MONITORING OF DISSOLVED ORGANIC MATTER IN MARINE SWEDISH WATERS - NEEDS AND METHODOLOGY

5 April 2004, credit: Jeff Schmaltz, MODIS Rapid Response Team, NASA/GSFC

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March 2016

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In the Baltic Sea, most of the nutrients flow is originating for the catchment. The rivers add massive amounts of nutrients, not only under inorganic forms but mostly under organic forms. One of the consequences is the concentrations dissolved organic carbon being three to four times higher in the Baltic Sea than in the open ocean. Dissolved organic nutrients represent the major proportion of the total pool of dissolved nutrients; as for example for nitrogen, for which inorganic forms exceed organic forms almost only in winter in marine Swedish waters.

In the Baltic Sea, pronounced spatial gradients over basins are observed. Total phosphorus concentration is three times higher in the south compared to the north, while humic substances concentration is two times higher in the north (Andersson et al. 2015). In parallel, primary production is ten times higher in the southern Baltic Sea compared to the Bothnian Bay, while bacterial production is more uniform over the entire Baltic Sea (Andersson et al. 2015). Dissolved organic matter originating from the land has a brown colour and contributes strongly to light attenuation in the water, decreasing severely the light availability for phytoplankton. The balance between bacterial and primary production is determined by a limitation of phosphorus in the north, which hampers phytoplankton production, and important dissolved organic matter loads in the north, which limit light availability for primary production and promote bacterial production.

The dynamics of dissolved organic matter is fundamental as structuring factor of marine food-webs, as dissolved organic matter impacts both bacteria and phytoplankton and shapes the transfer of energy to higher trophic levels.

Acknowledging the importance of dissolved organic matter for marine Swedish waters, this project aims at:

1) compiling current knowledge on dissolved organic matter (DOM) relevant to marine Swedish waters;
2) suggesting how DOM monitoring could be improved, regarding the “brownification” and eutrophication of the Baltic Sea, and the requirements to meet EU and national environmental directives;
3) describing the needs of data estimating chromophoric DOM for the validation of satellite products deriving chlorophyll concentrations.

I. Dissolved organic matter (DOM) in marine Swedish waters

I. 1. Panorama from international literature

In the Baltic Sea, the number of studies focusing on DOM has increased in the last decades for the Gulf of Bothnia, Gulf of Finland and Baltic Proper; however such studies are still very scarce for the Kattegat and Skagerrak regions. These studies report mainly data on dissolved organic carbon (DOC) and to a lesser extent on dissolved organic nitrogen (DON), dissolved organic phosphorus (DOP) and other variables such as lignin, yellow substances, humic substances (HS) or chromophoric dissolved organic carbon (CDOM) absorption parameters. In the case of CDOM absorption properties, drawing trend over time and space is almost impossible as the different parameters are reported in most of the studies.

The extensive detailed literature review on DOC, DON, DOP, CDOM absorption, humic substances and lignin is presented in Appendix 1, while the compiled summary of values for DOC, DON, DOP, CDOM absorption and humic substances are shown in Table 1.

Spatial distribution of DOM

Dissolved organic carbon (DOC)

In the Baltic Sea, the DOC concentrations range from 190 to 590 µmol C.l^{-1} in the surface water over open sea regions (Table 1, Appendix 1). The DOC concentrations of the rivers entering the Baltic Sea are noticeably higher than the Baltic Sea ranging from 290-1900 µmol C.l^{-1} (Fleming-Lehtinen et al. 2014, Räike et al. 2012, Stepanauskas et al. 2002). Therefore the DOC concentrations are generally higher in areas receiving high river inflow. Though DOC data are sporadic some spatial trend can be extrapolated at a basin scale.

The Gulf of Bothnia receives almost half of the freshwater inflow in the Baltic Sea, with high DOC concentrations from a peatland-dominated catchment (Räike et al. 2012, Stepanauskas et al. 2002). Consequently, the contribution of terrestrial DOC to total DOC decreases from the Bothnian Bay (70-87%) to the Baltic Proper (43-67%) (Alling et al. 2008, Deutsch et al. 2012). However, the DOC concentrations in the open-sea do not differ from the Gulf of Bothnia (240-325 µmol C.l^{-1}) to the Baltic Proper (Deutsch et al. 2012). Furthermore, a large part of terrestrial DOC seems to be lost in the river estuaries of the Baltic Sea (Fleming-Lehtinen et al. 2014, Markager et al. 2011), as a result a gradient of DOC concentrations is observed from the coast to open sea but not between open-sea waters over basins.

In the Baltic Proper, DOC concentrations range from 270 to 380 µmol C.l^{-1} in the open-sea where no spatial gradient is observed over the different basins (Nausch et al. 2008, Wedborg et al. 1994). DOC concentrations tend to be higher along the coast due to inputs of terrestrial DOC but also to increased autochthonous DOC production resulting from the riverine inputs of inorganic nutrients (Nausch et al. 2008; Maciejewska & Pempkowiak 2014). In the Baltic Proper the deeper waters originate from the North Sea, where DOC concentrations are much lower, resulting in lower DOC concentration below the halocline in the Baltic Proper (200-330 µmol C.l^{-1}, Maciejewska & Pempkowiak 2014; Nausch et al., 2008). Moreover, the DOC concentrations tend to slightly increase close to the bottom, due to diffusion of DOC from interstitial water or decomposition of organic matter on the sediment surface (Maciejewska & Pempkowiak 2014).

In the southern Baltic Proper, DOC concentrations decreases from east to west (Nausch et al. 2008) under the increasing influence of North Sea waters, from 170-390 µmol C.l^{-1} near the Dars Sill (Nausch et al. 2008; Lønborg & Søndergaard, 2009), to 90-260 µmol C.l^{-1} in the Kattegat (Osburn & Stedmon 2011, Wedborg et al. 1994), and 90-120 µmol C.l^{-1} in the North Sea (Kulinski et al. 2011).

Table 1. Summary of literature values of DOC (dissolved organic carbon), DON (dissolved organic nitrogen), DOP (dissolved organic phosphorus), a CDOM (absorption of chromophoric dissolved organic matter) and humic substances in the Baltic Sea and the Skagerrak. The detailed literature review, including references is presented in Appendix 1.

Basin		DOC (µM)	DON (µM)	DOP (µM)	a CDOM (m^{-1})	Humic subst ($µg.l^{-1}$)
Gulf of Bothnia						
Bothnian Bay	Open-sea	241-320		0.12	a(412)=1.04 ± 0.22	12
	Coast	347-520			a(350)= 6.60	19.9-47.7
Bothnian Sea	Open-sea	270-325	5-15	0.15±0.02	a(412)= 0.52 ± 0.07	8.8
	Coast	270-825		0.13	a(440)= 0.75-8.83	8.8
Baltic Proper						
Baltic Proper	Open-sea	267-458	16	0.2-0.40		7.7
Gotland Basin	Open-sea	300-390	14-16	0.2-0.52	a(300)=0.4±17.2	
E Gotland Basin	Coast Open-sea	330-380	12-24	0.50-0.90	a(440)= 0.33 - 4.12	
Bornholm Deep	Open-sea	403				
Arkona Sea	Open-sea	191-334	15		a(300)=0.1-16.6	
Southern Baltic	Open-sea	267-592			a(400)= 0.23-1.84	
Belt Sea	Coast	172-394	12-36	0.39-0.98	a(375) = 0.65-5.88	
Kattegat & Skagerrak						
Kattegat	Coast	79-265		015-0.36	a(375)= 1.42–4.65	5.1
	Open-sea				a(300) = 0.87-3.58	5.1
Skagerrak	Open-sea				a(375)= 0.09–0.42	3.4

Dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP)

Concentrations of DON and DOP are highly variable in the surface waters of the Baltic Sea ranging from 9 to 23 µmol $N.l^{-1}$ and 0.12 to 0.90 µmol $P.l^{-1}$ in the open-sea areas (Table 1). The sporadic data available for DON and DOP preclude the detection of general reproducible inter-basin variation pattern. So far, in the Baltic Proper no spatial variation was detected between basins for DON, from the Arkona Sea to the Gotland Basin (Nausch et al. 2008). However, DOP concentrations increase from the Bothnian Bay to the southern Gotland Basin (Nausch & Nausch 2011).

DOM transported by the rivers supplies DON and DOP to the coastal areas of the Baltic Sea (Mattsson et al. 2005). In river estuaries, the DON concentrations can be twice those in the open-sea surface water, however up to 60% of DON and DOP can be lost in estuaries (Markager et al. 2011).

DOM: lignin, humic substances, chromophoric DOM (CDOM)

In the Baltic Sea and the Skagerrak, there are few reports of lignin or humic substances in the literature (Table 1, Appendix 1), on the other hand reports of CDOM parameters are slightly more extensive. Though the parameters estimated from CDOM absorption differ among studies, some spatial patterns appear.

Over the different basins, the absorption of CDOM decreases from the Bothnian Bay to the Skagerrak (Berthon & Zibordi 2010) as the concentration of humic substances (Skoog et al. 2010) (Table 1, Appendix 1), reflecting a higher contribution of aromatic compound in the northern regions. At a basin scale, a gradient from higher CDOM absorption from the coasts to lower values in open-sea areas is also reflecting the impact of river inflow (Asmala et al. 2013, Ferrari et al. 1996, Kowalczuck 1999, Kowalczuck et al 2005, Kratzer & Tett 2009, Stedmon et al. 2000)

Seasonal variation of DOM

In the Baltic Sea, DOC concentrations during summer and autumn are higher than the winter levels (10 to 100% higher, Hoikkala et al. 2012, Kulinski et al. 2011, Maciejewska & Pempkowiak 2014, Markager et al. 2011, Zweifel et al. 1995). The seasonal accumulation of DOC in the surface waters emphasizes the vertical gradient in the Baltic Proper during the growing season (Hoikkala et al. 2012, Kuliński & Pempkowiak 2008, Maciejewska & Pempkowia, 2014). The seasonal DOC accumulation is due to both terrestrial sources and autochthonous production with a relative contribution varying spatially. In the coastal Bothnian Sea the seasonal DOC accumulation is mostly due to terrestrial inputs (Zweifel et al., 1995), while in the Baltic Proper or in Horsens Fjord the DOC accumulation is mainly attributed to primary production (Hoikkala et al. 2012; Maciejewska & Pempkowiak 2014, Markager et al. 2011). A large fraction of the DOC seasonally accumulated can be utilised by bacterial communities, suggesting that a large proportion of the DOC accumulated could be respired within few weeks (Hoikkala et al. 2015).

Seasonal trends seem to be variable for both DON and DOP. DON concentrations showed no seasonal variations in the Baltic Proper (Nausch et al. 2008) and Horsens Fjord (Markager et al. 2011), but accumulated during the productive season in the Gulf of Finland (Hoikkala et al. 2009, 2012). In the case of DOP, no seasonal variation was observed in Horsens Fjord (Markager et al. 2011), while DOP accumulated in surface waters in the Gulf of Finland (Hoikkala et al. 2009, 2012). In the Baltic Proper, DOP concentrations decreased over the growing season (Nausch and Nausch, 2006, 2007). Seasonal variations of DON and DOP might be basin dependent, however further studies would be required in order to identify reliable seasonal patterns.

As the variation of CDOM is highly influenced by river inflow, the absorption of CDOM is expected to display seasonal variations. Accordingly, CDOM absorption increases in the spring in the southern Baltic Proper with a more pronounced raise on the coast (Ferrari et al. 1996, Ferrari & Dowell 1998, Kowalczuck 1999, Kowalczuck et al. 2005, Kowalczuck et al. 2010).

Bioavailability of DOM

In the Baltic Sea, most of the DOC is refractory, leaving a variable fraction of labile DOC representing 0-17% of total DOC (Table 2). The labile DOC represents the DOC degradable by bacteria within days to weeks. The DOC from terrestrial origin is degraded by bacteria before it enters the Baltic Sea and result in being more refractory than autochthonous DOC (Hoikkala et al. 2015).

The proportions of labile DON and DOP are generally higher than that of DOC (Hoikkala et al. 2012, Lignell et al. 2008, Nausch & Nausch 2011), however they vary widely over space and time (Table 2). For example, the proportion of labile DOP increased from Bothnian Bay (8% of DOP) to the Baltic Proper (25–29% of DOP) (Nausch & Nausch 2011). The temporal variation in the proportions of labile DOP is also important, as in the Baltic Proper, where the proportion of labile DOP varied from 9% to 65% of DOP over the season (Nausch & Nausch, 2006, 2007). As well, in rivers flowing into the Baltic Sea, the proportions of labile DON and labile DOP varied widely among the rivers in summer (8–72%, average 25% for DON and 4–100%, average 75% for DOP; Stepanauskas et al. 2002). In the Baltic Proper, DON is estimated to represent on average 66% of the total nitrogen, which most is potentially available for remineralization processes (Nausch et al. 2008).

In the Baltic Sea, the concentrations of organic nutrients are high; hence organic nutrients may support autochthonous production for both bacteria and phytoplankton, and may contribute directly to eutrophication of the Baltic Sea (Hoikkala et al. 2015).

Table 2. Summary of literature values of biodegradability of the DOM pools by heterotrophic bacteria in the Baltic Sea and in rivers draining to the Baltic Sea reported in µM and in percentages. BDOC: biodegradable dissolved organic carbon; BDON: biodegradable dissolved organic nitrogen and BDOP: biodegradable dissolved organic phosphorous.

Area	Season	BDOC (µM)	BDOC (%)	BDON (µM)	BDON (%)	BDOP (µM)	BDOP (%)	Reference
Gulf of Bothnia								
Bothnian Bay	Spring–Summer					0.01–0.04	8	Nausch & Nausch (2011)
Bothnian Sea, coast	Spring–Autumn	23 ± 3	1–7					Zweifel et al. (1993)
Bothnian Sea, coast & open-sea	Spring–Summer	11–34	3–10					Zweifel et al. (1995)
Gulf of Finland								
Open-sea	Summer	4–20	1–5	0–6.5	14–21			Lignell et al. (2008)
Open-sea	Spring–Autumn	0–38	0–9		0–41			Hoikkala et al. (2012)
Open-sea	Spring–Summer					0.04–0.10	44–46	Nausch & Nausch (2011)
Gulf of Riga								
Coast	Spring–Summer	21–82	3–17					Zweifel (1999)
Baltic Proper								
Open-sea	Spring–Summer					0.03–0.34	9–65	Nausch & Nausch (2006)
Open-sea	Spring–Summer					0.04–0.12	33–60	Nausch & Nausch (2007)
Open-sea	Spring–Summer					0.02–0.10	10–29	Nausch & Nausch (2011)
Danish coast								
Horsens Fjord	Year round	8–193	22 ± 13	4–17	43 ± 10			Lønborg & Søndergaard (2009)
Dars Sill	Year round	14–65	14 ± 5	3–12	28 ± 12			Lønborg & Søndergaard (2009)
Rivers								
Rivers draining to the Baltic Sea	Summer			3.4–32.4	8–72	<0.01–0.31	4–100	Stepanauskas et al. (2002)
Kiiminkijoki	Late autumn	49–218	4–18					Hulatt et al. (2014)
3 river estuaries to the Gulf of Bothnia & Gulf of Finland	Spring–Autumn	53–98	7–12	1.2–8.5	10–22			Asmala et al. (2013)
Karjaanjoki	Spring–Autumn	10–123	2–17					Hoikkala et al. (2012)

I. 2. Additional knowledge from Swedish marine monitoring programs

All the information regarding dissolved organic matter from Swedish marine monitoring programs was extracted from the Sharkweb (http://sharkweb.smhi.se/) and dBotnia (http://www.umf.umu.se/miljoanalys/databasen-dbotnia/). The data used in this report cover the period of 1969 to 2014. Since the late 70's various characteristics of DOM have been measured, covering different time periods and regions.

The monitoring of DOM started with the measurement of variables such as lignin, urea and yellow substances, followed by humic substances and lately DOC.

Lignin, urea and yellow substances

The monitoring of lignin was performed from 1969 to 1992 but the measurements were fragmented. An extensive spatial sampling was performed covering all the basins of the Baltic Sea and the Skagerrak, with a focus on the Kattegat and Skagerrak and to a lesser extent on the Gulf of Bothnia (Table 3).

The concentration of urea has been monitored for a short period from 1978 to 1981, only for the Baltic Sea and not the Skagerrak (Table 4).

Yellow substances were estimated from 1971-1984, with a sporadic coverage in time and space (Table 5). Yellow substances have nowadays been replaced by the measurement of CDOM absorption. In the last years a program started to measure CDOM absorption over the Baltic Sea, however these data are not available yet.

As for lignin, data on urea and yellow substances were somewhat scattered, with few coinciding sampling occasions for these variables. Since there was no concomitant other measurement of organic carbon, organic nitrogen or organic phosphorus pools, the spatio-temporal distribution of lignin, urea and yellow substances will not be further described.

Humic substances

Humic substances started to be monitored in 1975 and are still estimated currently. During a first period from 1975 to 1992, humic substances were mostly estimated in the Skagerrak and Kattegat, and less in the Gulf of Bothnia and the other basins (Table 6). After a break, humic substances data are available from 1996 to 2014 (Table 7). During this second period, the sampling focused primarily on the Gulf of Bothnia, and less on the Gotland basin and Kattegat (Table 7). The values are 2 to 7-fold higher in the second period, therefore only the data from the second period (1996-2014) were used in this report. The data collected in the framework of monitoring programs give clear information on spatio-temporal variation of humic substances.

The concentrations of humic substances display strong spatial patterns (Figure 1), with high concentrations in the Bothnian Bay (17.0±2.8 $\mu g.l^{-1}$ at station F3 / A5) decreasing towards the southern basins of the Baltic Sea and the North Sea (4.0±1.7 $\mu g.l^{-1}$ at station Anholt E and 2.1±1 $\mu g.l^{-1}$ at station Å17). In each basin, concentrations are higher along the coast and decrease at the open-sea stations, as for example from 40.0±16.1 $\mu g.l^{-1}$ at station Råneå-1 to 14.9±4.1 $\mu g.l^{-1}$ at station F9 / A13 in the Bothnian Bay.

The vertical distribution of humic substances varies according to the region considered (Figure 2a and 2b). In the open-sea of the Gulf of Bothnia, concentrations are more variable in the surface waters compared to the deeper layers, though this difference tends to reduce in the south of the the Bothnian Sea. On the coast, concentrations are much higher at the surface compare to the bottom in all the Gulf of Bothnia. In the Baltic Proper, the concentrations are more similar between the surface and the deeper layers, though in the Western Gotland Basin (BY31 and BY38), humic substances are likely to accumulate in the deeper layers. In the Kattegat, humic substances show higher concentrations at the surface (station Anholt E).

Table 3. Sampling of lignin from 1969 to 1992: number of sampling occasions per year and basin, the number of stations sampled is between brackets. (OS: open-sea)

Lignin		1969	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990	1991	1992
Bothnian Bay	Coast																								
	OS							1 (1)	5 (1)		5 (3)		17 (11)	18 (11)	16 (1)	2 (1)	18 (1)	12 (12)	1 (1)	12 (11)	11 (9)	19 (1)	17 (1)	3 (2)	16 (8)
Bothnian Sea	Coast													11 (1)			11 (11)			1 (1)					
	OS										8 (5)		2 (12)	23 (13)	23 (13)	23 (12)	22 (12)	22 (12)	12 (12)	14 (12)	13 (11)	22 (12)	22 (12)		2 (12)
Åland Sea	OS										3 (1)		2 (1)	2 (1)	2 (1)	2 (1)	2 (1)	2 (1)	2 (1)	2 (1)	2 (1)	2 (1)	2 (1)		2 (1)
Gulf of Finland	OS	4 (4)									2 (1)		2 (2)												2 (1)
N Baltic Proper	Coast																								
	OS	8 (4)									6 (2)	3 (1)	7 (4)	3 (2)	3 (1)	5 (2)	6 (2)	5 (2)	3 (2)	3 (2)	5 (2)	4 (2)	4 (2)		
W Gotland Basin	Coast																								
	OS	15 (8)									9 (4)		15 (5)	47 (22)	6 (2)	9 (3)	9 (3)	7 (2)	6 (2)	8 (2)	9 (3)	6 (3)	5 (2)	2 (2)	7 (3)
E Gotland Basin	OS	25 (14)									7 (3)		11 (4)	1 (5)	5 (3)	7 (2)	8 (2)	5 (2)	4 (2)	8 (2)	9 (3)	4 (2)	5 (2)	2 (2)	4 (2)
Gdansk Basin	OS																								
Bornholm Basin	Coast	1 (1)																							2 (2)
	OS	9 (5)									5 (4)		11 (4)	11 (4)	7 (3)	12 (3)	1 (4)	12 (3)	9 (3)	12 (3)	12 (3)	8 (3)	9 (3)	4 (3)	6 (4)
Arkona Basin	Coast																								
	OS	6 (3)									3 (1)		3 (1)	3 (1)	3 (1)	4 (1)	4 (1)	4 (1)	4 (2)	5 (1)	5 (2)	2 (1)	4 (1)	2 (1)	2 (1)
Belt Sea	OS																1 (1)	3 (1)	2 (1)	3 (1)	6 (1)	3 (1)	2 (1)		
The Sound	Coast	5 (2)									2 (1)		2 (1)	2 (1)									1 (1)		
	OS	3 (3)																							
Kattegat	Coast	5 (2)						11 (1)	116 (3)	4 (1)	3 (2)		5 (2)	29 19)	23 (15)	8 (2)	9 (2)	7 (2)	9 (2)	11 (2)	14 (2)	8 (2)	1 (2)	2 (2)	1 (2)
	OS	7 (4)									2 (1)		6 (3)	8 (6)	6 (3)	7 (2)	9 (2)	6 (2)	9 (2)	11 (2)	13 (2)	9 (2)	1 (2)	3 (2)	12 (2)
North Sea	Coast	91 (45)			11 (11)						8 (8)		14 (11)	41 (17)	8 (6)	44 (16)	47 (17)	44 (16)	34 (17)	56 (16)	44 (16)	19 (16)	29 (14)		
	OS	3 (1)							15 (1)					9 (9)			3 (1)	4 (1)		6 (1)	5 (1)	2 (1)	39 (8)		2 (1)

Table 4. Sampling of urea from 1969 to 1992: number of sampling occasions per year and basin, the number of stations sampled is between brackets. (OS: open-sea)

Urea		1969	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990	1991	1992
Bothnian Bay	Coast																								
	OS										5 (3)	6 (3)	8 (5)	2 (2)											
Bothnian Sea	Coast																								
	OS										8 (5)	6 (4)	9 (5)	5 (5)											
Åland Sea	OS										3 (1)	2 (1)	2 (1)	1 (1)											
Gulf of Finland	OS										4 (2)	2 (1)	2 (2)												
N Baltic Proper	Coast																								
	OS										6 (2)	7 (3)	9 (4)	3 (3)											
W Gotland Basin	Coast																								
	OS										9 (4)	19 (5)	18 (5)	11 (5)	12 (12)										
E Gotland Basin	OS										8 (3)	16 (4)	12 (5)	10 (5)	4 (4)										
Gdansk Basin	OS																								
Bornholm Basin	Coast																								
	OS										7 (4)	16 (4)	12 (4)	8 (4)	2 (2)										
Arkona Basin	Coast																								
	OS										3 (1)	4 (1)	3 (1)	2 (1)	2 (2)										
Belt Sea	OS																								
The Sound	Coast										3 (1)	4 (1)	3 (1)	3 (1)											
	OS																								
Kattegat	Coast										3 (1)	5 (2)	4 (2)	4 (2)											
	OS										6 (2)	5 (2)	5 (2)	2 (2)											
North Sea	Coast																								
	OS																								

Table 5. Sampling of yellow substances from 1969 to 1992: number of sampling occasions per year and basin, the number of stations sampled is between brackets. (OS: open-sea)

Yellow substances		1969	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990	1991	1992
Bothnian Bay	Coast																								
	OS								5 (1)								2 (1)								
Bothnian Sea	Coast																12 (11)								
	OS																3 (3)								
Åland Sea	OS																								
Gulf of Finland	OS																								
N Baltic Proper	Coast																								
	OS													1 (1)											
W Gotland Basin	Coast																								
	OS									19 (15)				46 (19)											
E Gotland Basin	OS									39 (5)							2 (2)								
Gdansk Basin	OS									4 (4)															
Bornholm Basin	Coast			44 (44)		36 (36)	60 (50)																		
	OS			4 (4)		2 (2)	3 (3)			10 (6)							1 (1)	1 (1)							
Arkona Basin	Coast																								
	OS									6 (3)															
Belt Sea	OS																								
The Sound	Coast									2 (1)															
	OS																								
Kattegat	Coast						6 (6)		132 (31)	4 (2)							1 (1)								
	OS																								
North Sea	Coast			15 (14)	15 (15)	46 (7)	46 (7)									6 (6)	3 (3)								
	OS																1 (1)								

Table 6. Sampling of humic substances from 1969 to 1992: number of sampling occasions per year and basin, the number of stations sampled is between brackets. (OS: open-sea)

Humic substances		1969	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990	1991	1992
Bothnian Bay	Coast																								
	OS							4 (3)	6 (2)		3 (2)			2 (1)	1 (1)						3 (3)	8 (4)	6 (4)		9 (5)
Bothnian Sea	Coast													8 (8)			8 (8)			10 (10)					
	OS								5 (1)		6 (4)		11 (7)	11 (7)	10 (6)	11 (6)	10 (6)	10 (6)	6 (6)	7 (6)	7 (6)	13 (7)	13 (7)		13 (8)
Åland Sea	OS										3 (1)														
Gulf of Finland	OS										2 (1)														1 (1)
N Baltic Proper	Coast																								
	OS										3 (1)	3 (1)	5 (3)	2 (1)	3 (1)	3 (1)	4 (1)	3 (1)	2 (1)	2 (1)	5 (3)	4 (3)	4 (3)		4 (3)
W Gotland Basin	Coast																								
	OS										9 (4)		9 (4)	39 (22)	2 (2)	5 (3)	4 (2)	4 (2)	4 (2)	4 (2)	5 (3)	3 (3)	1 (1)	2 (2)	1 (1)
E Gotland Basin	OS										7 (3)	1 (1)	5 (4)	3 (3)	1 (1)	4 (2)	4 (2)	4 (2)	4 (2)	4 (2)	5 (3)	2 (2)	2 (2)	2 (2)	2 (2)
Gdansk Basin	OS																								
Bornholm Basin	Coast																								
	OS										5 (4)		7 (4)	7 (4)	4 (3)	8 (3)	7 (4)	8 (3)	7 (3)	8 (3)	8 (3)	5 (3)	5 (3)	4 (3)	1 (1)
Arkona Basin	Coast																								
	OS										3 (1)		1 (1)	1 (1)	1 (1)	2 (1)	2 (1)	2 (1)	3 (2)	2 (1)	2 (1)	2 (1)	1 (1)	2 (1)	2 (1)
Belt Sea	OS																	1 (1)			3 (1)	2 (1)	2 (1)		
The Sound	Coast										2 (1)		1 (1)												
	OS																								
Kattegat	Coast							11 (10)	110 (28)		2 (1)		2 (2)	21 (15)	15 (12)	1 (1)	4 (2)	4 (2)	4 (2)	2 (1)	3 (1)	3 (2)	3 (2)	1 (1)	1 (1)
	OS																								
North Sea	Coast										8 (8)		14 (11)	41 (17)	5 (5)	44 (16)	47 (17)	42 (16)	32 (17)	55 (16)	47 (16)	19 (16)	28 (15)		
	OS													11 (10)			3 (1)	4 (1)		6 (1)	5 (1)	2 (1)	3 (1)		2 (1)

Table 7. Sampling of humic substances from 1991 to 2014: number of sampling occasions per year and basin, the number of stations sampled is between brackets. (OS: open-sea)

Humic substances		1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014
Bothnian Bay	Coast											10 (2)	7 (2)	10 (2)	12 (2)	12 (2)	26 (17)	13 (2)	16 (2)	16 (2)	16 (2)	16 (2)	14 (2)	21 (5)	16 (2)
	OS		9 (5)					2 (2)	2 (2)	2 (2)	8 (3)	11 (4)	13 (4)	11 (3)	15 (5)	14 (5)	17 (5)	20 (4)	15 (4)	15 (4)	15 (4)	14 (5)	15 (4)	19 (5)	12 (2)
Bothnian Sea	Coast								4 (1)	18 (1)	17 (2)	18 (2)	18 (2)	18(2)	16 (2)	16 (2)	18 (2)	23 (3)	18 (3)	30 (3)	30 (3)	30 (3)	30 (3)	48 (21)	30 (3)
	OS		13 (8)					2 (2)	1 (1)	3 (3)	10 (5)	8 (4)	8 (4)	8 (4)	9 (5)	11 (7)	10 (4)	19 (5)	16 (4)	17 (5)	14 (4)	14 (4)	16 (4)	14 (2)	10 (2)
Åland Sea	OS															1 (1)									
Gulf of Finland	OS		1 (1)																						
N Baltic Proper	Coast																								
	OS		4 (3)													1 (1)									
W Gotland Basin	Coast																								
	OS	2 (2)	1 (1)					4 (2)	11 (2)	9 (2)	9 (2)		9 (2)	9 (2)	7 (2)	8 (2)	4 (2)	9 (2)	8 (2)	9 (2)	8 (2)	8 (2)	7 (2)	3 (2)	5 (2)
E Gotland Basin	OS	2 (2)	2 (2)					14 (2)	9 (2)	8 (2)	12 (2)		10 (2)	14 (2)	10 (2)	13 (3)	10 (2)	12 (2)	12 (2)	11 (2)	13 (3)	12 (2)	7 (4)	3 (2)	7 (2)
Gdansk Basin	OS																								
Bornholm Basin	Coast																								
	OS	4 (3)	1 (1)				4 (1)	12 (1)	5 (1)	5 (1)	5 (1)		6 (1)	7 (1)	6 (1)	6 (1)	5 (1)	6 (1)	6 (1)	6 (1)	6 (1)	6 (1)	4 (1)	2 (1)	4 (1)
Arkona Basin	Coast																								
	OS	2 (1)						3 (1)	5 (1)	4 (1)	6 (1)		4 (1)	7 (1)	4 (1)	6 (1)	5 (1)	6 (1)	6 (1)	6 (1)	6 (1)	6 (1)	6 (2)	2 (1)	4 (1)
Belt Sea	OS																								
The Sound	Coast															1 (1)									
	OS																								
Kattegat	Coast	1 (1)	1 (1)					5 (1)	6 (1)	6 (1)	9 (1)		7 (1)	10 (1)	10 (1)	9 (1)	6 (1)	7 (1)	11 1)	12 (1)	11 (1)	12 (1)	11 (1)	4 (1)	7 (1)
	OS	2 (2)	2 (1)					3 (1)								2 (2)									
North Sea	Coast																								
	OS		2 (1)				1 (1)									1 (1)									

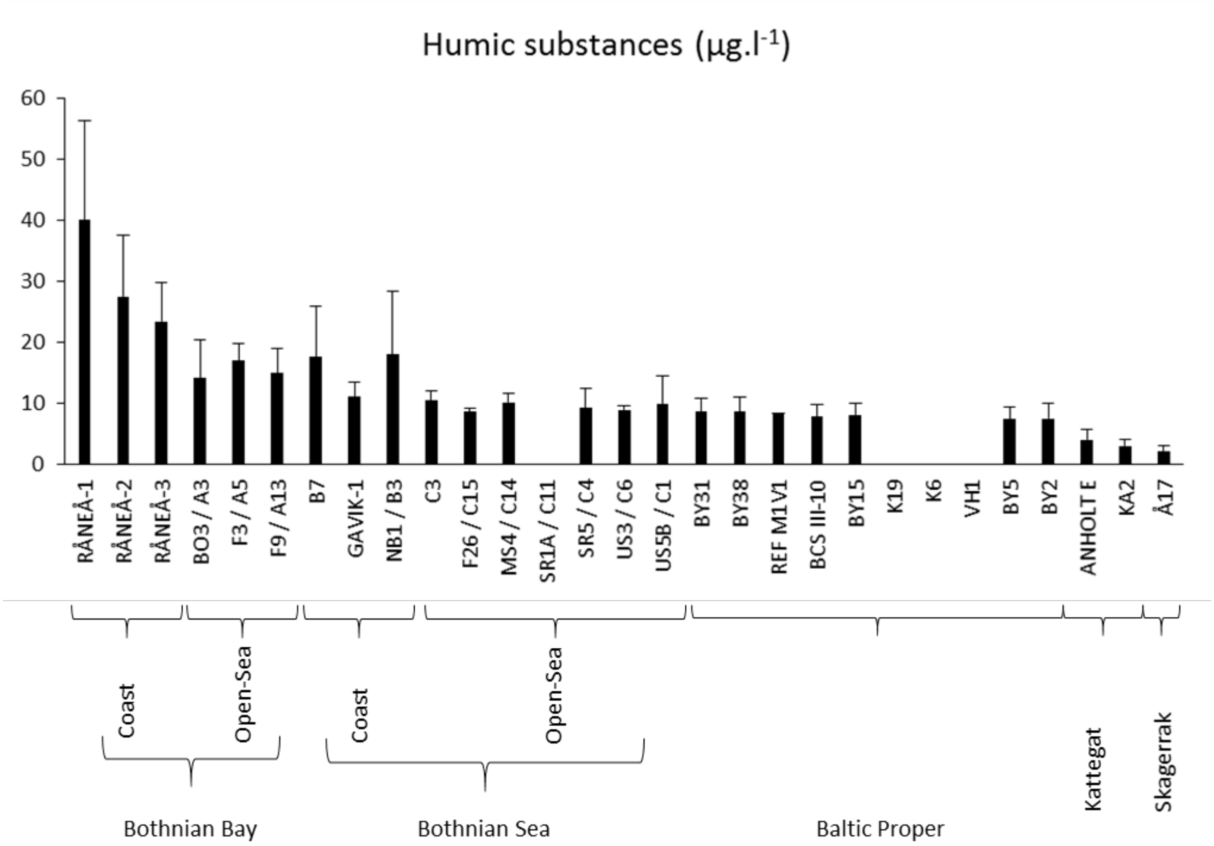

Figure 1. Average concentration of humic substances (in µg.l^{-1}) of the entire water column at each station from the Bothnian Bay to the Skagerrak. Error bars correspond to standard deviation. Station coordinates are presented in appendix 2.

The concentrations of humic substances display a strong seasonal pattern. In the open Baltic Sea, concentrations are minimal in summer, and progressively increase from autumn to the spring when concentrations are maximal (Figure 3a and 3b). At coastal stations, the seasonal pattern is even more pronounced in spring, when concentrations are extremely variable (for example at stations Råneå-2 of NB1 / B3 in the Gulf of Bothnia).

The variations of humic substances concentrations over time, region and depth seem to be mostly linked to hydrodynamic conditions, e.g. river inflow and circulation of water masses.

Humic substances (μg.l^{-1})

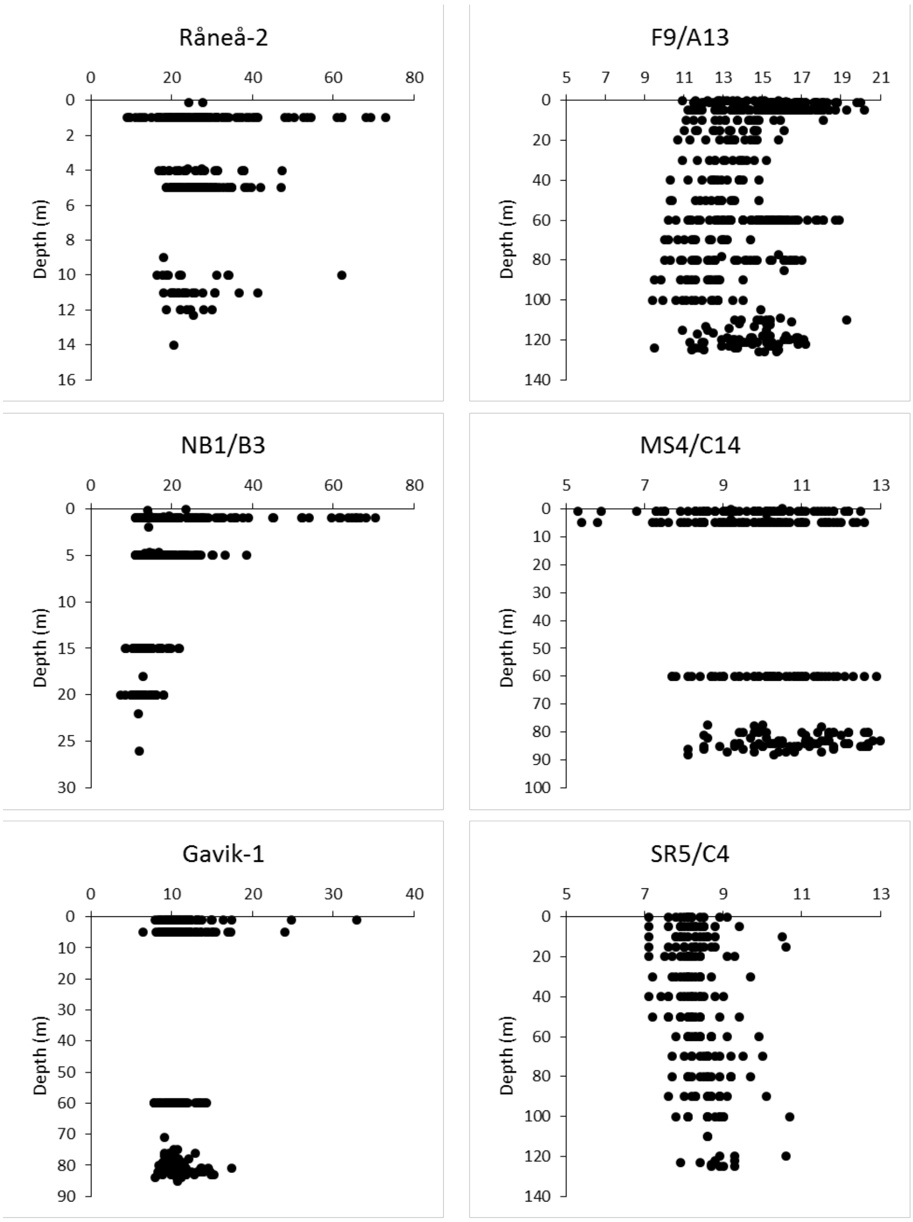

Figure 2a. Distribution of humic substances concentration (in μg.l^{-1}) over depth at stations: Råneå-2 (Bothnian Bay, coast), F9 / A13 (Bothnian Bay, open-sea), NB1 / B3 (Bothnian Sea, coast), MS1 /C14 (Bothnian Sea, coast), Gavik-1 (Bothnian Sea, coast) and SR5/C4 (Bothnian Sea, open-sea).

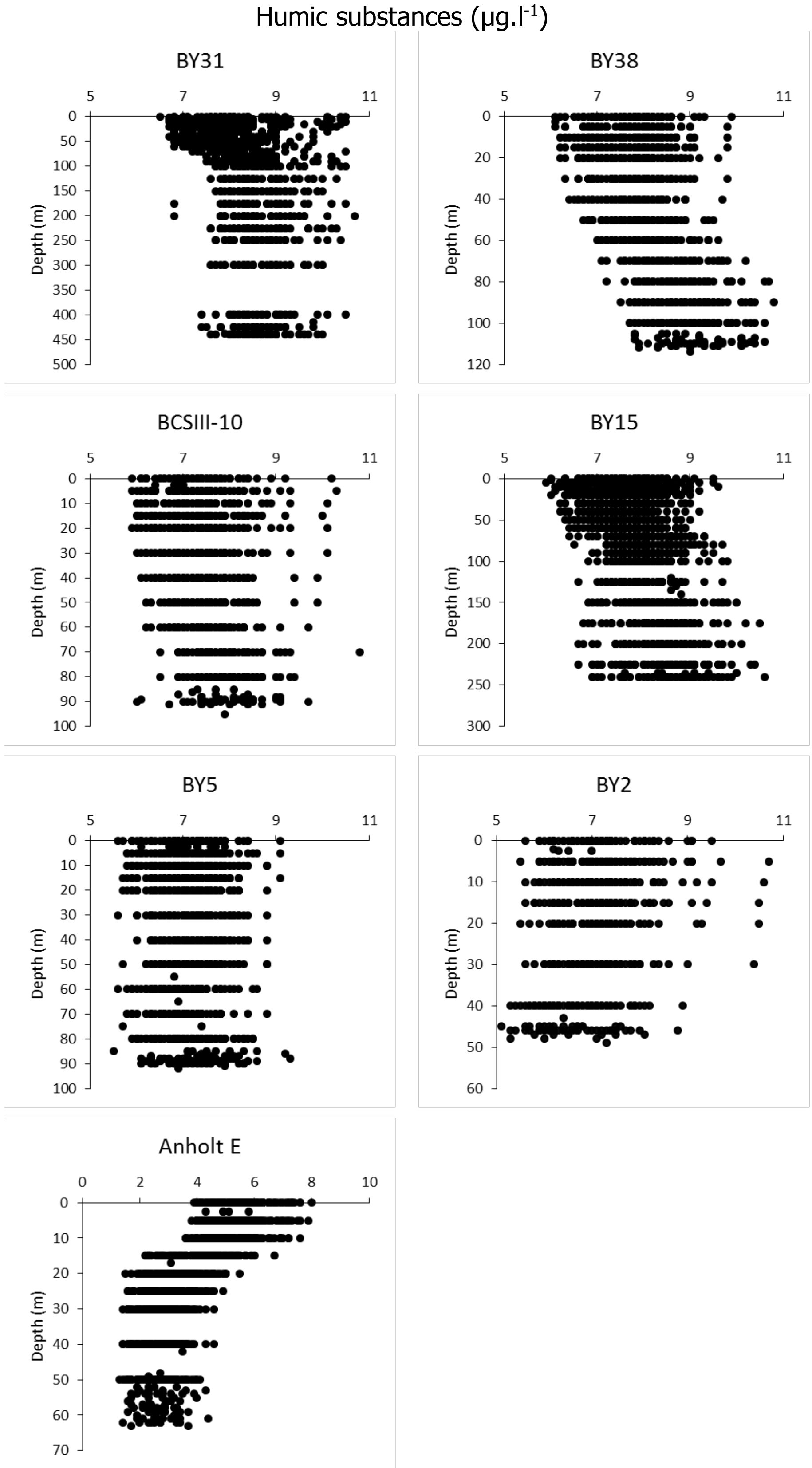

Figure 2b. Distribution of humic substances concentration (in µg.l^{-1}) over depth at stations: BY31 and BY 38 (Western Gotland Basin), BCSIII-10 and BY15 (Eastern Gotland Basin), BY5 (Bornholm Basin), BY2 (Arkona Basin) and Anholt E (Kattegat).

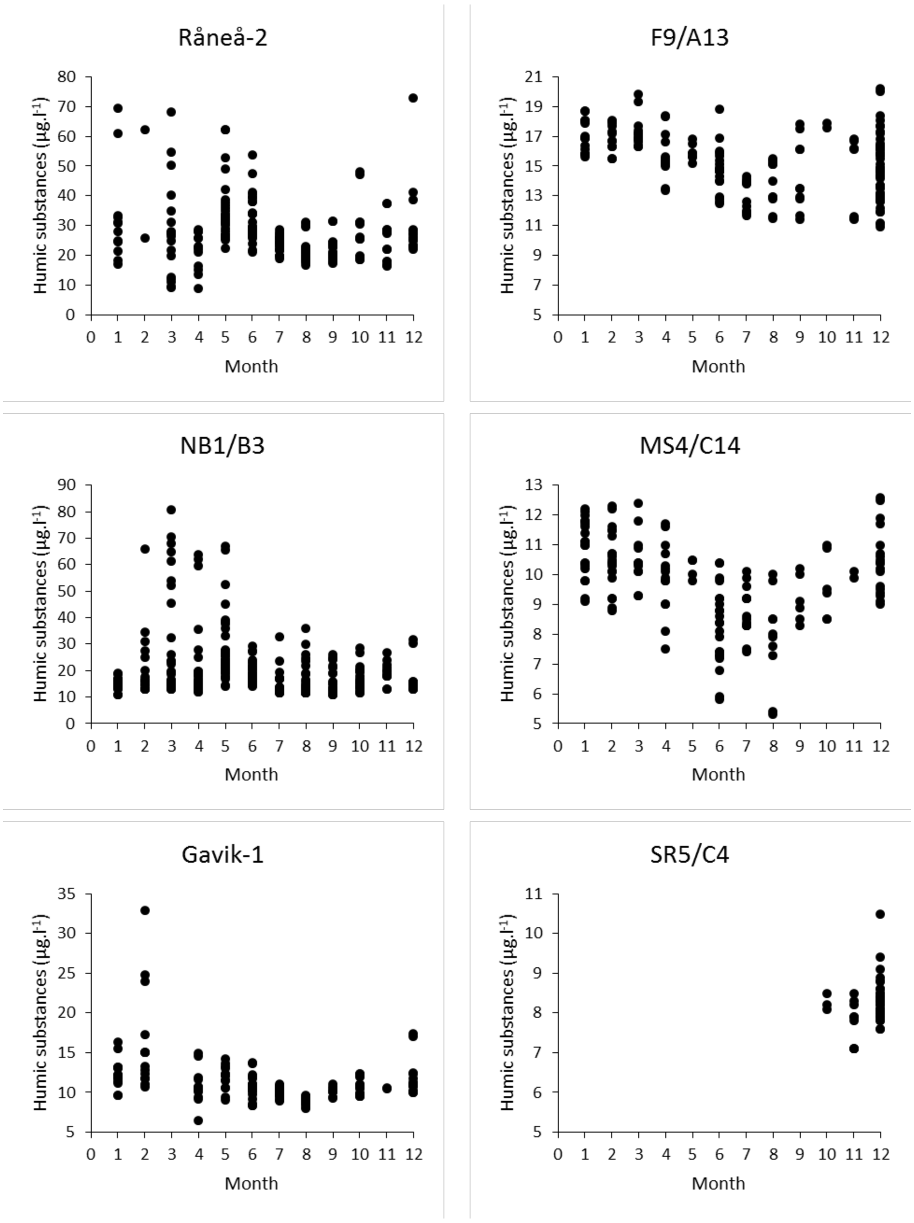

Figure 3a. Seasonal variation of humic substances concentration (in $\mu g.l^{-1}$) at stations: Råneå-2 (Bothnian Bay, coast), F9 / A13 (Bothnian Bay, open-sea), NB1 / B3 (Bothnian Sea, coast), MS1 /C14 (Bothnian Sea, coast), Gavik-1 (Bothnian Sea, coast) and SR5/C4 (Bothnian Sea, open-sea).

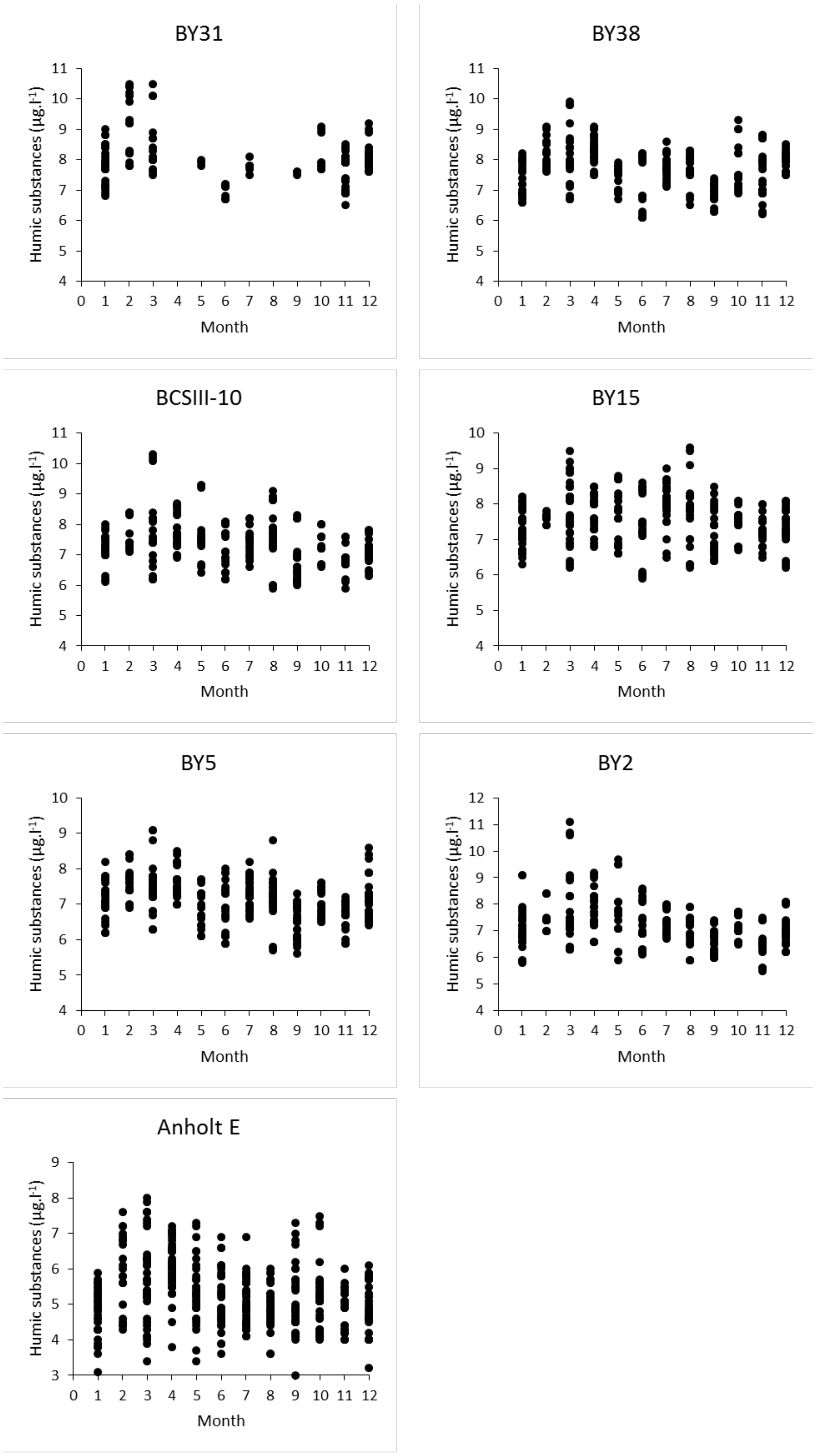

Figure 3b. Seasonal variation of humic substances concentration (in µg.l^{-1}) at stations: BY31 and BY 38 (Western Gotland Basin), BCSIII-10 and BY15 (Eastern Gotland Basin), BY5 (Bornholm Basin), BY2 (Arkona Basin) and Anholt E (Kattegat).

Dissolved organic carbon (DOC)

DOC monitoring started in 1991 and continues, though data were only available until 2014. Almost only the Gulf of Bothnia is covered, with an extensive sampling frequency (Table 8).

In the open-sea of the Gulf of Bothnia, DOC concentrations decrease from the north the south (Figure 4). DOC concentrations range from 389±69 µmol $C.l^{-1}$ at station F3 / A5 to 298±23 µmol $C.l^{-1}$ at station SR5 / C4. At a basin scale, DOC concentrations are higher at the coastal stations.

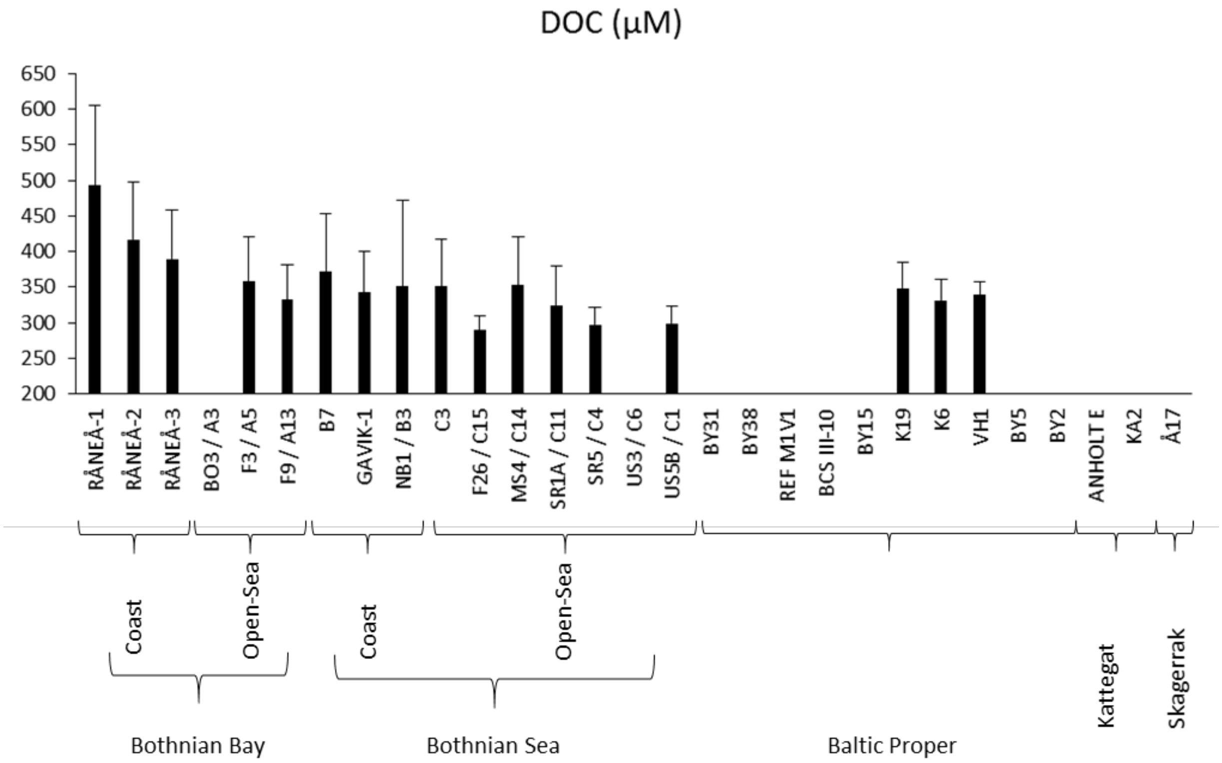

Figure 4. Average concentration of DOC (in µmol $C.l^{-1}$) of the entire water column at each station from the Bothnian Bay to the Skagerrak. Error bars correspond to standard deviation. Station coordinates are presented in appendix 2.

The vertical distribution of DOC is relatively similar on the coast or in the open-sea of the Gulf of Bothnia (Figure 5). The concentrations are higher at surface compared to the deeper layers.

The seasonal variations of DOC are less pronounced than for humic substances, however the spring is also displaying most of the variability (Figure 6). At the coast, maximal concentrations are observed in spring, and later in summer; while in the open-sea maximal concentrations are reached in summer.

The variations of DOC concentrations over time, region and depth appear to be linked to hydrodynamic and biological metabolism.

Table 8. Sampling of dissolved organic carbon, DOC, from 1991 to 2014: number of sampling occasions per year and basin, the number of stations sampled is between brackets. (OS: open-sea)

DOC		1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014
Bothnian Bay	Coast							2 (2)	9 (2)	10 (2)	10 (2)	10 (2)	9 (2)	10 (2)	12 (2)	12 (2)	27 (17)	14 (2)	16 (2)	16 (2)	16 (2)	16 (2)	14 (2)	21 (5)	16 (2)
	OS	16 (2)	4 (1)	24 (3)	12 (3)	16 (1)	20 (1)	6 (2)	5 (1)	5 (1)	10 (3)	10 (3)	17 (3)	10 (3)	13 (3)	12 (3)	16 (4)	18 (3)	14 (3)	11 (2)	12 (2)	12 (3)	12 (2)	17 (4)	12 (2)
Bothnian Sea	Coast	17 (1)	17 (1)	20 (1)	15 (1)	21 (1)	23 (1)	5 (1)	11 (2)	12 (2)	17 (3)	16 (3)	19 (3)	14 (3)	17 (3)	17 (3)	14 (3)	20 (3)	22 (3)	23 (3)	24 (3)	24 (3)	24 (3)	24 (3)	24 (3)
	OS	20 (2)	2 (1)	26 (3)	30 (3)	18 (1)	20 (1)	5 (1)			4 (2)	5 (2)	14 (2)	6 (2)	6 (2)	6 (2)	8 (2)	14 (2)	14 (2)	20 (3)	12 (2)	12 (2)	14 (2)	14 (2)	10 (2)
Åland Sea	OS																								
Gulf of Finland	OS																								
N Baltic Proper	Coast																								
	OS																								
W Gotland Basin	Coast								1 (1)																
	OS																								
E Gotland Basin	OS																								
Gdansk Basin	OS																								
Bornholm Basin	Coast								8 (8)															35 (3)	
	OS																								
Arkona Basin	Coast																								
	OS																								
Belt Sea	OS																								
The Sound	Coast																								
	OS																								
Kattegat	Coast																								
	OS																								
North Sea	Coast																								
	OS																								

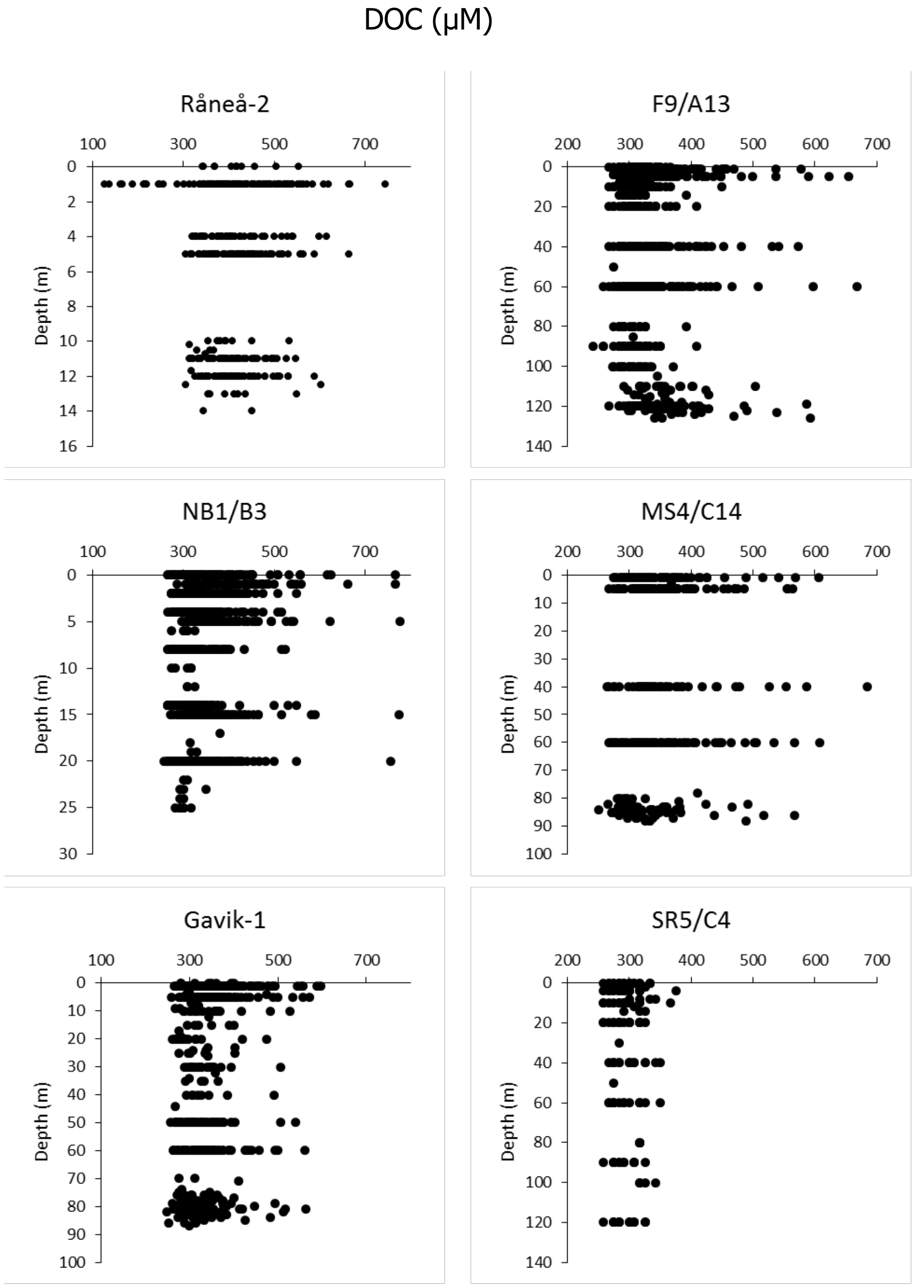

Figure 5. Distribution of DOC concentrations (in µmol C.l^{-1}) over depth at stations: Råneå-2 (Bothnian Bay, coast), F9 / A13 (Bothnian Bay, open-sea), NB1 / B3 (Bothnian Sea, coast), MS1 /C14 (Bothnian Sea, coast), Gavik-1 (Bothnian Sea, coast) and SR5/C4 (Bothnian Sea, open-sea)

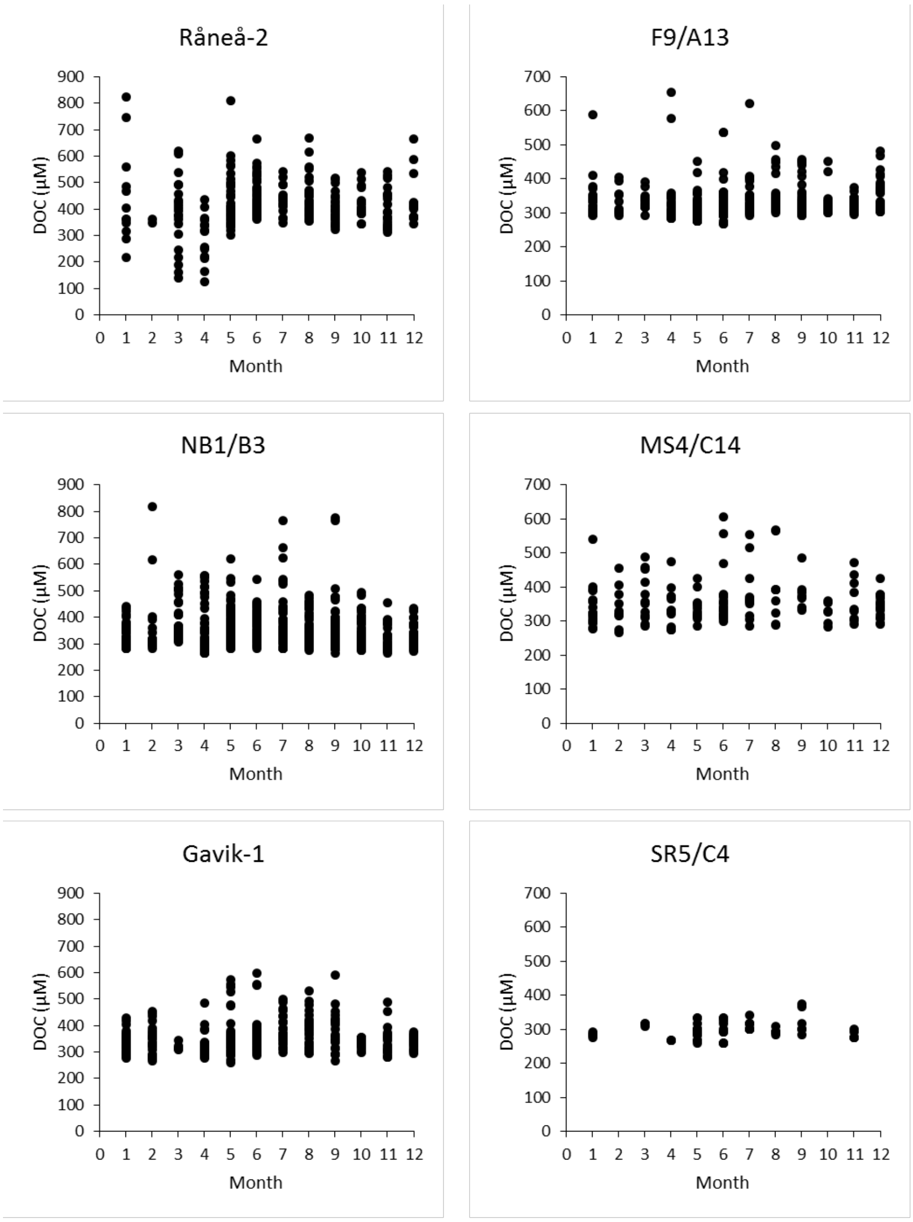

Figure 6. Seasonal variation of DOC concentrations (in µmol C.l^{-1}) at stations: Råneå-2 (Bothnian Bay, coast), F9 / A13 (Bothnian Bay, open-sea), NB1 / B3 (Bothnian Sea, coast), MS1 /C14 (Bothnian Sea, coast), Gavik-1 (Bothnian Sea, coast) and SR5/C4 (Bothnian Sea, open-sea).

II. Monitoring program in practice

Information on DOM in marine Swedish waters are only partially available, and gives so far only a limited certainty on the significance and relevance of any conclusion at this stage. However, to improve the knowledge on DOM spatio-temporal variations in Swedish marine waters, some recommendations regarding the spatial and temporal sampling coverage of DOM related characteristics can be suggested.

II. 1. Spatial coverage

In the Baltic Sea, a large proportion of DOM originates from the land; though most of this DOM is lost in the coastal regions a significant fraction reaches the open-sea especially in the northern basins. Future climate scenario forecast an increase in river run off especially in the north of the Baltic Sea; however the composition of DOM flowing into the sea is more likely to be altered and the future distribution of DOM at the basin scale is unknown. Taking in account the gaps in our knowledge and the changing environment, it seems to be essential to monitor DOM parameters both along the coast and in the open-sea.

At the moment, the monitoring program of water mass is including both coastal and open-sea stations. Nevertheless, the spatial coverage presents some gaps. In some basins, the number of stations on the coast or in the open-sea is insufficient.

In the Bothnian Bay, 2 stations are sampled on the coast (Råneå-1, Råneå-2), and 2 in the open-sea (A5, A13). The 2 coastal stations are receiving freshwater from the same river, and the coast of the southern Bothnian Bay is not covered. A coastal station in the southern part would be relevant to evaluate if there is a significant decrease in DOM runoff with latitude.

In the Bothnian Sea, 2 stations are sampled at the coast (Gavik-1, B3/B7) and 2 in open-sea (C3, C14). Only the northern part of the Bothnian Sea is covered. The 2 open-sea stations are also quite close to each other at the basin scale, leaving the southern half of the basin not sampled. An additional station on the coast and in open-sea in the southern part of the Bothnian Sea would be interesting to address the dilution and/or loss of DOM from the important freshwater inputs from the Gulf of Bothnia.

The Gotland Basin is represented by 2 coastal stations (B1 Askö, REF M1V1) and 3 open-sea stations (BY15, BY29, BY31). Based on the data from the monitoring programs and on literature, DOM does not display important variations in the open-sea of this Gotland basin; hence the spatial coverage might be sufficient to monitor DOM. However, almost no information is available on DOM on the coast; it is therefore not possible to assure that the number of coastal station would be sufficient.

In the Bornholm and Arkona basins, only the open-sea is sampled (station BY5 in Bornholm Basin and BY2 in Arkona Basin). As for the Gotland Basin, information is not available to evaluate the relevance of a coastal sampling. Though a gradient is observed in the colour of the waters flowing into the Baltic Sea, with darker waters in the north and lighter in the south, the rivers from the south are more likely carrying nutrients from agricultural land and contributing to eutrophication. A preliminary study of DOM on the southern coast of Sweden would be prerequisite to make appropriated recommendations on the sampling spatial coverage.

In the Kattegat and the Skagerrak, 1 station on the coast and 1 station in open-sea are sampled for each basin (Kattegat: N14 Falkenberg on the coast and Anholt E in open-sea; Skagerrak: Slaggö on the coast and Å17 in open-sea). The lack of information makes difficult to address the relevance of the spatial coverage.

In general, the current spatial distribution of the sampling stations in the open-sea seems adequate to properly address DOM variations, despite a gap in the southern Bothnian Sea. However, for the coast it would be necessary to evaluate the monitoring of new stations.

II. 2. Variables

Carbon

In the Baltic Proper, DOC concentrations are on average 48 higher than those of particulate organic carbon (Nausch et al., 2008). However, along the coast the rivers are carrying significant particle loads that increase the particulate organic carbon. As well, during strong phytoplankton blooms the particulate organic carbon might significantly increase. Therefore, to avoid any interference, the monitoring of DOC would be recommended over the measurement of total organic carbon (TOC).

Nitrogen

In the Baltic Proper, nitrogen is present under three forms: 5% under dissolved inorganic nitrogen (DIN), 13% under particulate organic nitrogen (PON) and 66% as dissolved organic nitrogen (DON) (Nausch et al. 2008). Organic forms of nitrogen represent most of the nitrogen budget, and the particulate fraction of nitrogen is quite important, thus measurement of DON would be recommended over that of total nitrogen (TN).

The DON pool is only partly constituted by molecules such as urea or amino acids. These molecules give good information on the DON pool that is extremely labile; however in the Baltic Sea bacterial communities are adapted to degrade complex molecules (Figueroa 2016). Hence, the quantification of the entire DON pool and not only a small set of extremely labile molecules, as urea or amino acids, would me more relevant to address ecosystem problematics, e.g. ecosystem production and function.

Phosphorus

As for nitrogen, a large part of the phosphorus is under organic forms in the Baltic Sea. Furthermore in summer during blooms of filamentous cyanobacteria, a variable fraction of phosphorus is represented in the particulate fraction. The variable proportion of phosphorus under particulate form would lead to recommend the measurement of DOP over total phosphorus (TP).

Organic matter

Currently, organic matter has been studied through the estimation of humic substances concentration and of CDOM optical properties (absorption or fluorescence). In the Baltic Sea, humic substances are a good proxy of river inflow both quantitatively and qualitatively and consequently a good proxy for brownification. Humic substances could also be a good proxy for light attenuation; however CDOM absorption would be a more accurate proxy.

CDOM is usually estimated by measuring the absorption spectra ideally from UV wavelength to >800 nm or by fluorometric methods using excitation-emission matrices. The excitation-emission matrices (EEMs) allow the distinction of peaks characteristics of certain group of compounds, for example one of these peaks correspond to humic substances. However, these peaks display different excitation/emission maximal coordinates depending on the quality of DOM. Moreover, there is no standard method and consensus on data correction and processing at the moment. The EEMs method gives qualitative information; however, quantification of DOM in biomass or in fluorescence emission is not possible at the stage of development of this method to achieve quality insurance standards required by monitoring programs. On the other hand, CDOM absorption gives a quantitative estimate and is complementary to humic substances estimation.

We used data from the ECOCHANGE research program to evaluate the relationships between DOC, humics substances and CDOM. The Rånefjärden was sampled in 2010 in May, June, July and August at the surface of 18 stations. The Örefjärden was sampled in 2010, 9 times from May to September, at the surface of 18 stations. The entire Baltic Sea was sampled in August 2011 and March 2012 at the surface of 14 stations from the Kattegat to the Bothnian Bay. The relationships between DOC concentrations, humic substances concentrations and g440 (absorption of CDOM at 440 nm) are presented (Figure 7). Each couple of parameters shows good relationships. The power of each relation ship differed when considering each dataset separately; however, the relationships were very strong for each couple of variables when all data were considered. Harvey et al. (2015) found difference in relationships between DOC and g440 between coastal bays of the Gulf of Bothnia and coastal bays the Baltic Proper. This illustrates the independence of the variables estimated and the necessity to have at the same time DOC concentration and humic substances and/or CDOM absorption, as characteristics of DOM.

Humic substances and CDOM absorption give complementary information. Nevertheless, humic substances concentration is an easy variable to estimate, and has also a slightly lower analysis cost than CDOM absorption. Thus, the measurement of humic substances would be recommended following HELCOM recommendations. However, the inclusion of CDOM absorption in monitoring programs should be evaluated.

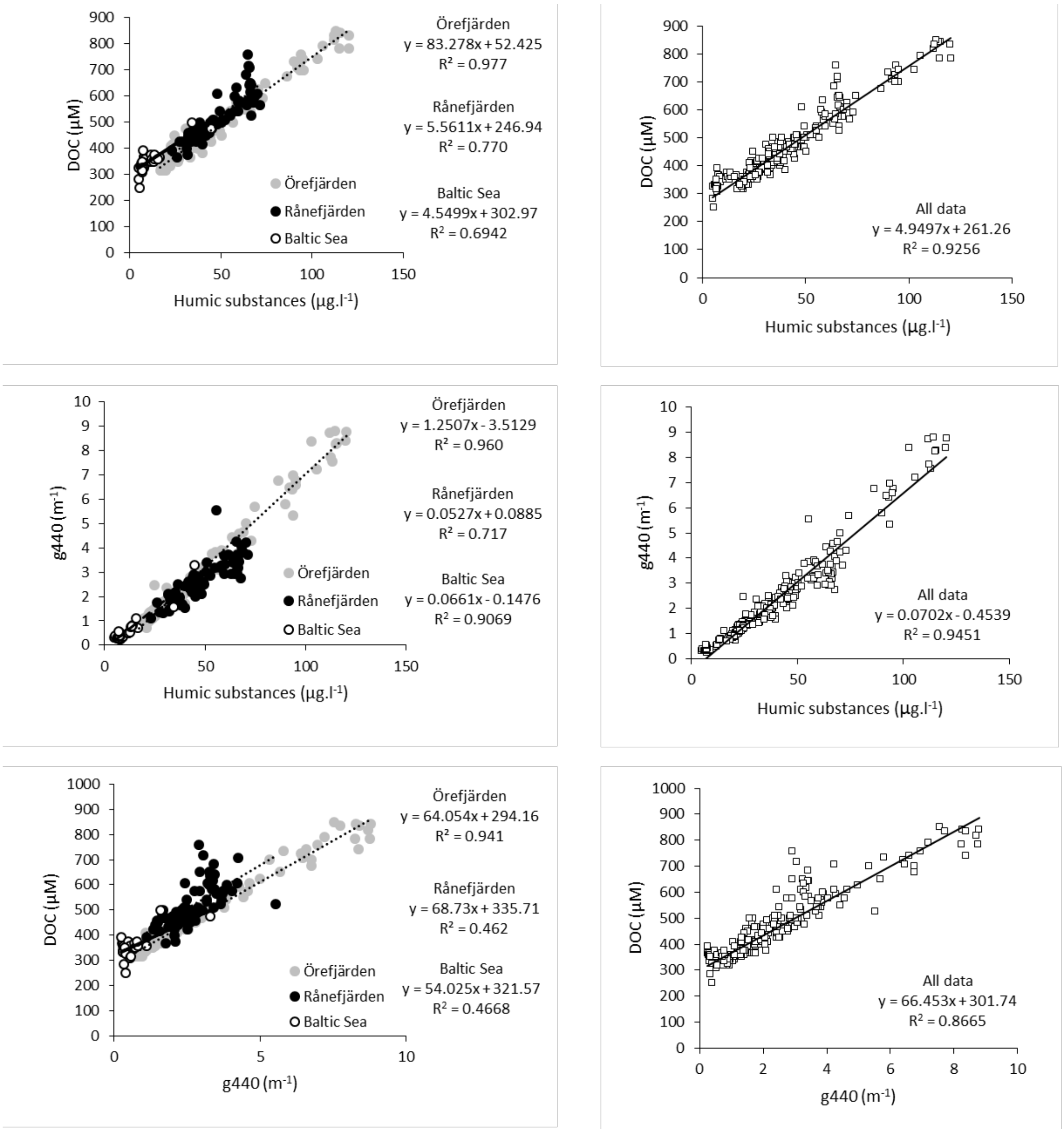

Figure 7. Relationships between DOC concentrations (µmol C.l^{-1}), humic substances (µg.l^{-1}) and g440 (m^{-1}) from ECOCHANGE datasets from Rånefjärden (Bothnian Bay), Örefjärden (Bothnian Sea) and a transect over the entire Baltic Sea. The right panel is a zoom of the left panel representing the Baltic Sea transect.

II. 5. Recommended methodology

Dissolved organic carbon (DOC)

DOC concentration is directly measured by high temperature catalytic oxidation as recommended by HELCOM. Water samples are filtered on 0.22 µm membrane filters and acidified to pH 4 in order to remove inorganic carbon. The prepared sampled are later analysed on TOC analyzer using HTCO method as described in Sugimura & Suzuki (1988) and Cauwet (1999).

Dissolved organic nitrogen (DON)

DON is estimated indirectly after the measurement of total dissolved nitrogen (TDN) and dissolved inorganic nitrogen (DIN), as DON = TDN – DIN.

DIN is directly measured on the sample by standard colorimetric methods (Hansen & Koroleff 1999). For TDN, the sample is filtered on a 0.22 µm pore size membrane filter and oxidized with peroxodisulphate to transform organic nitrogen into nitrate (Hansen & Koroleff 1999). The sample is later analysed with colorimetric method as DIN.

Dissolved organic phosphorus (DOP)

As for DON, DOP is estimated indirectly after the measurement of total dissolved phosphorus (TDP) and dissolved inorganic phosphorus (DIP), as DOP = TDP – DIP.

DIP is directly measured on the sample by standard colorimetric methods (Hansen & Koroleff 1999). For TDP, the sample is filtered on a 0.22 µm pore size membrane filter and oxidized with peroxodisulphate to transform organic phosphorus into phosphate (Hansen & Koroleff 1999). The sample is later analysed with colorimetric method as DIP.

Humic substances

Humic substances concentration is directly measured on untreated water samples by fluorescence (Coble et al. 1990). Humic substances fluorescence are measured using a fluorometer at 350/450 nm excitation/emission wavelengths and the fluorescence is standardized to quinine sulphate as described in Hoge at al. (1993).

Chromophoric dissolved organic matter (CDOM) absorption

CDOM absorption is measured by spectrophotometry. Samples are filtered through 0.22 µm pore size polycarbonate filters. A dual beam spectrophotometer with integrating-sphere attachment is ideal (Mitchell et al. 2000). The absorption spectra should be measured from 350 to 800 nm as described in Mitchell et al. (2000) and Tilstone et al. (2002).

III. Needs for the validation of satellite data for chlorophyll products

Ocean colour satellite sensors measure the spectral reflectance of the ocean surface. In the last years new high-resolution sensors were designed for coastal waters with further applications for the Baltic and North Seas. The sensor "MEdium Resolution Imaging Spectrometer" (MERIS) from the European Space Agency (ESA) satellite ENVISAT gives high-resolution images. As well, the moderate-resolution imaging spectroradiometer (MODIS) was launched on board the Aqua (EOS PM) satellite by the National Aeronautics and Space Administration (NASA).

The ocean colour sensors have several spectral bands designed for specific application for the atmosphere, land and ocean. In the marine waters, several constituents absorb light in the same spectral band, as for example CDOM and chlorophyll. It is therefore crucial to properly estimate CDOM concentrations, which are also exclusively absorbing light in a specific spectral band, in order to get a reliable retrieval of chlorophyll concentrations.

As ocean colour sensors measure ocean surface reflectance, water samples for validation purposes should be taken just below the surface. As well, the sampling spatial coverage should be representative of all the range of variation of CDOM. The estimation of CDOM would be recommended at all coastal and open-sea stations covered by monitoring program, as baseline information is missing for most of the marine Swedish waters. Additionally, intensive measurements campaign with extensive spatial and time coverage might be needed to improve processing algorithms for the Baltic and North Seas.

Sweden is situated at relatively high latitude where satellite images are not generated for the whole year due to solar incidence angle, moreover ocean colour data is not retrieved under sea-ice. In the south of the Baltic Sea, ocean colour satellite data are available from February to November, while in the north this period could be limited from March to October. Therefore, the monitoring of CDOM would be restricted to the period from spring to autumn.

For the validation ocean colour products, the standard method of CDOM estimation is the measurement of CDOM spectral absorption (Doerffer 2002, Tilstone et al. 2003). As CDOM absorption and humic substances concentrations showed strong relationships in the Baltic Sea (Figure 7), the use of humic substances concentrations determined by fluorescence could be evaluated for satellite products validation. However, the relationship would require to be established on a dataset reasonably large and representative of the conditions encountered in marine Swedish waters. In that case, humic substances would be a proxy of CDOM absorption and could increase errors and uncertainties in satellite products. Furthermore, CDOM absorption is the only valid measurement accepted by the ESA and the NASA for satellite product validation.

In the Baltic and North Seas, CDOM absorption measurements are missing and are essential to deliver reliable satellite products such as secchi depth, and CDOM and chlorophyll concentrations.

SUMMARY

Information on DOM in the Baltic Sea is very scarce considering its importance for marine food-webs. Allochthonous DOM is increasing light absorption in the water and transporting nutrients to the sea. In the Baltic Sea, most of the nutrients are under organic forms, which can have a high bioavailability.

DOM is only partly included in the regular monitoring of marine Swedish waters. In general, the spatio-temporal coverage of the monitoring program is relatively extensive, though some regions could be included in the monitoring program.

Nutrients are monitored under forms of total nutrients or dissolved inorganic nutrients. As the information on the dissolved organic forms is missing, the inclusion of DOC, DON and DOP should be evaluated. For example, an intensive survey over time space over a year could be informative to give relevant recommendations for monitoring programs.

Humic substances are a good indicator of terrestrial inputs, and were monitored for a long period for brownification. However, if the monitoring program aims at providing data for the validation of satellite products, the inclusion of CDOM absorption measurement in the program should be evaluated.

The input of allochthonous DOM to the Baltic Sea is determining the balance between bacterial and primary production and the energy channelling though the food-web. Future climate scenarios forecast a change in riverine inputs to the Baltic Sea, in terms of quantity and frequency. Therefore, the inclusion of DOM in marine monitoring programs is fundamental to address ecological status and ecosystem change in the marine Swedish waters.

ACKNOWLEDGEMENTS

This project was financed by the Swedish agency for marine and water management and the marine strategic research environment EcoChange, via the Swedish Research Council FORMAS.

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Appendix 1. Literature data on dissolved organic carbon (DOC), dissolved organic nitrogen (DON), dissolved organic phosphorous (DOP), absorption of chromophoric dissolved organic matter (a CDOM, slope of absorption spectra between 275 and 295 nm, SUVA (specific ultra-violet absorption) at 254 nm), humic substances and lignin in the Baltic Sea (exclusive of the Gulf of Finland and Gulf of Riga) and the North Sea.

Area	Season	Year	DOC	DON	DOP	a CDOM	a CDOM	a CDOM	Humic Subst.	Lignin	Reference
							Slope275-295	Suva 254			
			(µm)	(µm)	(µm)	(m-1)	(µm-1)	(mg.L-1.m-1)	(µg.l-1)	(µg.l-1)	
Gulf of Bothnia											
Whole gulf, coast & OS	Year round	1977–1978	241–483								Perttilä and Tervo (1979)
Bothnian Bay											
Bothnian Bay, coast & OS	May–early June	1992							12		Skoog et al. (2011)
Bothnian Bay, coast & OS	August–September	2009		14.8 ± 3.0							Korth et al. (2011)
Bothnian Bay, coast & OS	March, August–September	2009	308								Deutsch et al. (2012)
Bothnian Bay, coast	May–early June	1997	390–520						19.9-47.7		Gustafsson et al. (2000)
Bothnian Bay, coast (Oulu)	September	2005	347	7.8		a(350)= 6.60					Stedmon et al. (2007)
Bothnian Bay, coast	May–early June	2005	464 ± 2								van Dongen et al. (2008)
Bothnian Bay, coast	Apr–May, Aug, Oct	2010	393 ± 27								Asmala et al. (2013)
Bothnian Bay, OS	June	1995	517								Porcelli et al. (1997)
Bothnian Bay, OS	May–early June	1997	290				7.3±1.5	3.47±0.27			Gustafsson et al. (2000)
Bothnian Bay, OS	May–early June	2005	288–320								van Dongen et al. (2008)
Bothnian Bay, OS	August	2007				a(412)=1.035 ± 0.218					Berthon and Zibordi 2010
Bothnian Bay, OS	June–July	2008			0.12 ± 0.03						Nausch and Nausch (2011)
Bothnian Sea											
Bothnian Sea, coast & OS	May–early June	1992							8.8		Skoog et al. (2011)
Bothnian Sea OS	May–June	1992	300–325								Wedborg et al. (1994)
Bothnian Sea, OS	Year round	1991–1992	270–335								Zweifel et al. (1995)
Bothnian Sea, OS	August	2007				a(412)= 0.519 ± 0.065					Berthon and Zibordi 2010
Bothnian Sea, OS	June–July	2008–2009			0.13 ± 0.02						Nausch and Nausch (2011)
Bothnian Sea, OS	February–March				0.18 ± 0.02						
Bothnian Sea, OS	March, August–September	2009	316								Deutsch et al. (2012)
Bothnian Sea, coast	Year round	1990–1992	270–400								Zweifel et al. (1995)
Bothnian Sea, coast	Spring–Autumn	1991–1992	320 ± 9	13 ± 3	0.13 ± 0.25						Zweifel et al. (1993)
Bothnian Sea, Örefjärden, coast	March	2004	272-655	5.5-15.1		a(350)= 3.0-22.4					Stedmon et al. (2007b)
Bothnian Sea, coast	Apr–May, Aug, Oct	2010–2011	417 ± 67				2.35±0.18	12.9±3.5			Asmala et al. (2013)
Bothnian Sea, Örefjärden, coast	Spring	2010	367-850			a(440)= 1.51-8.83					Harvey et al. (2015)
Bothnian Sea, Örefjärden, coast	Summer	2010	317-825			a(440)= 0.75-7.58					Harvey et al. (2015)

Appendix 1 (continued)

Area	Season	Year	DOC	DON	DOP	a CDOM	a CDOM	a CDOM	Humic Subst.	Lignin	Reference
							Slope275-295	Suva 254			
			(µm)	(µm)	(µm)	(m-1)	(µm-1)	(mg.L-1.m-1)	(µg.l-1)	(µg.l-1)	
Baltic Proper											
Baltic Proper–Bothnian Bay, OS	March, August–September	2009	273–351								Deutsch et al. (2012)
Åland Sea, Östhammar, coast	Summer	2010-2013	342-567			a(440)= 0.48-1.24					Harvey et al. (2015)
Northern Baltic Proper, OS	Summer	2001-2002				a(440)= 0.40 ± 0.04					Kratzer et al. (2009)
Baltic Proper, coast & OS	May–early June	1992							7.7		Skoog et al. (2011)
Baltic Proper-Gulf of Finland, coast & OS	Spring	2004, 2008-2009	288.5–831.7			a(370)= 0.70–7.94					Kowalczuk et al. (2010)
Baltic Proper-Gulf of Finland, coast & OS	Summer	2008-2009	303.7–559.2			a(370)= 1.06–6.54					Kowalczuk et al. (2010)
Baltic Proper-Gulf of Finland, coast & OS	Autumn-winter	2008-2009	266.7–583.3			a(370)= 0.93–5.56					Kowalczuk et al. (2010)
Baltic Proper, OS	June–October	1977	308–458								Perttilä and Tervo (1979)
Baltic Proper, OS	May–June	1992	300–325c								Wedborg et al. (1994)
Baltic Proper, OS	August–September	2009		15.9 ± 1.2							Korth et al. (2011)
Northern Baltic, coast and OS	July	2008				a(440)= 0.53 ± 0.19					Kratzer and Vinterhav (2010)
Western Gotland Basin, Himmerfjärden, coast	Summer	2001-2002				a(440)= 0.48 ± 0.10					Kratzer et al. (2009)
Western Gotland Basin, Himmerfjärden, coast	Spring	2010-2013	342-417			a(440)= 0.33-0.60					Harvey et al. (2015)
Western Gotland Basin, Himmerfjärden, coast	Summer	2010-2013	358-450			a(440)= 0.34-1.57					Harvey et al. (2015)
Western Gotland Basin, Nyköping, coast	Summer	2010-2013	358-1067			a(440)= 0.45-4.12					Harvey et al. (2015)
Western Gotland Basin, Nyköping, coast	Summer	2010-2013	375-617			a(440)= 0.36-1.95					Harvey et al. (2015)
Baltic Proper, OS	May–July	2005			0.20–0.30						Nausch and Nausch (2007)
Baltic Proper, OS	June–July,	2008–2009			0.21 ± 0.05						Nausch and Nausch (2011)
Baltic Proper, OS	February–March				0.32 ± 0.04						
Baltic Proper, OS	August	2007				a(412)= 0.410 ± 0.099					Berthon and Zibordi 2010
Northern Baltic Proper, OS	March, August–September	2009	299								Deutsch et al. (2012)
Eastern Gotland Basin, OS	Year round	1994–2006	320 ± 20	16 ± 2							Nausch et al. (2008)
Eastern Gotland Basin, OS	May–July	1999		12–24	~0.50–0.90						Põder et al. (2003)
Eastern Gotland Basin, OS	March–September	2001	330–380	18–203							Schneider et al. (2003)
Eastern Gotland Basin, OS	May–July	2001			0.20–0.52						Nausch and Nausch (2006)
Eastern Gotland Basin, OS	Average of three seasons	2006–2007	371 ± 22	14.5 ± 0.5		a(300)=0.4±17.2					Aarnos et al. (2012)
Eastern Gotland Basin, OS	March–October	2009–2011	361 ± 74								Maciejewska and Pempkowiak (2014)
Bornholm Basin, OS	April–October	2009–2011	403 ± 74								Maciejewska and Pempkowiak (2014)
Southern Baltic Proper, OS		1970s	267–517								Jurkowskis et al. (1976)
Southern Baltic Proper, OS	September	1983	383–592								Pempkowiak et al. (1984)
Southern Baltic Proper, OS	April	1994	435 ± 54			a(350)= 1.44 ± 0.32					Ferrari et al. (1996)
Southern Baltic Proper, OS	August	1994				a(350)= 1.4 ± 0.08					Ferrari et al. (1996)
Southern Baltic Proper, OS	September	1994				a(350)= 1.54 ± 0.06					Ferrari et al. (1996)
Southern Baltic Proper, coast & OS	September	1994	472 ± 46								Ferrari et al. (1996)
Southern Baltic Proper, OS	Spring	1994-1997				a(400)= 0.25-1.84					Kowalczuk 1999
Southern Baltic Proper, OS	Summer	1994-1997				a(400)= 0.38-1.65					Kowalczuk 1999
Southern Baltic Proper, OS	Autumn-winter	1994-1997				a(400)= 0.23-0.87					Kowalczuk 1999
Southern Baltic Proper, OS	Spring	1993-2001				a(400)= 0.25-1.84					Kowalczuk et al. (2005)
Southern Baltic Proper, OS	Summer	1993-2001				a(400)= 0.37-1.65					Kowalczuk et al. (2005)
Southern Baltic Proper, OS	Autumn-winter	1993-2001				a(400)= 0.23-1.27					Kowalczuk et al. (2005)
Southern Baltic Proper, OS	May	2006	322–341								Kuliński and Pempkowiak (2008)
Southern Baltic Proper, OS	Year round	1994–2006	270–325	14–17							Nausch et al. (2008)
Arkona Sea, OS	February-June	1998				a(375)= 0.711–0.896					Stedmon et al. (2000)
Arkona Sea, OS	August	2005	316	10.2		a(350)= 1.49					Stedmon et al. (2007)
Arkona Sea, OS	Average of three seasons	2006–2007	334 ± 22	14.7 ± 0.4		a(300)=0.1±16.6					Aarnos et al. (2012)
Arkona Sea, OS	August, September, February	2006–2007	191-325			a(300)=3.79-5.10				5.97-6.83	Osburn and Stedmon (2011)

Appendix 1 (continued)

Area	Season	Year	DOC	DON	DOP	a CDOM	a CDOM	a CDOM	Humic Subst.	Lignin	Reference
							Slope275-295	Suva 254			
			(µm)	(µm)	(µm)	(m-1)	(µm-1)	(mg.L-1.m-1)	(µg.l-1)	(µg.l-1)	
Belt Sea, The Sound											
Belt Sea, OS	February-June	1998				a(375)= 0.681–0.995					Stedmon et al. (2000)
The Sound, OS	February-June	1998				a(375)= 0.664–0.901					Stedmon et al. (2000)
Kattegat and Skagerrak											
Kattegat and Skagerrak , OS	Summer, winter–early spring	2008–2009			0.15–0.36						Nausch and Nausch (2011)
Kattegat and Skagerrak , coast & OS	March, September, October	1992				a(380) = 0.02-1.5					Hojerslev et al. (1996)
Kattegat and Skagerrak , coast & OS	March, September, October	1992				a(310) = 0.2					
Kattegat and Skagerrak , coast & OS	March, September, October	1992				a(450) = 0.02-0.03					
Kattegat											
Kattegat, coast & OS	May–early June	1992							5.1		Skoog et al. (2011)
Kattegat	May–June	1992	200								Wedborg et al. (1994)
Kattegat , coast & OS	February-June	1998				a(375)= 0.464–0.915					Stedmon et al. (2000)
Kattegat, OS	August, September, February	2006	79-265			a(300) = 0.87-3.58				0.97-4.78	Osburn and Stedmon (2011)
Skagerrak											
Skagerrak , coast & OS	February-June	1998				a(375)= 0.091–0.423					Stedmon et al. (2000)
Skagerrak , coast & OS	May–early June	1992							3.4		Skoog et al. (2011)
Coastal Danish sites											
Belt Sea, Aarhus Bay , coast	June	1992			0.48–0.98						Thingstad et al. (1996)
Belt Sea , Horsens Fjord, coast	February-June	1998				a(375)= 1.02–1.50					Stedmon et al. (2000)
Belt Sea, Horsens Fjord, coast	Year round	2001–2002	194–309	17-29	0.39-0.67	a(375) = 0.65-1.60					Markager et al. (2011)
Belt Sea, Horsens Fjord, coast	Year round	2004–2005	172–394	12–35							Lønborg and Søndergaard (2009)
Belt Sea, Dars Sill, coast	Year round	2004–2005	186–324	17–36							Lønborg and Søndergaard (2009)
Belt Sea, Kolding Fjord, coast	February-June	1998				a(375)= 0.83–4.94					Stedmon et al. (2000)
Kattegat, Mariager Fjord, coast	February-June	1998				a(375)= 1.42–3.43					Stedmon et al. (2000)
Belt Sea, Nærå Strand, coast	February-June	1998				a(375)= 2.98–3.13					Stedmon et al. (2000)
Belt Sea, Nyborg Fjord, coast	February-June	1998				a(375)= 3.16–5.88					Stedmon et al. (2000)
Belt Sea, Odense Fjord, coast	February-June	1998				a(375)= 1.08–3.96					Stedmon et al. (2000)
Kattegat , Roskilde Fjord, coast	February-June	1998				a(375)= 3.53–3.39					Stedmon et al. (2000)
Kattegat , Randers Fjord, coast	February-June	1998				a(375)= 1.97–4.65					Stedmon et al. (2000)
Belt Sea, Vejle Fjord, coast	February-June	1998				a(375)= 0.64–0.87					Stedmon et al. (2000)

Appendix 2. Coordinates of stations mentioned in the report.

Basin	Station name	Latitude	Longitude
Bothnian Bay	RÅNEÅ-1	65.8075	22.375
Bothnian Bay	RÅNEÅ-2	65.73	22.4467
Bothnian Bay	RÅNEÅ-3	65.6353	22.5743
Bothnian Bay	BO3 / A3	64.305	22.3583
Bothnian Bay	F3 / A5	65.1673	23.2327
Bothnian Bay	F9 / A13	64.7083	22.0652
Bothnian Sea	B7	63.525	19.8082
Bothnian Sea	GAVIK-1	62.8635	18.2643
Bothnian Sea	NB1 / B3	63.4997	19.819
Bothnian Sea	C3	62.6528	18.9523
Bothnian Sea	F26 / C15	61.9833	20.0667
Bothnian Sea	MS4 / C14	62.0998	18.5513
Bothnian Sea	SR1A / C11	61.2333	17.6667
Bothnian Sea	SR5 / C4	61.0833	19.5833
Bothnian Sea	US3 / C6	62.75	19.2
Bothnian Sea	US5B / C1	62.5867	19.975
Northern Baltic Proper	BY29	58.8833	20.3167
Western Gotland Basin	B1 Askö	48.118	37.507
Western Gotland Basin	BY31 LANDSORTSDJ	58.5833	18.2333
Western Gotland Basin	BY38 KARLSÖDJ	57.1167	17.6667
Western Gotland Basin	REF M1V1	56.37083	16.20167
Eastern Gotland Basin	BCS III-10	55.555	18.4
Eastern Gotland Basin	BY15 GOTLANDSDJ	57.3132	19.9348
Bornholm Basin	K19 / TORHAMNS SKÄRGÅRD	56.0815	15.8187
Bornholm Basin	K6 / S KASEN	56.1115	14.8237
Bornholm Basin	VH1 / HANÖ-1	55.9832	14.5138
Bornholm Basin	BY5 BORNHOLMSDJ	55.25	15.9833
Arkona Basin	BY2 ARKONA	55	14.0833
Kattegat	N14 FALKENBERG	56.94	12.21167
Kattegat	ANHOLT E	56.6667	12.1167
Kattegat	KA2	57.1917	11.6667
North Sea	Slaggö	58.2603	11.4367
North Sea	Å17	58.275	10.5133