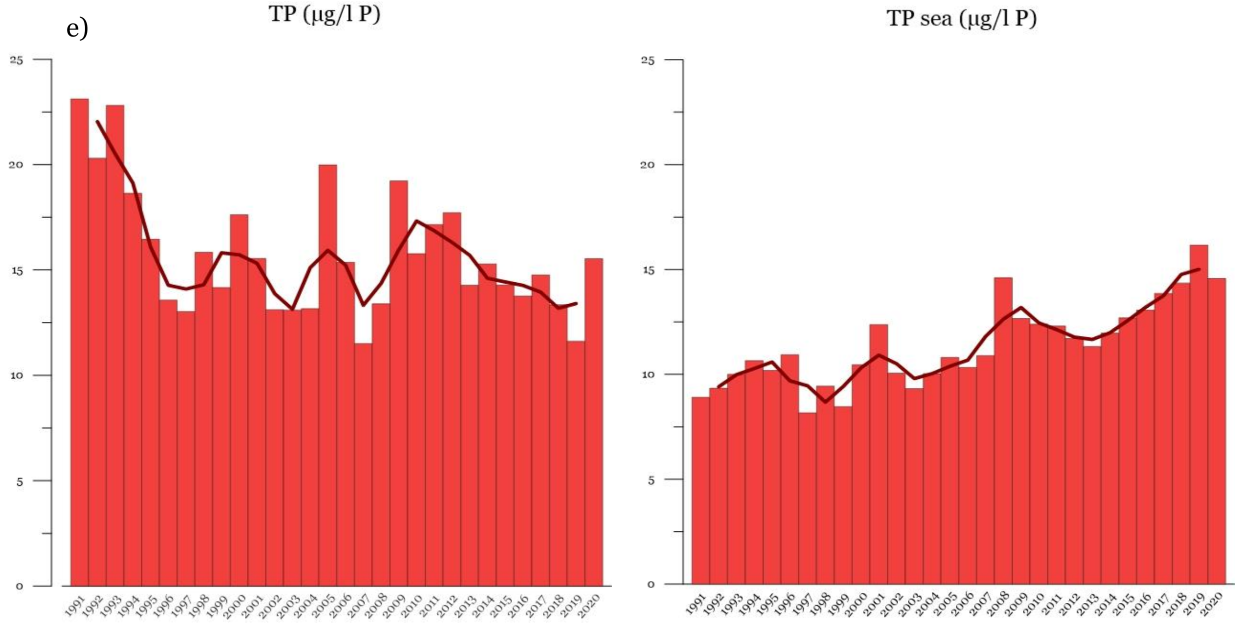
a)


River flow (m^3/s)
NO_2+NO_3 (µg/l N)
NO_2+NO_3 sea (µg/l N)
PO_4 (µg/l P)
PO4 sea (µg/l P)

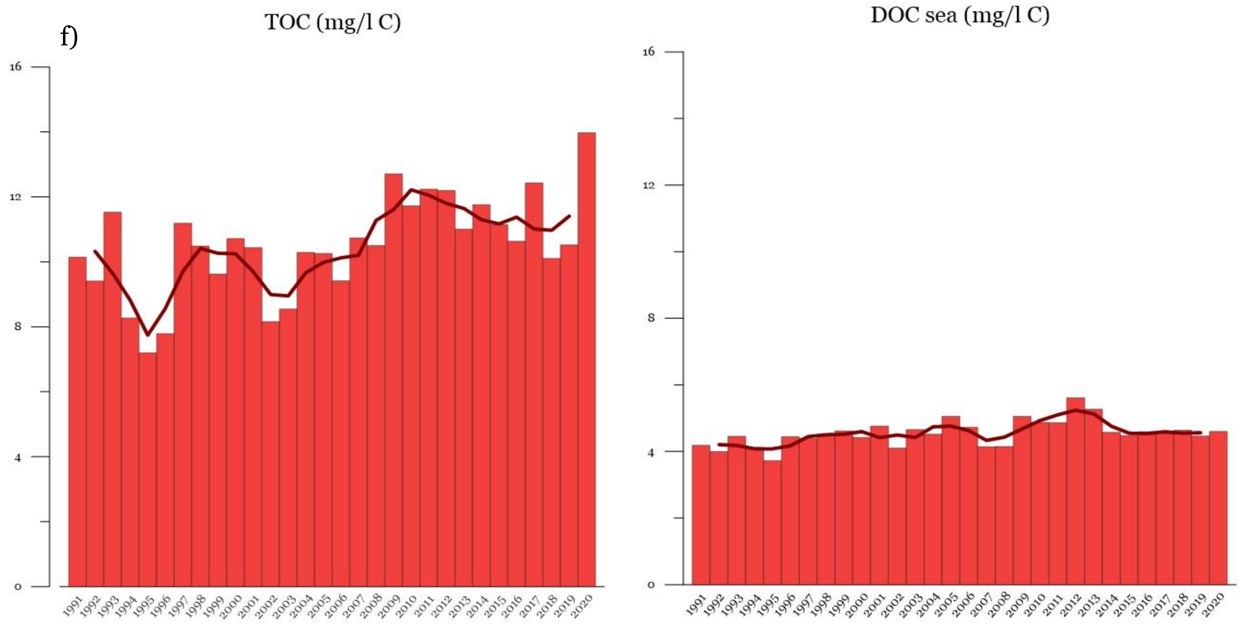
d)


TN (µg/l N)
TN sea (µg/l N)
0
100
200
300
400
500
1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013 2014 2015 2016 2017 2018 2019 2020

e)


TP (µg/l P)
TP sea (µg/l P)
0
5
10
15
20
25
1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013 2014 2015 2016 2017 2018 2019 2020

f)


TOC (mg/l C)
DOC sea (mg/l C)
0
4
8
12
16
1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013 2014 2015 2016 2017 2018 2019 2020

g)

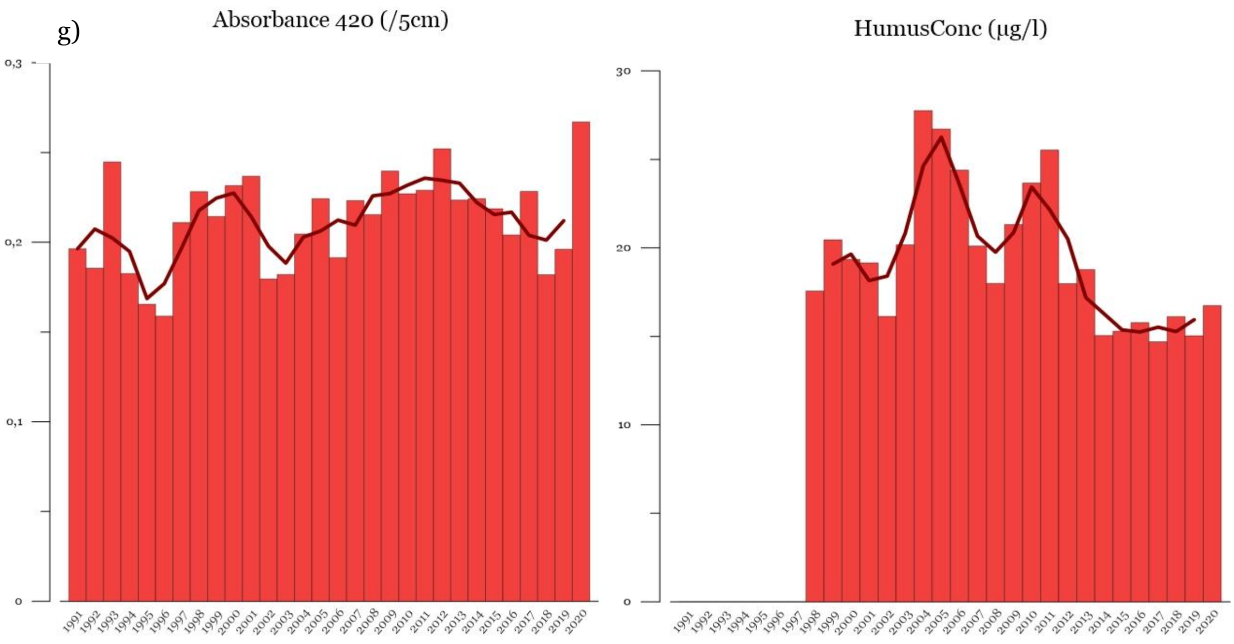


Figure 2. Bar plots and line plots (bars represent annual means, while lines represent 3-years moving means; x axis: year, y axis: concentration value). a) river flow; b) concentration of nitrates in the river (left) and in the sea (right); c) concentration of phosphates in the river (left) and in the sea (right); d) total nitrogen in the river (left) and in the sea (right); e) total phosphorus in the river (left) and in the sea (right); f) TOC in the river (left) and DOC in the sea (right); g) absorbance 420 in the river (left) and humic substances concentration in the sea (right).

Phosphates, on the other hand, did not show a regular and uniform trend, but they rather fluctuated over time. Values ranged from 1.4 µg l^{-1} in 2015 to 9.4 µg l^{-1} in 1993 in the river, and from 1.7 µg l^{-1} in 1997 to 4.0 µg l^{-1} in 2019. It should also be noted that the phosphate concentration in the river was generally higher than in the sea, and that it showed less pronounced changes in the later location (Fig. 2c).

Regarding to total nitrogen, the situation seems totally different by looking at the graphics: in the river there were some variations, but in the sea the values remained almost constant for the last 29 years. Means varied between 283 µg l^{-1} (2007), and 421 µg l^{-1} (1998) in the river, and from 225 µg l^{-1} (1997) to 278 µg l^{-1} (2001) in the sea. There was not any noticeable peak, but in the river the total nitrogen concentration slightly increased from 1994 to 1997 (Fig. 2d).

In another way, total phosphorus showed a trend, although it was different for the river and sea. In the river, the highest values were shown during the first years of the study, i.e., the lowest is 11.5 µg l^{-1} in 2017, followed by 11.6 µg l^{-1} in 2019, while the highest mean was 23.1 µg l^{-1} in 1991. Conversely, in the sea, the highest concentration was found on the latest years, and the lowest during the first ones. As an example, the lowest was 8.2 µg l^{-1} in 1997, and the highest mean was 16.2 µg l^{-1} in 2019 (Fig. 2e).

For the organic carbon, TOC was taken to study the river, and DOC the sea. Both of them fluctuated with time, but there was positive trend in both. First, in the river, the lowest mean (7.2 µg l^{-1}) was found during 1995, and the highest (14.0 µg l^{-1}) was found in year 2020. In the sea, the lowest mean was found in 1995 (3.7 µg l^{-1}), and the highest was found in 2012 (5.6 µg l^{-1}) (Fig. 2f).

Last of all, for the absorbance in the river, the means values ranged between 0.159 /5cm and 0.267 /5cm, but this has fluctuated over time. In the river, the absorbance slightly increased from 1997 to 2001, from 2004 to 2005, and from 2007 to 2012. On the other hand, the humic substances concentration in the sea ranged from 14.7 µg l^{-1} to 27.8 µg l^{-1} (Fig. 2g).

DIN:DIP ratio (Fig. 3) results show higher values around the shift of millennium and from 2014 to 2020 in the river. Specifically, the ratio in the river was lower than 16 in the following years: 1993, 2004, 2005, 2006, 2007, 2009, 2010, 2012 and 2013 and higher in the rest of them. On the other hand, the ratio in the sea was higher than 16 in the years 1991, 1993, 1995, 1998, 2000, 2001, 2002, 2003, 2004 and 2006, but lower in the rest of them. Generally, the DIN:DIP ratio in the river was higher than in the sea, since there were some high values during the first years of the data and around the shift of the millennium, but these decrease on the last years.

The A420:TOC ratio (Fig. 4) does not show remarkable differences. Although slightly, the ratio has decreased with time, presenting its maximum in 1995 and its minimum in 2018. However, even though for the HS:DOC ratio data were only available from 1998, it seems that the ratio has decreased. The first six available years remained roughly stable, but in 2004, the ratio reaches its maximum. Then, it slowly decreases until 2010, when the humic substances predominate over DOC for two years and decreases to remain again stable for the last 9 years.

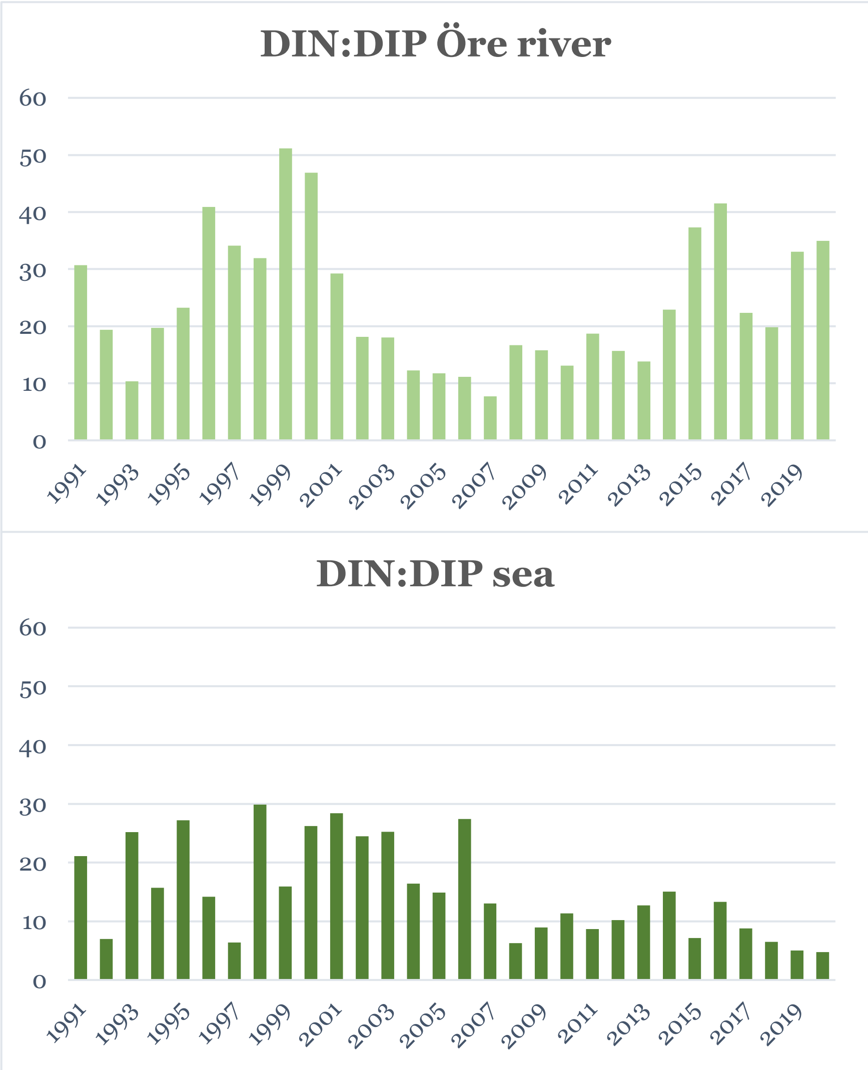


Figure 3. DIN:DIP molar ratio in the river (above) and in the sea (below).

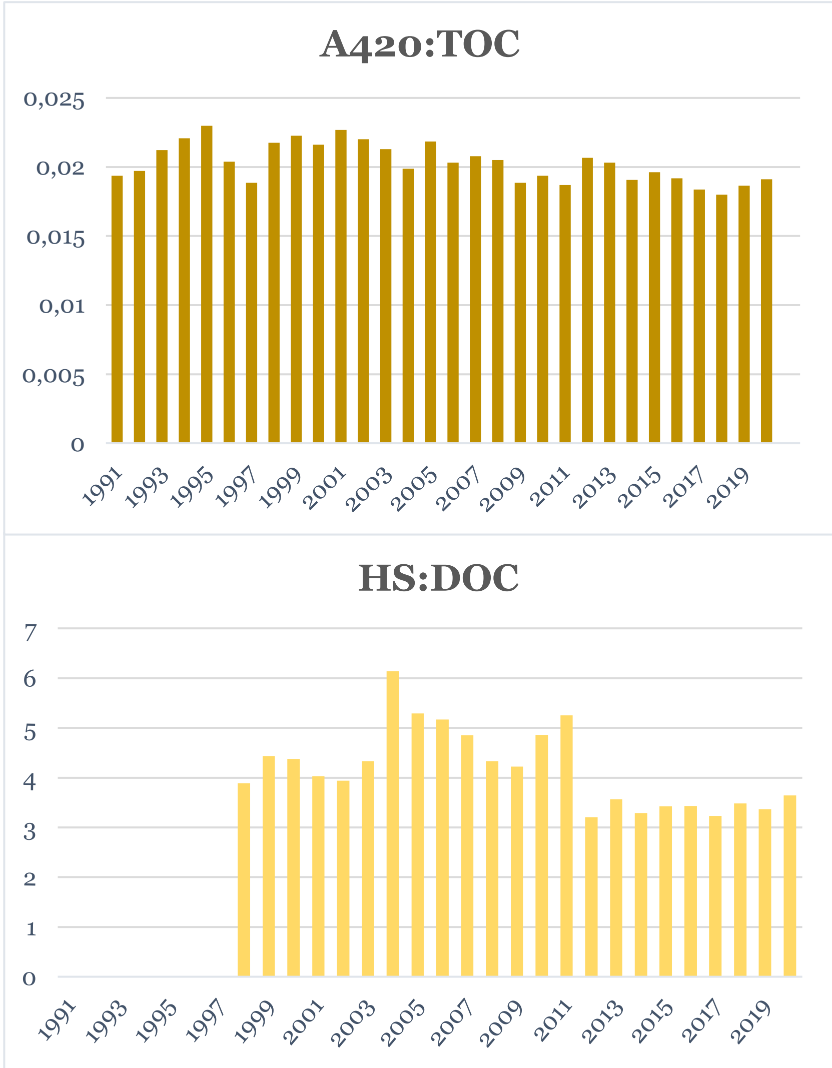


Figure 4. A420:TOC ratio in the river (above) and humic substances:DOC ratio in the sea (below)

3.2. Trend analysis

The Mann-Kendall test (Tab. 1) confirmed the trends on the graphs above. It showed a significant positive trend for TOC in the river, and TP and DOC in the sea; and a significant negative trend for NO2+NO3, and TP in the river, and NO2+NO3 and humic substances in the sea. The rest of the environmental parameters did not show any significant trend.

The DIN:DIP ratio in the river does not have any significant trend, however the DIN:DIP ratio in the sea has a significant negative trend. In the same way, A420:TOC in the river and HS:DOC in the sea, have both a significant negative trend.

Table 1. Mann-Kendall test results. S determine if there is a positive or negative trend; the p-value determines if the trend is significant ($p \leq 0.05$) or not ($p > 0.05$). (Green colour: significant positive trend; orange: significant negative trend).

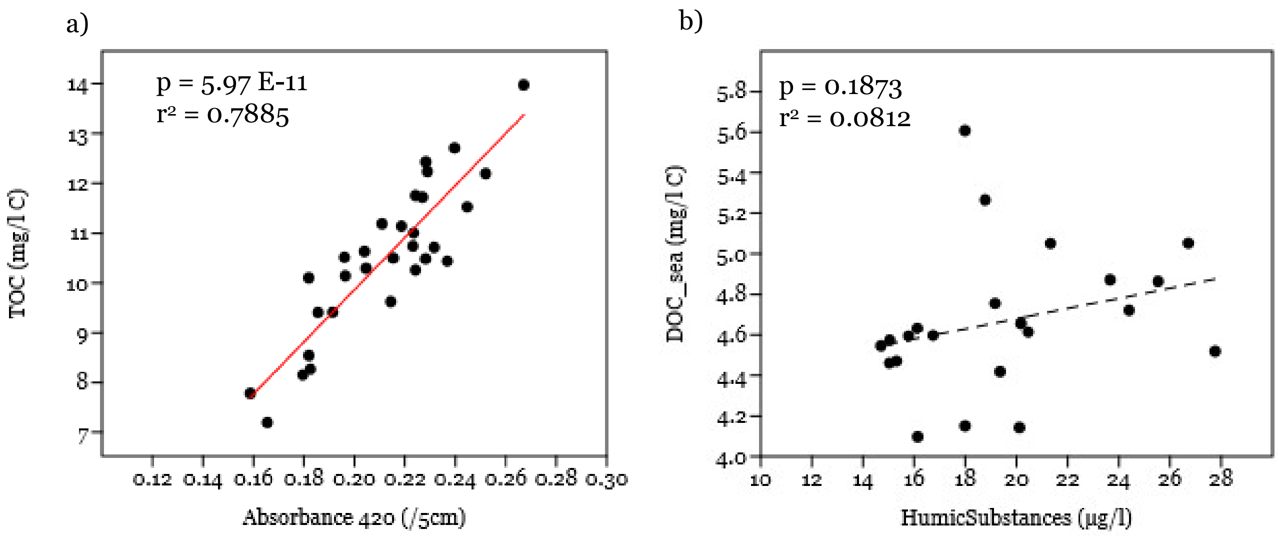
	River flow	NO2+NO3	PO4	TN	TP	TOC	A420
S :	-37	-243	-103	-63	-119	171	89
p:	0,5196	1,6E-05	0,0688	0,2687	0,0353	0,0024	0,1164

	NO2+NO3_sea	PO4_sea	TN_sea	TP_sea	DOC_sea	HS_sea
S :	-209	51	-23	279	151	-99
p:	0,0002	0,3724	0,6947	7E-07	0,0074	0,0057

	DIN:DIP river	DIN:DIP sea	A420:TOC	HS:DOC
S :	-1	-185	-191	-89
p:	1	0,0010	0,0012	0.0201

3.3. Linear regression

In the river, TOC turned out to have a strong relationship with the absorbance ($p = 5.96E-11$; $r^2 = 0.7885$). The analogous linear regression in the sea, i.e., humic substances and DOC, did not show a significant relation between these two variables ($p = 0.1873$; $r^2 = 0.0812$). Lastly, the DOC in the sea also showed a low positive correlation ($p = 0.0024$; $r^2 = 0.2853$) to the TOC in the river (Fig. 5).



c)

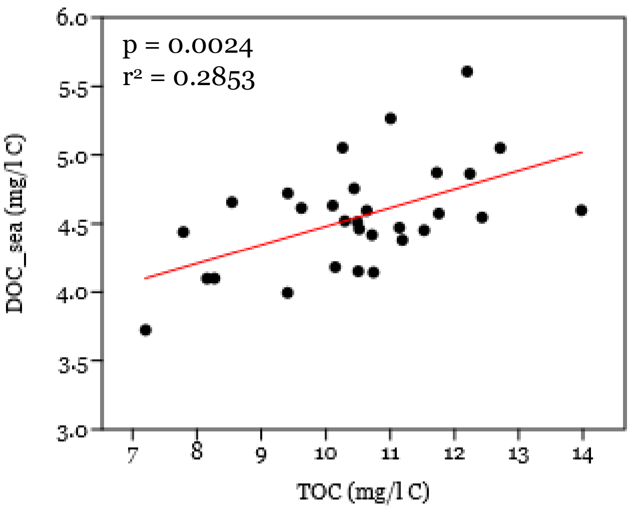


Figure 5. Linear regression (black dots: mean values for each year; red line: trendline; black dashed line: 'trendline', no correlation). a) Relation between absorbance 420 (/5cm) and TOC (mg/l C) in the river; b) Relation between humic substances concentration (µg/l) and DOC (mg/l C) in the sea; c) Relation between TOC (mg/l C) in the river and DOC (mg/l C) in the sea.

4. DISCUSSION

This section aims to elucidate how the data series under study might act as a signal or serve as an indicator of how the activities taking place in the river catchment, and associated processes affecting the transport of chemicals into the Öre River, are influencing the river and coastal waters it flows into.

As described above, almost 80% of the catchment area serving the Öre River are forests. Forest fertilization (with nitrogen) has been a method of boosting forest growth, to increase the timber production and economic profit. Forest growth is generally constrained by the limited nitrogen availability in Swedish boreal forests (Lundin and Nilsson, 2021). This technique has been applied to Swedish soils since the 1950s, it became popular during the 1960s, and it reached its maximum in the mid-1970s (circa 190.000 hectares per year were fertilized in Sweden). Even so, the technique gradually lost popularity and during the 1990s and early 2000s less than 50.000 hectares per year were fertilized (Lindkvist, et al., 2011).

It is difficult to establish a direct link between fertilization of the forest and the data supporting this analysis as the processes affecting the dissemination of nitrates (nitrates leaching throughout the soil, runoff or ammonia volatilization and deposition) are complex. In addition, data before 1991 were not evaluated, however, results showed a decreasing trend of nitrate concentration since 1991 (Fig. 2b, Tab. 1). The river flow has not varied, and was therefore not likely to act as significant factor affecting nitrate concentration, neither in the river nor in the recipient coastal waters (Fig. 2a).

Another potential factor influencing nitrate concentration could be the significant area coverage by marshes and other wetlands (16%), which could be acting as a buffer for atmospheric nitrogen (N_2) deposition initially, and leach to the layers below with rainfall events (Rubol et al., 2012). There is also 1% of the basin covered by clays, which could have act as a contributing factor to the storage of nitrogen in the upper layers for years, with this being slowly released by weathering years later (Hoffmann and Johnsson, 1999).

A follow-up analysis to examine some of the processes described above can be valuable, perhaps by the use of longer data series which will allow a better comparison with nitrate concentrations before the period covered in this analysis.

The Swedish Forestry Act (1979:429) was revised in 1993. This new revision included stringent environmental clauses, rather than productivity aspects, and both factors were given the same importance. This might support a decline in the fertilization of forests during the period 1990-2000. Another reason contributing to the decline of forest fertilization could be the rise of nitrogen deposition leaded by airborne pollution, mainly from other European countries, and especially in southern Sweden before the 1990s decade (Finstad et al. 2016).

However, because of arising of the environmental concerns during the last three decades over increasing air pollution, and consequently N_2 deposition, is now in decline, and some forest's owners had reinitiated the practice to boost the growth of their trees again with fertilizers (Lundin and Nilsson, 2021). All of this, combined with the recent interest in rapid growth to deliver ecosystem services, such as carbon mitigation, or to obtain biofuels (Lindkvist, et al., 2011), could be the reason for the slight augment of nitrate concentrations and total nitrogen in the river observed during the last two years of the data series (Fig. 2b). It will be therefore interesting to conduct a follow up analysis to investigate if this trend continues in future years.

Although there could be a number of confounding factors, the wide extension of forests in the basin, and its fertilization, seems a possible explanation to interpret the trend observed for the concentration of nitrates, and the higher values measured in the river compared to the receiving coastal waters. The nitrates and nitrites have high solubility when bound to other compounds (Gehle, 2013). The predominant soil in the catchment area (podzol, characterized by high percolation) could have contributed to these through soil leaching in the groundwater, and later on, to the river (Schad, 2016).

Farming land on the other hand, only represents a 1% of land coverage in the river catchment. Google Earth was used to characterise the different types of farms in the catchment area, and this include mainly arable crops, cattle, poultry, or fish farms. Arable crops are usually subject to the addition of fertilizers and pesticides. These can be in the form of natural sources (e.g., manure), or artificial sources. These practices can contribute to the dissemination of dangerous and toxic compounds, including phosphates, nitrates and organic carbon to soils and water bodies (Shrestha et al., 2008). Pollution effects can be worsened by poor fertilizer management practices (Shrestha et al., 2008).

Even though it was not possible to produce an in-depth analysis of the type of farms in the area, the use of google Earth enables to distinguish some specific farming practices taking place in the watershed. There is at least one cattle farm (Burén, 2021), one moose farm (https://algenshus.se/), and a horse centre (3.5 km away from Bjurholm towards north, http://www.backforsgard.se/) (satellite image, Google Earth, v.9.150.0.2). A timber factory was also found near to Angnäs, next to the river (https://www.norratimber.se/kontakt/agnas-stolpfabrik).

Another conclusion that can be deducted from the data analysis is that the limiting element in the river water tends to be dominated by phosphorus concentration (higher number of years limited by phosphorus, n = 21 year), while the coastal area under study would be nitrogen limited (higher number of years with nitrogen limitation conditions, n = 20). That is to say that DIN:DIP ratio has been above the Redfield ratio (> 16:1) during more years in the river, and lower (< 16:1) during more years in the coastal waters. The Redfield ratio is the optimal DIN:DIP ratio that Alfred Redfield calculated for phytoplankton growth (Redfield, 1934; Danish Environmental Protection Agency and National Environmental Research Institute, 2021). This could be a response to forests and farms fertilization, and the phosphorus capacity to bind and be transported within the sediment. Afterwards, it can be released again to water with anoxic conditions in the water column (Andersson et al., 2015).

Phosphorus load in the Baltic Sea, on the other hand, was only 38.300 tonnes (2010), of which only 5% were air-borne introduced (HELCOM, 2013). The river flow and phosphorus transported by the river did not show high values, and neither the air-borne load was high, suggesting other sources of phosphorus to the coast. Research by Forsgren and Jansson (1993), demonstrated that phosphorus sedimentation in the Öre estuary was higher than the riverine load of allochthonous particle phosphorus.

Much of the phosphorus load in the study area might be sourced from the Baltic Proper, as it is close and interconnected with the Bothnian Sea, where anoxic seabeds are common. These conditions favour the release of phosphorus from sediments (Andersson et al., 2015). These processes are favouring to the proliferation of cyanobacterial blooms and can develop eutrophicated ecosystems, especially with higher average temperature conditions, which is the expected scenario for the forthcoming years with climate change (Forsgren and Jansson, 1993; Andersson et al., 2015). In fact, total phosphorus has increased in the last seven years at the marine stations, and it showed a general positive trend over the 1991-2020 period, while in the river the same parameter has decreased (Fig. 2e).

Recent analysis of the zone in which the estuary is located has shown higher concentrations of phosphorus than other northern or offshore monitoring stations (Jiménez, 2020). Some cyanobacteria, like the Nostocales order, thrive in nitrogen-limited environments as they can fixate atmospheric nitrogen, but need high amounts of phosphorus to function (Mann and Carr, 2012; Munn, 2019). Species from this order are responsible for the release of dangerous toxins in aquatic ecosystems such as paralytic shellfish poisons (Saxitoxins), neurotoxins produced by *Aphanizomenon* spp, among others (Codd et al., 2005). Cyanobacteria growth is an important process to take in consideration, since it causes economic losses, it is a risk to animal and human health, and it can lead to the depletion of ecosystems health, e.g., by modifying the food chain (Paerl and Huisman, 2009).

The food web efficiency can act as an indicator of ecosystem health, i.e., an ecosystem where phytoplankton-based diet predominates over bacterial-based diet is healthier (Lefébure et al., 2013). Besides limiting nutrients like nitrogen and phosphorus, there are others, such as TOC and DOC that also influence the base of the food chain. DOC is a fraction of the dissolved organic matter (DOM), and TOC in turn is the sum of DOC and particulate organic carbon (POC). In addition, DOC is composed by humic substances like humic acids, fulvic acids and humin, which serves as nourishment for heterotrophic organisms (Fondriest Environmental, 2017).

Wetlands are the main source of TOC for boreal rivers, but the amount of TOC input also depends on where the wetland is located. For example, Laudon et al. (2004) studied seven catchment areas in northern Sweden, and one of them showed a lower TOC export compared to the extent surface within the watershed. The reason could be that in this area the wetland was located in the upper reaches of the catchment, far from the stream and not connected with it, while the other studied areas, comprised riparian wetlands, or were located in the valley bottoms close to the water flow. In northern Sweden the riparian wetlands follow along the water channels in forested areas. They occupy less than 5% but are still an important source of TOC when runoff is high (Laudon et al.,2004). In the same study they shown that TOC export is larger during the spring flood in forested basins than in the wetland dominated basins during the same period, as it is more distributed during the year.

In the Öre River, there is a 79% of land covered by forests and 16% covered by marshes and other wetlands. Even though the exact location of these habitats is hard to establish, both landscapes are presumably producing and transporting terrestrial organic matter to the river, increasing TOC concentration. In the last two to three decades TOC has increased in northern and boreal freshwaters, i.e., it has created what is called 'browning' effect (Finstad et al. 2016). This is a response of the ecosystems to different factors such as the reduction of acid rain (less airborne sulphur pollution), jointly with the 'greening' phenomenon, which is the increasing vegetation cover due to warmer temperatures, more precipitation and changes in land use (Finstad et al. 2016).

It is noticeable in the results that the TOC in the data series showed a significant positive trend. Yet, the absorbance (generally linked to the TOC concentration) did not show a significant positive trend (Fig. 2g), although it was strongly correlated with TOC (Fig. 5a). The reason for this could be an increasing load of TOC explained by the current 'browning' phenomenon, although the composition of TOC could have changed. This new composition would be likely less coloured, leading to a lower absorbance 420:TOC ratio and a negative trend for this ratio, although further research would be needed to affirm this assumption.

Similarly, the same trends can be seen in the sea for DOC and the humic substances, although in this case DOC has increased (Fig. 2f), while humic substances, and the humic substances:DOC ratio have decreased (Fig. 2g; Fig. 4). The linear regression (Fig. 5b) did not show a relationship between these parameters which is an interesting finding, as this could mean that the DOC increase would consist of autochthonous DOC, rather than DOC transported from further afield. Generally, these molecules are coloured particles, which prevent light from penetrating in the water column, especially the humic substances (Fondriest Environmental, 2017). Higher absorbance at 440 nm was observed to be more influenced by freshwater input and allochthonous DOC (i.e., coming from terrestrial sources) in a research near to the study area (Harvey et al., 2015). It is however possible that part of the DOC is allochthonous, as it shows a weak positive correlation with the TOC in the river (Fig. 5c), while the rest is autochthonous DOC.

4.1. Conclusions

- While the river flow did not significantly change in the studied period, other environmental parameters such as nitrates, total phosphorus, organic carbon and humic substances show substantial variation.
- The processes influencing the concentration of these parameters in the river and the recipient coastal waters are varied (climate change, anthropogenic nutrient inputs, changes in land use, reduction of acid rain, among others), and in some cases there is a high level of uncertainty on their overall impact.
- The river tends to be more phosphorus limited, and the studied coastal area is usually nitrogen limited, as marshes and other wetlands provide nitrogen directly to the river, and phosphorus is released from the estuary sediments when anoxic conditions are given.
- It is important to keep monitoring the nutrient levels and water colour, as rivers play a critical part in the adequate functioning of the ecosystems supporting the Baltic Sea, which is very sensitive and is prone to algal and cyanobacteria blooms.

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