Chapter 4
Research on Carbon Cycling in the Baltic: Quantification of the Carbon Fluxes

4.1 Carbon Exchange Between the Baltic Sea and the North Sea

Considerations presented in this chapter are based on the comprehensive study performed by Kuliński et al. (2011). The details of the methodology used for the quantification of carbon exchange between the Baltic Sea and the North Sea are presented in Sect. A.1 (this volume, Appendixes).

The key element that determines carbon exchange between the Baltic and the North Sea is the direction and volume of water flows between two basins. "End members" method allows to distinguish these two water masses within the total water volume that enters the Danish Straits and to verify the respective carbon contributions to export/import to/from the Baltic. Simultaneously, the method allows disentangling of the mixing process complexity occurring within the Danish Straits.

Annual variability of water exchange for the period from June 1, 2002, to May 31, 2006, is illustrated by series of diurnal flows of the Baltic (Fig. 4.1) and the North Sea water masses (Fig. 4.2). In both cases, negative values indicate the water flowing from the Baltic to the North Sea, while positive values indicate an opposite direction. During the entire considered period, the direction and the volume of the flowing water are subjected to significant variability. The Baltic daily water flows range from 17.1 km^3 day^{-1} (December 7, 2002) to 17.5 km^3 day^{-1} (February 13, 2005), compared to -13.3 km^3 day^{-1} (January 15, 2005) to 20.4 km^3 day^{-1} (November 15, 2006) for the North Sea.

In order to estimate the annual magnitude of carbon exchange variability between the Baltic and the North Sea, four yearly intervals have been distinguished, based on the hydrological data, for the period from June 1 to May 31 (Table 4.1). Altogether, during four years (June 1, 2002 to May 31, 2006) the North Sea received 5658.6 km^3 of water from the Baltic. During the same period

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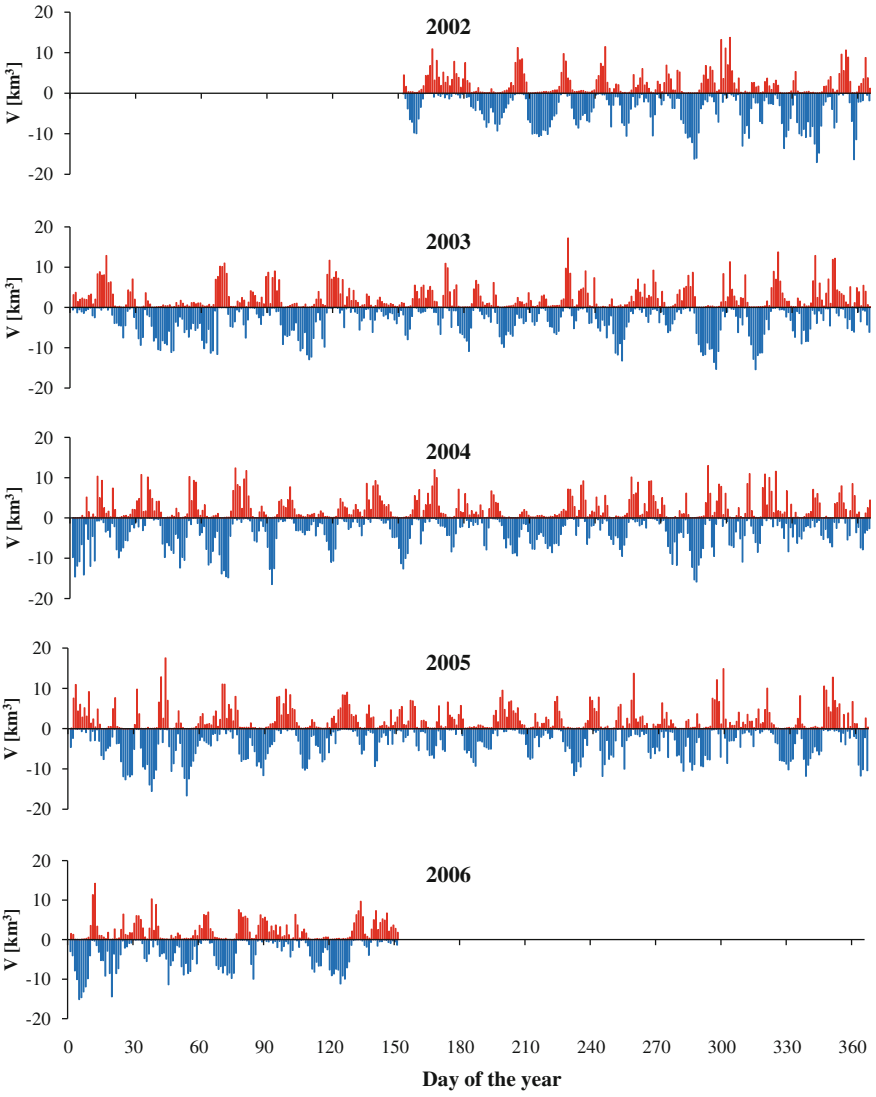

Fig. 4.1 Seasonal variations of the daily Baltic water flows during the period from June 1, 2002, to May 31, 2006, calculated based on the data generated by CMOD hydrological model and the "end members" method. Negative values (*blue*) indicate the Baltic water flowing into the North Sea, positive values (*red*) indicate the Baltic water returning to its source (modified after Kuliński et al. 2011)

of time, the volume of 3594.0 km^3 of the Baltic water returning to its source was recorded, which constitutes 63% of the export. Annual volumes of the Baltic water exported to the North Sea ranged from -1333.9 km^3 $year^{-1}$ for the period of

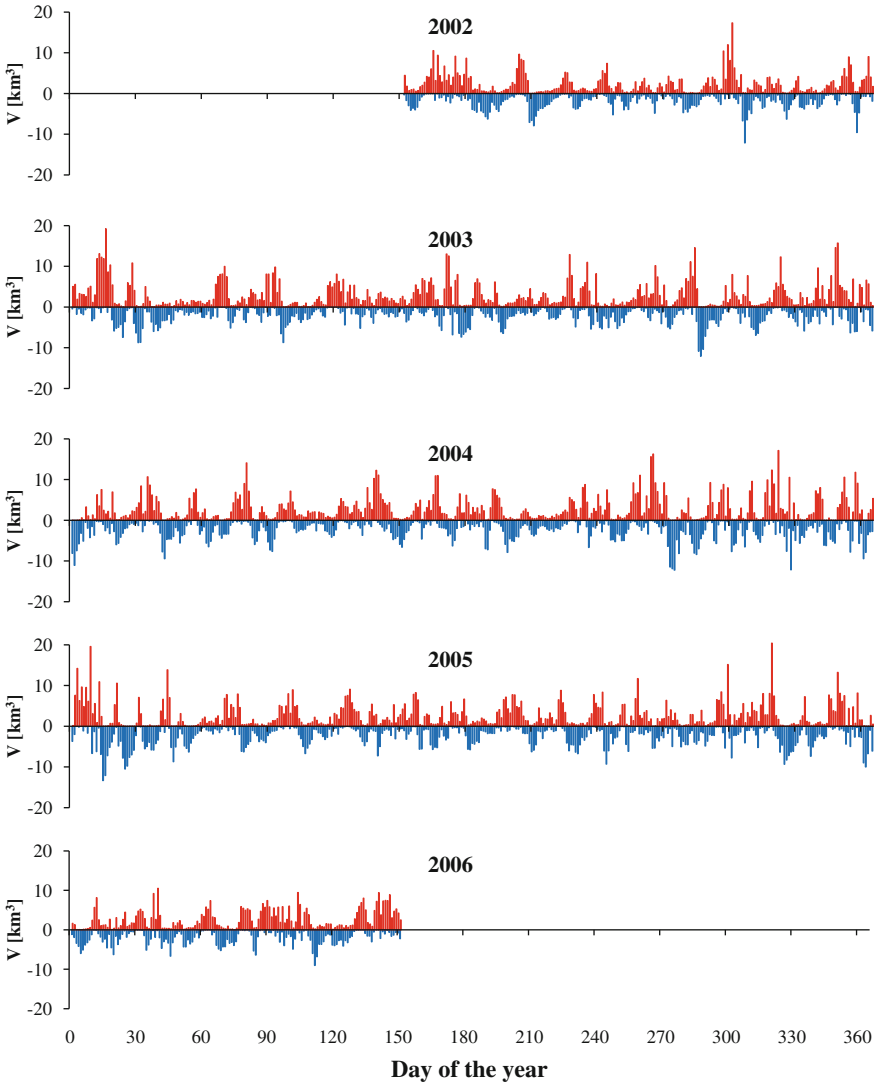

Fig. 4.2 Seasonal variations of the daily North Sea water flows during the period from June 1, 2002, to May 31, 2006, calculated based on the data generated by CMOD hydrological model and the "end members" method. Positive values (*red*) indicate the North Sea water inflows to the Baltic, negative values (*blue*) indicate the North Sea water returning to its source (modified after Kuliński et al. 2011)

2005/2006 to −1496.9 km^3 $year^{-1}$ during 2002/2003, while volumes of the Baltic water returning to its source varied from 854.4 km^3 $year^{-1}$ during 2005/2006 to 929.0 km^3 $year^{-1}$ during 2004/2005. The Baltic Sea water net export to the North

Table 4.1 Water exchange between the Baltic Sea and the North Sea (Kuliński et al. 2011)

Period	Baltic water			North Sea Water		
	Exported from Baltic (km^3)	Imported to Baltic (km^3)	Net export from Baltic (km^3)	Imported to Baltic (km^3)	Exported from Baltic (km^3)	Net import to Baltic (km^3)
2002/2003	−1496.9	886.6	−610.3	965.6	−749.8	206.8
2003/2004	−1422.0	924.0	−498.0	1035.0	−876.9	158.1
2004/2005	−1405.8	929.0	−476.8	1059.0	−981.4	77.6
2005/2006	−1333.9	854.4	−479.5	1008.7	−857.1	151.6
Average	−1414.6	898.5	−516.1	1014.8	−866.3	148.5
SD[a]	66.9	35.0	63.5	40.0	95.0	53.3

[a] Standard deviation

Sea falls within a range of -476.8 km^3 year^{-1} for 2004/2005 and -610.3 km^3 year^{-1} for 2002/2003, which corresponds to 34% and 41% of the total volume of water transported during these years. The average value of -516.1 ± 63.5 km^3 year^{-1} characterizes the Baltic water flow to the North Sea in the period of investigations.

During the entire period, from June 1, 2002, to May 31, 2006, the volume of 4068.3 km^3 of the North Sea water was transported to the Baltic (Table 4.1); in the same time 85% of this water volume (-3465.2 km^3) returned to its source. Annual volumes of the North Sea water entering the Baltic range from 965.6 km^{3}year^{-1} for 2002/2003 to 1059.0 km^{3}year^{-1} for 2004/2005, compared to averages of returning fluxes: -749.8 km^{3}year^{-1} for 2002/2003 and -981.4 km^{3}year^{-1} for 2004/2005. The net import of the North Sea water to the Baltic oscillates between 77.6 km^{3}year^{-1} for 2004/2005 and 206.8 km^{3}year^{-1} for 2002/2003. These values correspond, respectively, to 7% and 21% of the total North Sea water flowing to the Baltic for the above−mentioned periods. On the average 148.5 ± 53.3 km^{3}year^{-1} of the North Sea water enters the Baltic Sea.

4.1.1 Dissolved Inorganic Carbon

Seasonal fluctuations of DIC concentration for MB (the Baltic end member, see Sect. A1 for explanations) and MP (the North Sea end member, see Sect. A1 for explanations) stations are presented in Fig. 4.3. Literature data (Prowe et al. 2009; Thomas and Schneider 1999) were further confirmed by our own measurements performed during various seasons in recent years.

Both stations are characterized by explicit distinct seasonal variability of DIC concentrations, with distinct summer minimum and winter maximum. This is related to the atmospheric CO_2 solubility changes in the sea water dependant on the water temperature and the phytoplankton activity, leading to the dissolved CO_2 uptake during the photosynthesis (Sect. 2.2.3.2). DIC concentrations for MB

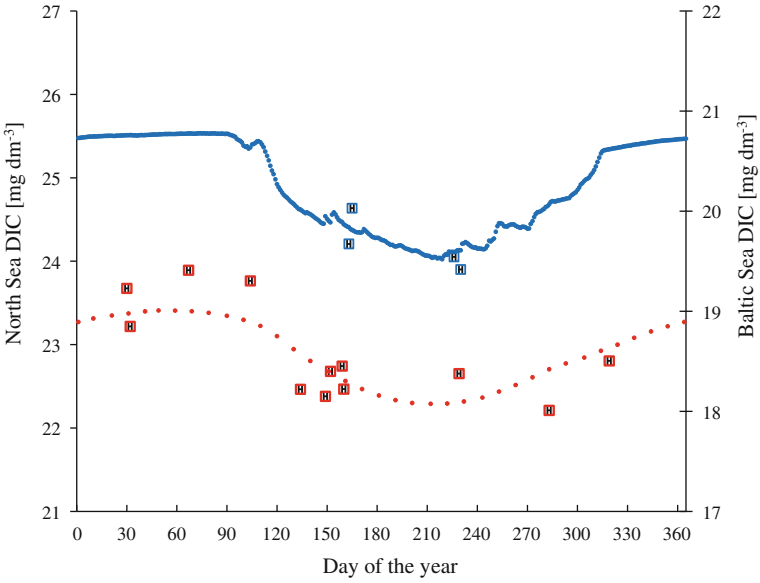

Fig. 4.3 DIC concentrations seasonal variability, curves: MP station—*blue* (Prowe et al. 2009), and MB station—*red* (Thomas and Schneider 1999). Squares—DIC concentrations based on our own data obtained during the r/v Oceania 2006–2009 research cruises (modified after Kuliński et al. 2011)

station vary from 18.1 ± 0.3 mg dm^{-3} to 19.0 ± 0.3 mg dm^{-3} estimated for 212 and 49 day of the year, respectively (July 31 and February 18). In the case of MP station, DIC concentrations oscillate at higher levels, with an amplitude of changes ranging between 24.0 ± 0.4 mg dm^{-3} for summer and 25.2 ± 0.4 mg dm^{-3} for winter (Prowe et al. 2009).

The literature data concerning DIC seasonal variations at the MB and MP stations, and daily sea water flows calculations based on the Baltic and North Sea components, enabled estimation of the annual (June 1 to May 31) DIC flows for the considered 4 years long period. The results are summarized in Table 4.2. Average Baltic DIC export to the North Sea amounts to −9.70 ± 1.13 Tg C $year^{-1}$, while the subsequent annual averages range from −8.98 Tg C $year^{-1}$ for 2005/2006 to −11.39 Tg C $year^{-1}$ for 2002/2003. The annual North Sea DIC loads imported to the Baltic are smaller and reveal more variability. Values oscillate between 1.65 Tg C $year^{-1}$ during the period of 2004/2005 and 5.41 Tg C $year^{-1}$ during- 2002/2003, which gives the period average equal to 3.70 ± 1.55 Tg C $year^{-1}$ of DIC transported from the North Sea to the Baltic.

In order to illustrate seasonal variability of the magnitude and direction of DIC fluxes, including their monthly averages with standard deviation, the Baltic and North Sea DIC loads were calculated for the entire 4 year period of studies (Fig. 4.4). Only for May and June, does the Baltic DIC flux reveal positive values,

Table 4.2 Summary of the annual (June 1 to May 31) Baltic and North Sea DIC fluxes

Period	Baltic DIC (Tg C year^{-1})	North Sea DIC (Tg C year^{-1})	Total DIC (Tg C year^{-1})
2002/2003	−11.39	5.41	−5.98
2003/2004	−9.23	3.97	−5.26
2004/2005	−9.18	1.65	−7.53
2005/2006	−8.98	3.76	−5.22
average ± SD	−9.70 ± 1.13	3.70 ± 1.55	−6.00 ± 1.08

Negative values indicate DIC export from the Baltic to the North Sea, positive values indicate DIC import from the North Sea to the Baltic (Kuliński et al. 2011)

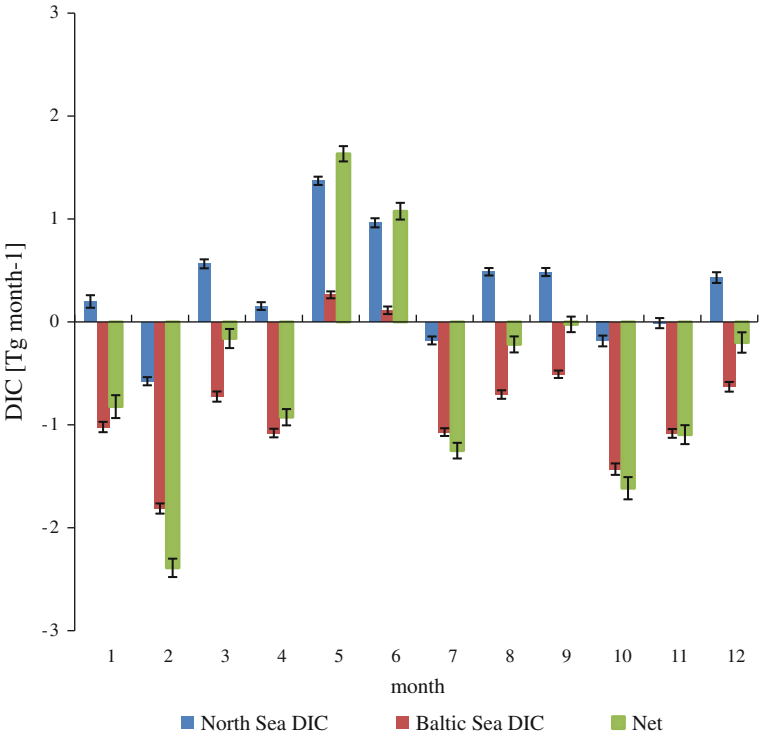

Fig. 4.4 Monthly averages of the Baltic and North Sea DIC loads and net load values for the period from June 1, 2002, to May 31, 2006. Negative values indicate DIC export from the Baltic, positive values indicate DIC import from the North Sea to the Baltic (modified after Kuliński et al. 2011)

0.26 ± 0.03 Tg C month^{-1} and 0.11 ± 0.04 Tg C month^{-1}, respectively. This indicates an intensive inorganic carbon returning flux to the Baltic from the North Sea, while for the remaining months, a DIC export to the North Sea is observed.

Monthly averages of the export range from -0.51 ± 0.04 Tg C month^{-1} in September to -1.81 ± 0.05 Tg C month^{-1} in February. Despite higher DIC concentrations, the North Sea DIC flux absolute values are somewhat smaller, which has its source in smaller volumes of the North Sea water flowing into the Baltic. The most intensive DIC fluxes from the North Sea, illustrated by monthly averages, are recorded for May and June, amounting to 1.37 ± 0.04 Tg C month^{-1} and 0.96 ± 0.04 Tg C month^{-1} respectively. During the subsequent 6 months (January, March, April, August, September, December), the DIC import from the North Sea to the Baltic is also observed, amounting to the monthly averages ranging from 0.15 ± 0.04 Tg C month^{-1} in April to 0.56 ± 0.04 Tg C month^{-1} in March. Results obtained for the remaining months indicate the North Sea DIC loads returning to its source, ranging from -0.01 ± 0.05 to -0.58 ± 0.04 Tg C month^{-1}. Monthly average totals of DIC flux presented in Fig. 4.3 as net values reveal positive values only for the month of May and June (similarly to the Baltic DIC flux). This fact clearly points to the Baltic DIC export as the determining factor for the inorganic carbon exchange between the Baltic and the North Sea. Net monthly averages of DIC exchange between basins range from -2.39 ± 0.09 Tg C month^{-1} in February to 1.63 ± 0.07 Tg C month^{-1} in May.

4.1.2 Dissolved Organic Carbon

The DOC concentrations measured in the near-shore zone, results of analysis of samples collected at both the MP and MB stations, as well as the known concentrations at the MP station (Suratman et al. 2009) allowed to estimate the DOC concentrations variability for the North Sea (MP station) and for the Baltic Sea (MB station) end members (Fig. 4.5). DOC concentrations at all stations exhibit a seasonal trend that is opposite to the DIC one (Sect. 4.1.1), characterized here by summer maximum and winter minimum. This situation is related to factors determining DOC concentrations in sea water.

DOC concentrations in the nearshore zone are characterized by significant seasonal fluctuations (Fig. 4.5). The amplitude of these changes ranges between 3.1 ± 0.2 mg dm^{-3} in the winter time and 5.0 ± 0.7 mg dm^{-3} in the summer—July and August. The estimates are charged with relative standard deviation extending from 2.3% for June 29 to 11.5% for November 8. DOC concentrations at the MB station during the winter season are comparable to those observed for the nearshore station, indicating most likely similar concentrations of refractory DOC for both regions. Seasonal changes of DOC concentrations at the MB station range from 3.1 ± 0.2 to 4.3 ± 0.2 mg dm^{-3}.

In the case of the North Sea, little dynamics of DOC concentrations during a year span was recorded (Fig. 4.5), with values ranging from 1.1 ± 0.1 mg dm^{-3} to 1.6 ± 0.1 mg dm^{-3}. This is related to lower phytoplankton activity than that in the Baltic, as well as significant influence from the North Atlantic, which shapes the North Sea water chemistry (Thomas et al. 2005).

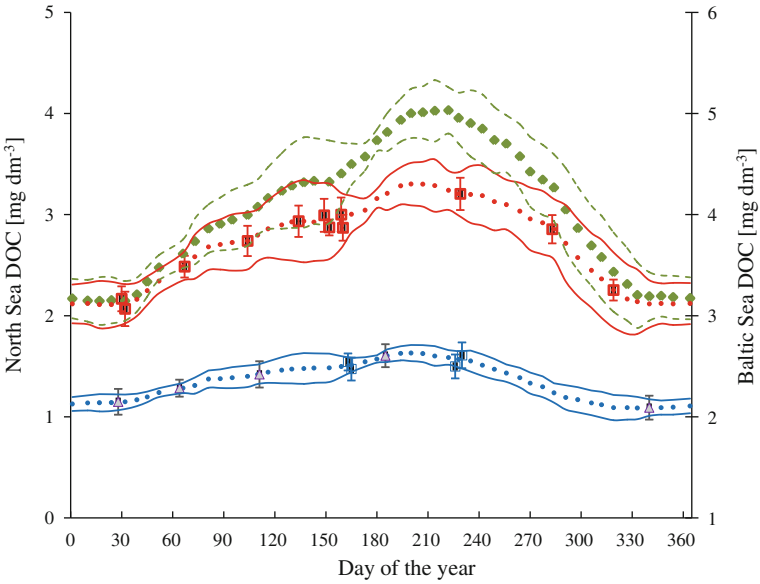

Fig. 4.5 The DOC concentrations variability: measured concentrations (*green rhombuses*), concentrations extrapolated to the MB station (*red dots*) and to the MP station (*blue dots*). Squares represent the DOC concentrations measured at MB and MP stations, triangles—DOC data from the literature (Suratman et al. 2009). *Dashed lines* define the range of the measured DOC uncertainty, whilst *solid lines*—the range of the extrapolated DOC concentrations uncertainties as given by RSD (modified after Kuliński et al. 2011)

The seasonal variability of DOC concentrations measured for MB and MP stations and calculations of daily Baltic and North Sea seawater flows, allowed to determine the annual DOC fluxes for the considered period of time. The obtained results are summarized in Table 4.3. Net values of the Baltic DOC export to the North Sea fall within -1.72 Tg C year^{-1} for 2005/2006 and -2.21 Tg C year^{-1} for 2002/2003, with the average of -1.88 ± 0.22 Tg C year^{-1}. Annual loads of the North Sea DOC entering the Baltic are definitely lower, oscillating between

Table 4.3 Summary of the annual (June 1 to May 31) Baltic and North Sea DOC fluxes

Period	Baltic DOC (Tg C year^{-1})	North Sea DOC (Tg C year^{-1})	DOC Total (Tg C year^{-1})
2002/2003	−2.21	0.28	−1.93
2003/2004	−1.80	0.23	−1.57
2004/2005	−1.79	0.11	−1.68
2005/2006	−1.72	0.22	−1.50
average ± SD	−1.88 ± 0.22	0.21 ± 0.07	−1.67 ± 0.19

Negative values indicate DOC export from the Baltic to the North Sea, positive values indicate DOC import from the North Sea to the Baltic (Kuliński et al. 2011)

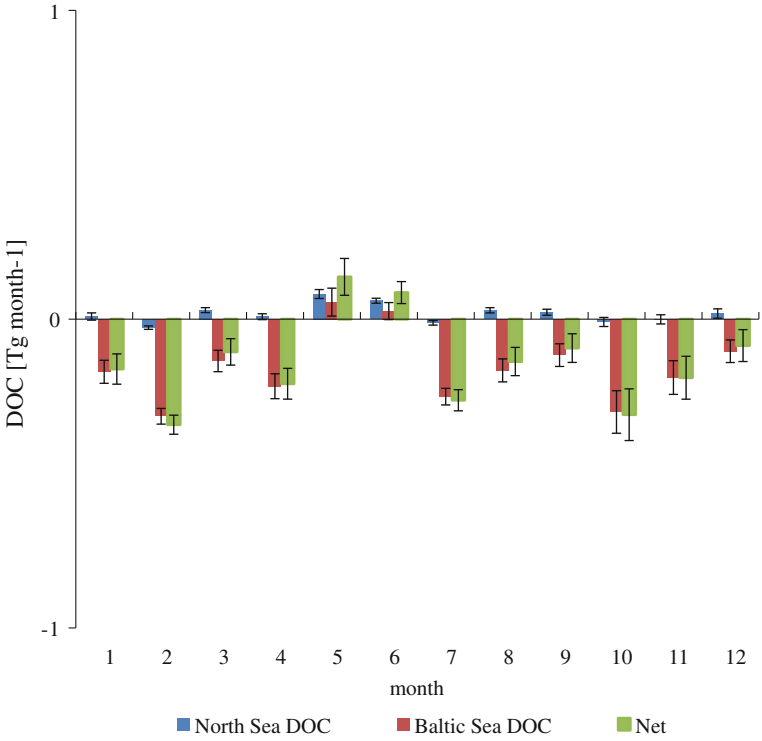

Fig. 4.6 Monthly averages of the Baltic and North Sea DOC fluxes and net flux values for the period from June 1, 2002, to May 31, 2006. Negative values indicate DOC export from the Baltic to the North Sea, positive values indicate DOC import from the North Sea to the Baltic (modified after Kuliński et al. 2011)

0.11 Tg C year^{-1} during 2004/2005 and 0.28 Tg C year^{-1} during 2002/2003. The total of the Baltic and the North Sea DOC loads, expressing quantitatively the DOC net exchange between the two basins, vary from -1.50 Tg C year^{-1} for 2005/2006 to -1.93 Tg C year^{-1} for 2003/2004, with the average of -1.67 ± 0.19 Tg C year^{-1}.

The monthly averages for the Baltic and the North Sea DOC fluxes, as illustrated in Fig. 4.6, indicate a dominant role of the former in shaping the organic carbon exchange between the two basins. The North Sea DOC load is less important and its values fall within standard deviation of the estimated net results. Similarly to DIC fluxes, it is only during May and June that positive values for monthly averages of the Baltic DOC fluxes are observed, and amount to 0.05 ± 0.04 and 0.03 ± 0.03 Tg C month^{-1}, respectively. Monthly averages of DOC for the remaining months range from -0.10 ± 0.03 Tg C month^{-1} in December to 0.30 ± 0.07 Tg C month^{-1} in October.

4.2 Carbon Inflows with River Runoff

Considerations presented in this chapter are based on the comprehensive study performed by Kuliński and Pempkowiak (2011a). The data (monthly means of water flows and carbon concentrations) used for the computation of carbon fluxes were taken from the database created and provided by Baltic-C—a FP6 BONUS funded project. This database contains the results obtained by national monitoring programmes carried out by the Baltic Sea countries.

Summary of the total inorganic carbon (TIC) and the total organic carbon (TOC) carried by (63) major rivers flowing into the Baltic Sea is presented in Table 4.4. Annually, rivers discharge, to the Baltic, 8.78 Tg of carbon, out of which more than 62% (5.49 Tg) is represented by the inorganic fraction. Among considered rivers, fifty seven (57 or 90%) enter the Baltic from the Swedish and Finnish territory. These rivers carry only 10% (0.53 Tg) of inorganic carbon and less than 40% (1.31 Tg) of organic carbon, of the total carbon load introduced to

Table 4.4 Summary of total inorganic carbon load (TIC) and total organic carbon load (TOC) carried by major rivers flowing into the Baltic Sea (Kuliński and Pempkowiak 2011a)

L. p.	River	Country	TIC (Gg year^{-1})	TOC (Gg year^{-1})	Water volume (km^3 year^{-1})
1	Ahtava	Finland	1.2	6.9	0.5
2	Ångermanälven	Sweden	37.5	84.6	16.3
3	Ätran	Sweden	7.0	19.3	1.8
4	Aura	Finland	1.7	4.1	0.2
5	Botorpström	Sweden	1.1	2.6	0.2
6	Daugava	Latvia	1068.9	210.7	20.8
7	Delångersån	Sweden	1.0	2.6	0.4
8	Emån	Sweden	4.3	16.8	1.1
9	Eura	Finland	0.9	2.7	0.2
10	Gide	Sweden	1.0	9.2	0.9
11	Göta	Sweden	63.8	80.5	18.1
12	Helgeån	Sweden	7.3	27.0	1.5
13	Iijoki	Finland	12.9	66.5	5.7
14	Indalsälven	Sweden	61.1	57.0	13.9
15	Kalajoki	Finland	2.6	26.9	1.1
16	Kalix	Sweden	20.5	59.0	10.1
17	Kemijoki	Finland	1.3	2.1	0.3
18	Kiiminki	Finland	2.9	25.8	1.5
19	Kiskonjoki	Finland	0.7	2.7	0.2
20	Kokemaenjoki	Finland	28.0	75.0	7.0
21	Koskenkyla	Finland	1.0	1.9	0.2
22	Kuivajoki	Finland	1.3	7.5	0.5
23	Kymi Ahven	Finland	21.9	46.2	5.8

(continued)

Table 4.4 (continued)

L. p.	River	Country	TIC (Gg year^{-1})	TOC (Gg year^{-1})	Water volume (km^3 year^{-1})
24	Kymi Kokon	Finland	17.9	38.5	5.1
25	Lagan	Sweden	4.8	37.9	2.8
26	Lapuanjoki	Finland	1.7	19.1	0.9
27	Lestijoki	Finland	0.5	6.2	0.3
28	Ljungan	Sweden	15.2	19.2	3.2
29	Ljungbyån	Sweden	0.3	3.4	0.2
30	Ljusnan	Sweden	0.9	0.5	0.2
31	Lule	Sweden	31.6	44.4	16.1
32	Lyckebyån	Sweden	0.4	3.8	0.2
33	Merikarvia	Finland	0.9	11.7	0.6
34	Mörrumsån	Sweden	1.7	12.8	0.9
35	Motala	Sweden	33.0	24.3	3.2
36	Mustijoki	Finland	1.3	3.6	0.2
37	Narpionjoki	Finland	0.5	7.2	0.3
38	Narva	Estonia	384.5	190.9	12.7
39	Neman	Lithuania	609.1	123.4	11.9
40	Neva	Russia	1295.2	1209.5	77.6
41	Nissan	Sweden	3.0	24.5	1.6
42	Nyköpingsån	Sweden	5.5	6.4	0.6
43	Oder	Poland	431.8	75.5	13.1
44	Öre	Sweden	1.2	13.7	1.1
45	Oulujoki	Finland	17.4	87.3	8.9
46	Paimionjoki	Finland	2.4	2.3	0.2
47	Perhonjoki	Finland	0.6	10.1	0.6
48	Pite	Szwecja	8.9	22.4	5.5
49	Porvoonjoki	Finland	3.6	5.5	0.4
50	Pyhajoki	Finland	2.3	20.0	1.0
51	Råne	Sweden	2.1	11.7	1.4
52	Rickleån	Sweden	0.7	5.8	0.5
53	Rönneån	Sweden	5.4	4.1	0.4
54	Siikajoki	Finland	3.1	29.3	1.4
55	Simojoki	Finland	3.6	20.3	1.5
56	Sirppujoki	Finland	0.1	1.1	0.1
57	Skellefte	Sweden	6.0	8.2	3.4
58	Torne	Sweden	28.9	102.4	14.2
59	Ume	Sweden	35.9	63.8	14.9
60	Uskelanojoki	Finland	1.4	2.6	0.2
61	Vantaa	Finland	4.7	8.9	0.6
62	Virojoki	Finland	0.4	2.5	0.1
63	Vistula	Poland	1168.1	175.6	28.5
	Total		5486.6	3297.9	344.9

the basin. The decisive role is played by the continental rivers: Neva, Vistula, Daugava, Neman, Narva and Odra. The continental rivers are characterized by the largest catchment areas and greatest volume of water transported to the Baltic; Neva introduces annually 77.6 km^3 $year^{-1}$ of water and 1.29 Tg TIC and 1.21 Tg TOC to the Gulf of Finland. It represents 24% and 36% of the total inorganic and organic carbon load, respectively, entering the Baltic Sea with the considered rivers.

The major rivers entering the Baltic Sea deliver 345 km^3 of water every year, which represents 80% of the total river runoff into the basin, estimated at 428 km^3 $year^{-1}$ (Lass and Matthäus 2008). Assuming the representativeness of the carbon load carried by the considered rivers, it was estimated that every year 6.81 Tg TIC $year^{-1}$ and 4.09 Tg TOC $year^{-1}$ enter the Baltic Sea with the runoff, which amounts to the annual flux, of land-originating total carbon, equal to 10.90 Tg.

4.3 Carbon Deposition to the Baltic Sea Sediments

Considerations presented in this chapter are based on the studies performed by Kuliński (2010) and Kuliński and Pempkowiak (2011b). The details of the methodology used for the quantification of carbon deposition, mineralization and burial in the Baltic Sea sediments are presented in Sect. A.2 (this volume, Appendix).

The organic carbon deposition rates to the Baltic Sea sediments are summarized in Table 4.5. The negative values of carbon flux indicate its export from the water column to sediments. The total depositional area of the sea amounts to more than 101×10^3 km^2 (Algesten et al. 2006; Błaszczyszyn 1982; Emeis et al. 2000). Each

Table 4.5 Summary of carbon loads reaching the sediments within different depositional regions, surface areas of the regions and organic carbon accumulation rates

Depositional region	Surface area (km^2)	TOC accumulation rate (g C m^{-2} $year^{-1}$)	Annual carbon deposition to sediments (Tg $year^{-1}$)
Arkona Basin	3 200[a]	20[b]	−0.064
Bornholm Deep	13 170[a]	58[c]	−0.764
Gdansk Deep	12 150[a]	60[b]	−0.729
Gotland Deep	28 240[a,b]	40[b]	−1.130
Gulf of Riga	890[a]	40[e]	−0.036
Gulf of Finland	940[a]	40[e]	−0.038
Gulf of Bothnia	42 440[d]	24[d]	−1.018
Total	101 030	–	−3.779

Negative values indicate carbon export from the water column to sediments (Kuliński 2010)
[a] (Błaszczyszyn 1982)
[b] (Emeis et al. 2000)
[c] (Christoffersen et al. 2007)
[d] (Algesten et al. 2006)
[e] Values adapted from the Gotland Deep

year, −3.78 Tg C is deposited to the sediments within the depositional areas. Due to its largest area among the regions considered, the Gulf of Bothnia is characterized by the greatest deposition loads, equal to −1.13 Tg year^{-1}. The smallest amount of carbon is deposited within the Gulf of Riga and the Gulf of Finland (−0.04 Tg year^{-1}). Accumulation rates for the organic carbon oscillate from 20 to 24 g m^{-2} year^{-1} for the Arkona Basin and the Gulf of Bothnia, and from 58 to 60 g m^{-2} year^{-1} for the Bornholm Deep and the Gdansk Deep, respectively.

4.3.1 Carbon Return Flux from the Bottom Sediments

Figures 4.7, 4.8, 4.9, 4.10, 4.11 present DIC and DOC concentrations in pore water and the above-sediment water layer for 5 among 7 considered depositional areas in the Baltic Sea. To cover all of the depositional areas of the Baltic, results characterizing the Gotland Deep were extended for the Gulf of Riga and the Gulf of Finland. In all cases, both DIC and DOC concentrations demonstrated decreasing trends in the direction of the water/sediment interface. The dependences between concentrations and depths were approximated by linear regression plots. The strength of correlation is described by the determination coefficient R^2. The coefficient values for DIC profile, ranging from 0.88 for in the Arkona Basin (Fig. 4.7) to 0.98 for the Bornholm Deep (Fig. 4.8) and Gotland Deep (Fig. 4.10), indicate a very high level of linear correlation for DIC concentration changes with depth. Subsequent profiles are characterized by varying slope, described by directional coefficients a in equation $y = ax + b$, in other words—the gradient of

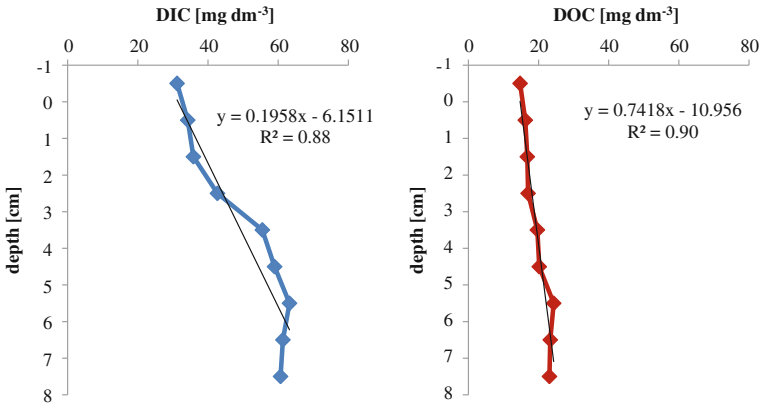

Fig. 4.7 The DIC and DOC concentration profiles in pore water from the upper layers of sediments of the Arkona Basin. The determination coefficients (R^2) indicate the linear correlaton strength. Accuracy of DIC and DOC concentrations analysis is described by relative standard deviation equal to 1.8% and 2.4%, respectively (n = 3) (modified after Kuliński and Pempkowiak 2011b)

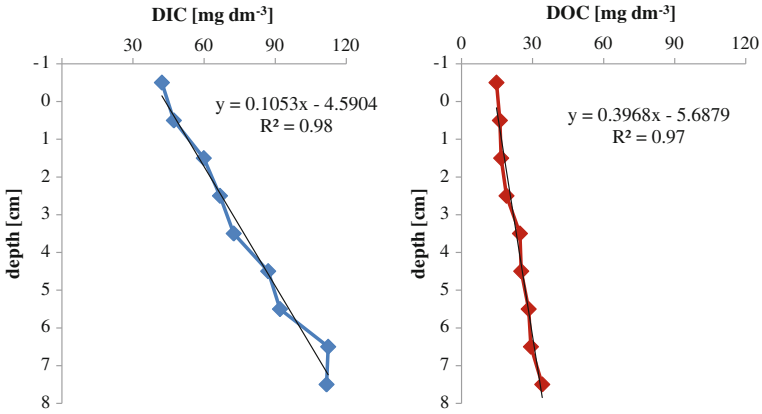

Fig. 4.8 The DIC and DOC concentration profiles in pore water from the upper layers of sediments of the Bornholm Deep. The determination coefficients (R^2) indicate the linear correlation strength. Accuracy of DIC and DOC concentrations analyses is described by relative standard deviation equal to 2.2% and 3.1%, respectively (n = 3) (modified after Kuliński and Pempkowiak 2011b)

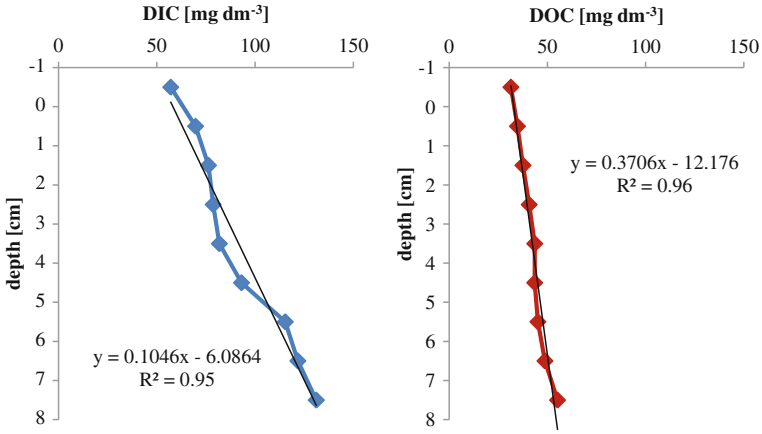

Fig. 4.9 The DIC and DOC concentration profiles in pore water from the upper layers of sediments of the Gdańsk Deep. The determination coefficients (R^2) indicate the linear correlation strength. Accuracy of DIC and DOC concentrations analyses is described by relative standard deviation equal to 2.2% and 2.8%, respectively (n = 3) (modified after Kuliński and Pempkowiak 2011b)

analyte concentration changes. Values of coefficient *a* tend to be lower for the DIC than for the DOC concentrations profiles, in agreement with higher values of the DIC gradients in pore water. The smallest DIC concentrations gradient is observed

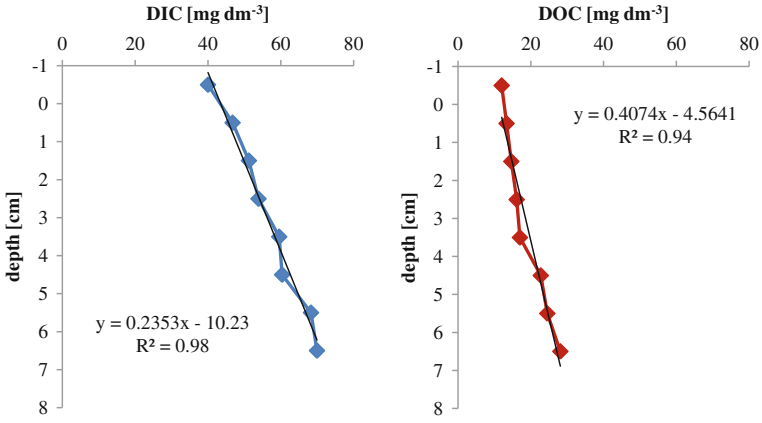

Fig. 4.10 DIC and DOC concentration profiles in pore water from the upper layers of sediments of the Gotland Deep. The determination coefficients (R^2) indicate the linear correlation strength. Accuracy of DIC and DOC concentrations analyses is described by relative standard deviation equal to 1.6% and 2.9%, respectively (n = 3) (modified after Kuliński and Pempkowiak 2011b)

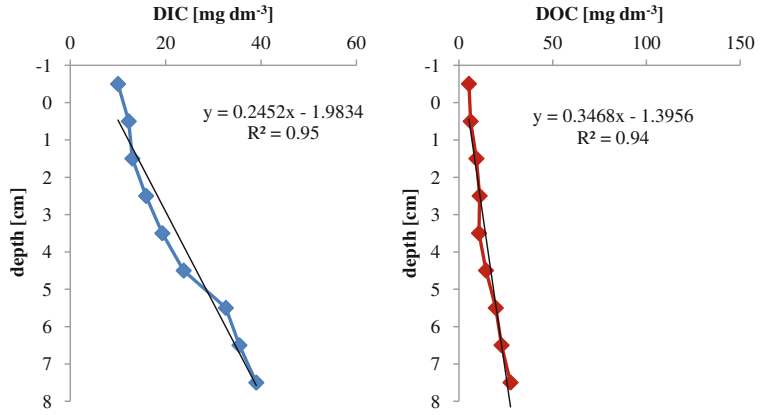

Fig. 4.11 The DIC and DOC concentration profiles in pore water from the upper layers of sediments of the Gulf of Bothnia. The determination coefficients (R^2) indicate the linear correlation strength. Accuracy of DIC and DOC concentrations analyses is described by relative standard deviation equal to 1.7% and 1.8%, respectively (n = 3) (modified after Kuliński and Pempkowiak 2011b)

for the sediment core from the Gulf of Bothnia (Fig. 4.11). Concentrations of DIC, in the investigated cores, oscillate from 10.2 ± 0.2 mg C dm^{-3} in the above-sediment water to 39.0 ± 0.7 mg C dm^{-3} at the 7–8 cm depth below sediment–water interface. In contrast, the Gdansk Deep DIC profile revealed the biggest DIC concentration changes (Fig. 4.9), with values ranging from 57.1 ± 1.2 mg C dm^{-3}

Table 4.6 Summary of diffusion magnitude and return fluxes of DIC and DOC from different depositional areas of the Baltic (Kuliński 2010)

Depositional area	Surface area (km^2)	C diffusion rate from sediments (g C m^{-2} $year^{-1}$)		C diffusion flux from sediments (Tg $year^{-1}$)		
		DIC	DOC	DIC	DOC	Total
Arkona Basin	3 200[a]	9.7	0.5	0.031	0.002	0.033
Bornholm Deep	13 170[a]	18.0	0.9	0.237	0.012	0.249
Gdansk Deep	12 150[a]	18.1	1.0	0.220	0.012	0.232
Gotland Deep	28 240[a,b]	8.6	0.9	0.243	0.025	0.268
Gulf of Riga	890[a]	8.6	0.9	0.008	0.001	0.009
Gulf of Finland	940[a]	8,6	0.9	0.008	0.001	0.009
Gulf of Bothnia	42 440[c]	7.0	1.0	0.297	0.042	0.339
Total	101,030	–	–	1.044	0.095	1.139

[a] (Błaszczyszyn 1982)
[b] (Emeis et al. 2000)
[c] (Algesten et al. 2006)

in the above-sediment water to 131.1 ± 2.9 mg C dm^{-3} in pore water collected at 7–8 cm.

In the case of DOC profiles, the highest *a* coefficient value was observed in pore water from the Arkona Deep (Fig. 4.7). Concentrations of DOC there vary between 14.7 ± 0.3 mg C dm^{-3} in the above-sediment water to 23.3 ± 0.5 mg C dm^{-3} in the layer at a depth of 6–7 cm. The biggest DOC concentrations gradient was observed in the pore water profile from the Gulf of Bothnia (Fig. 4.11), where DOC concentrations range between 5.3 ± 0.1 mg C dm^{-3} in the above-sediment water to 27.5 ± 0.5 mg C dm^{-3} at 7–8 cm depth.

Fluxes of dissolved carbon species, calculated based on the Fick's law of diffusion (see Appendix A.2 for details), are summarized in Table 4.6. The results indicate a strong return flux of carbon from sediments to the water column. Moreover, they point at DIC as the primary carrier of the carbon that returns from sediments to water, and, thus, at a dominance of mineralization processes over hydrolysis of organic matter deposited to the sediments. Diffusive fluxes of DIC range from 7.0 g C m^{-2} $year^{-1}$ in the Gulf of Bothnia to 18.1 g C m^{-2} $year^{-1}$ for the Gdansk Deep. Diffusive fluxes of DOC are an order of magnitude smaller and do not exceed 1.0 g C m^{-2} $year^{-1}$, as obtained for the Gdansk Deep and the Gulf of Bothnia. The minimum of 0.5 g C m^{-2} $year^{-1}$ is observed for the Arkona Basin Region.

The total carbon load released from sediments of the considered areas to the overlaying water amounts to 1.14 Tg C $year^{-1}$ (Table 4.6). The DOC flux contributes just 0.10 Tg C $year^{-1}$ (< 9%). The remaining 1.04 Tg C $year^{-1}$ reaches the water column as DIC. Depositional area characterized by the greatest absolute load of carbon is the Gulf of Bothnia, where the value amounts to 0.34 Tg C $year^{-1}$, which corresponds to nearly 30% of the total carbon released from the Baltic

sediments to the above-sediments water. Regions characterized by the lowest contribution of the return flux are the Gulf of Riga and the Gulf of Finland. The contribution of both to the total carbon return flux from the sediments does not exceed 1%.

4.3.2 Labile Organic Matter Decomposition in Sediments

An independent method was used in order to confirm the magnitude of the carbon return flux from sediments. A sediment core collected in the Gdańsk Deep was stored for 12 months. In the course of the storage, organic carbon was measured in subsequent layers of the core at 4 month intervals. The core was dated by means of the ^{210}Pb method, and the modelled deposition ages were validated with ^{137}Cs distribution in the core (Pempkowiak 1991; Szczepańska et al. 2011).

Organic carbon concentration profiles in sediments after successive stages of incubation against deposition time are presented in Fig. 4.12. Data uncertainties for the subsequent series are expressed by the relative standard deviation (RSD) varying from 1.0% to 1.7% for samples of the second and the third incubation stages

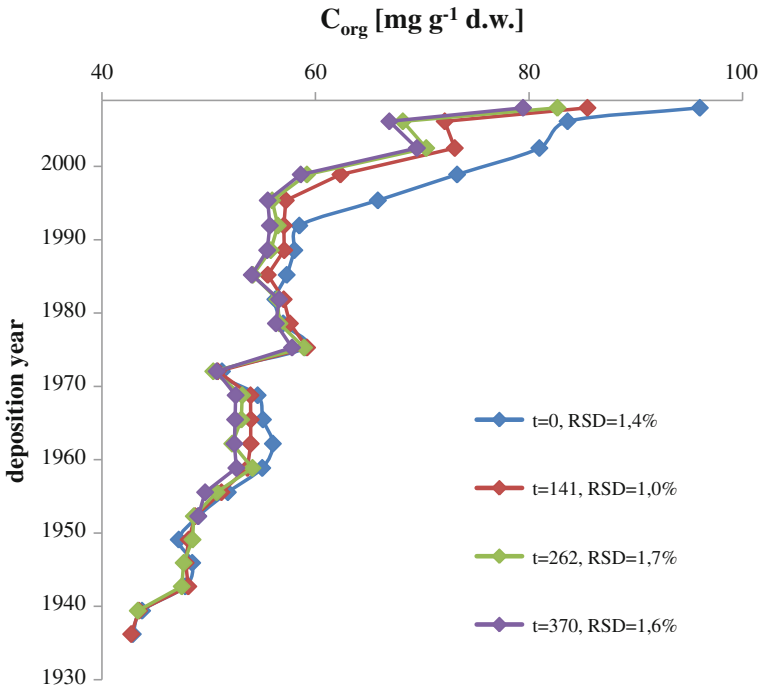

Fig. 4.12 Organic carbon concentration profiles in a Gdansk Deep core for the four incubation stages (Kuliński 2010)

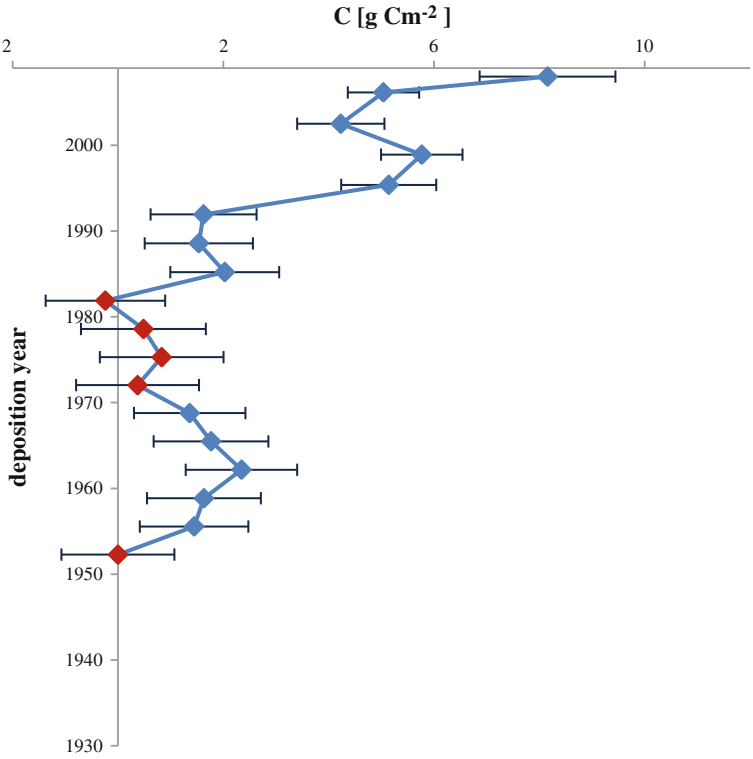

Fig. 4.13 Profile of the total organic carbon losses in the incubated sediment core from the Gdansk Deep. Red squares indicate sediment layers characterized by negative values of the lower uncertainty intervals (Kuliński 2010)

respectively. The highest concentrations of organic carbon in the analyzed sediment cores are found in samples analyzed at the beginning of the incubation time (t = 0), with values ranging from 42.9 ± 0.6 mg C g^{-1} d.w. for the layer deposited in 1936 to 96.0 ± 1.34 mg C g^{-1} d.w. for semi-liquid, topmost layer ("fluffy layer"), deposited in 2008. The lowest values were observed for core incubated for 370 days and varied from 49.0 ± 0.8 mg C g^{-1} d.w. in the layer dated on 1952 to 79.4 ± 1.3 mg C g^{-1} d.w. in the "fluffy layer". All four profiles are characterized by a noticeable concentration increase during the early 1990s, when also the biggest differences between subsequent layers of the sediment core are recorded. In sediments deposited before 1990, concentration values are more comparable, and the decrease with depth is less pronounced. For all analyzed cores, a characteristic drop in the organic carbon concentration occurs in the layer dated on 1972. This situation could be a result of sediments re-suspension and re-deposition event in the early seventies. The lack of differences between the organic carbon concentrations at successive stages of

incubation indicate that the sediments in the layer are actually older than suggested by ^{210}Pb dating method. Below this level, up to a layer dated on 1956, a slightly higher organic carbon concentrations are observed, as well as distinct differences in concentrations for the subsequent stages of incubation are recorded. The deeper layers are characterized by lower carbon concentrations, lacking of statistically significant differences for successive stages of incubation, which indicate organic matter mineralization and decomposition processes to be completed or nearly completed.

Organic carbon total losses (C_{min}) from successive 1 cm layers of the analyzed sediment core are expressed as g C m^{-2}, as presented in Fig. 4.13. Values are extrapolated to the temperature of 4°C. For the entire incubation experiment, the most significant losses in organic carbon occurred for layers deposited after 1992, when C_{min} ranges from 4.2 ± 0.8 g C m^{-2} for the layer deposited in 2003 to 8.2 ± 1.3 g C m^{-2} for the freshly deposited "fluffy layer". Significant organic carbon losses in this part of the core indicate intensive organic matter mineralization and decomposition taking place during a time scale of less than 15 years. Below this depth in the core, carbon losses from the sediments are still occurring, but the scale of the process is less significant than in the upper level and does not exceed 2.3 ± 1.0 g C m^{-2} in a layer dated on 1962. Despite the fact that the analyzed data encompass the period until 1952, due to a shorter time span characterizing the fourth phase of incubation, it can be assumed that in the deeper layers the organic matter mineralization and decomposition processes are no longer present. The explanation comes from a lack of statistically significant differences between the organic carbon concentration differences, in the considered core fragment, during earlier phases of incubation (Fig. 4.12). Figure 4.13 emphasizes four layers (marked in red) for which negative, or close to negative values of carbon losses were observed. Such sediments are characterized by organic matter that can be regarded as chemically stable under the storage conditions, as well as the absence or close-to-minimum rate of mineralization and decomposition processes. Based on the results obtained, the total organic carbon loss was estimated to be 35.5 ± 11.8 g C m^{-2}. The loss can be attributed to the mineralization of labile, and semi-stable fractions of organic matter spread along the core.

The results of organic carbon loss rates (v) for the sediment core are based on the first degree kinetic equation that represents the organic matter mineralization velocity (Fig. 4.14). The fastest rates are observed during the first phase of incubation, especially in the upper sediment layer, deposited after 1992. Values range here from 22.1 mg C m^{-3} day^{-1} in a layer dated for 2003 to 39.5 mg C m^{-3} day^{-1} for the "fluffy layer". In the course of the further stages of the experiment the observed rates of the organic matter losses are slower within the upper segment of the core, that is, in sediments deposited in the period from 1995 to 2008. The obtained results vary in the range from 1.9 mg C m^{-3} day^{-1} for sediments deposited in 1995 to 15.2 mg C m^{-3} day^{-1} for the "fluffy layer"—both recorded during the third phase of incubation. An average rate calculated for the entire

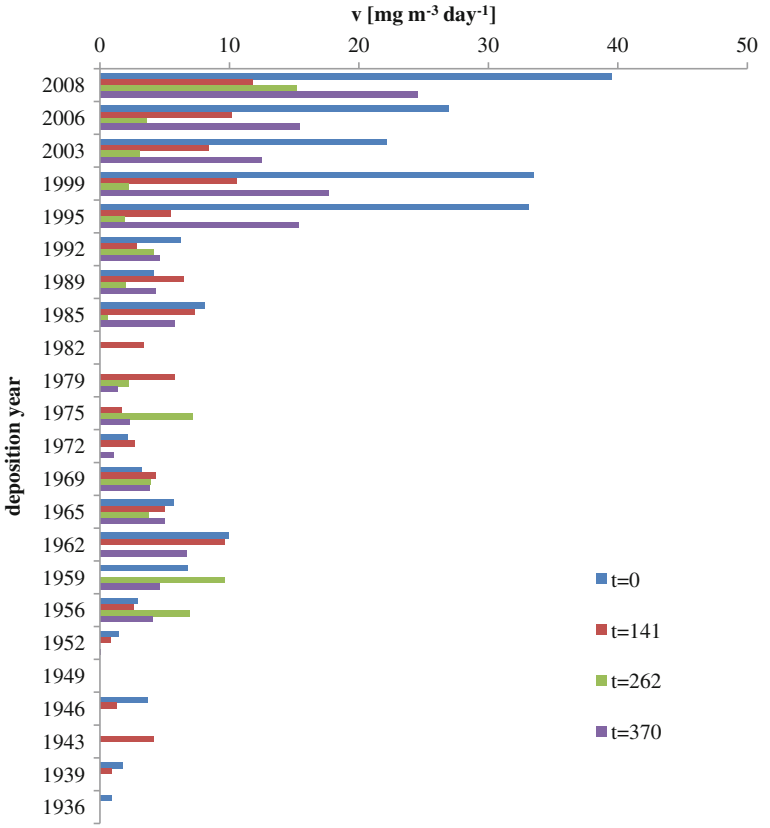

Fig. 4.14 Daily rates of the organic carbon loss during the successive phases of the sediment core incubation (Kuliński 2010)

experiment is driven by its high values observed for the first phase, and the obtained results fall between 12.5 mg C m^{-3} day^{-1} for the sediment deposited in 2003 to 24.5 mg C m^{-3} day^{-1} for the "fluffy layer". Below the uppermost sediment layers, the daily rates of the organic carbon loss are smaller, not exceeding 9.9 mg C m^{-3} day^{-1}, estimated during the first phase of incubation, for the material deposited in 1962. Slight differences are found for specific phases of the experiment, as well as for the average of the entire period during which the experiment was run. A pronounced increase in the organic matter decomposition rates, similar to those for organic carbon concentrations and C_{min} (Fig. 4.13), is observed in layers deposited between 1956 and 1969. However, differences in the organic carbon loss rates at successive stages of the experiment are minor for this core segment, in contrast to the uppermost layer of sediments. A different situation is observed in the

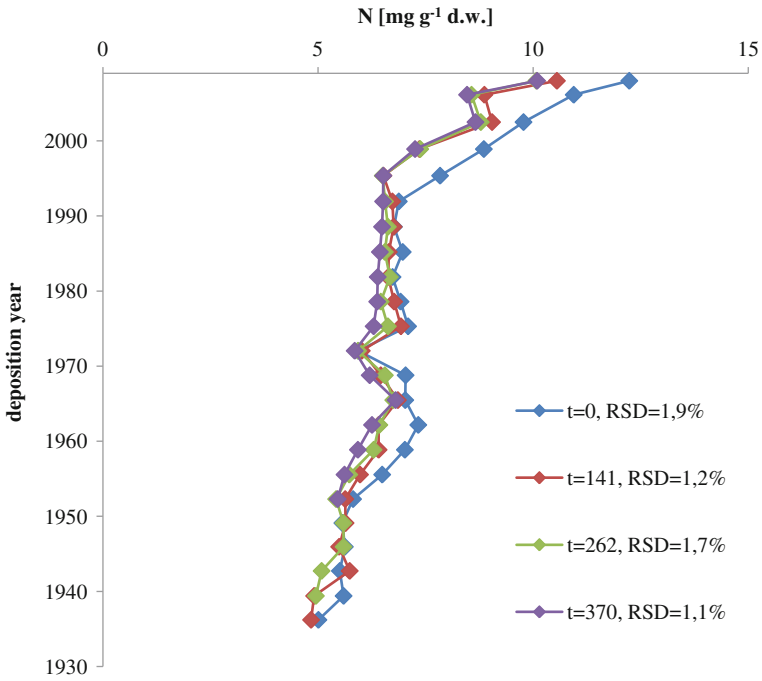

Fig. 4.15 Total nitrogen profile obtained for successive phases of the Gdansk Deep sediment core incubation (Kuliński 2010)

uppermost layer of the core, where the rates of mineralization during the second and the third phase of incubation are three times higher than those during the first phase. The results obtained in the experiment indicate the presence of semi-stabile organic matter whose contribution gradually decreases with depth and, at the same time, with the sediment age; its half-time is estimated at to be 55–60 years. Within the first 15 years the mineralization rate is significantly more intensive.

Profiles of the total nitrogen and phosphorus in the sediment cores subjected to the incubation (Figs. 4.15, 4.16) are in close agreement with the organic carbon concentrations profiles (Fig. 4.12). Relative standard deviations (RSD) characterizing the successive measurement series vary from 1.1 to 1.9% and from 1.6 to 2.2% for nitrogen and phosphorus, respectively. In the uppermost sediment layers deposited after 1992, the concentration of N and P increases, reaching its maximum in the most recently deposited sediment layers, amounting to 12.2 ± 0.2 mg N g^{-1} d.w. and 0.90 ± 0.02 mg P g^{-1} d.w. Similarly to the organic carbon profiles, N and P concentrations in a layer dated on 1972 are characterized by a distinct decrease, reaching 5.9 ± 0.1 mg N g^{-1} and

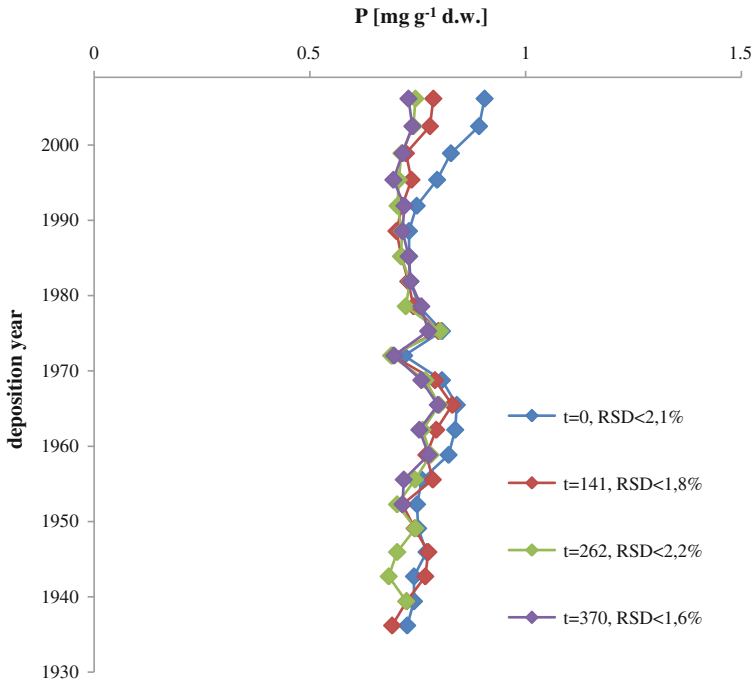

Fig. 4.16 Total phosphorus profile obtained for successive phases of the Gdansk Deep sediment core incubation (Kuliński 2010)

0.72 ± 0.2 mg P g^{-1}, whereas for the subsurface sediment layers, deposited between 1956 and 1969, a slight increase of N and P concentrations is observed, as well as an increase in concentration amplitude between subsequent incubation stages.

An analysis of C/N molar ratios (Table 4.7) reveals rather steady values in vertical profiles that range from 8.9 in layers dated on 1962 and 2006 to 10.1 in layers dated on 1943 and 1972, with an average of 9.6. A small increase is observed during the course of incubation for the subsequent sediment layers. The end of the experiment is characterized by values that oscillate in the range from 9.2 for the "fluffy layer" to 10.5 for the layer dated on 1952. Another pattern represents the C/P molar ratios profile, exceeding even 110 for the cores upper layer, and a value smaller than 80 in the deepest layers. Similar 'depth' trend is characteristic of the N/P molar ratios. In both cases, C/P and N/P profiles do not reveal any systematic changes with time.

Table 4.7 Summary of C/N, C/P and N/P molar ratios at different incubation stages of the Gdansk Deep sediment core (Kuliński 2010)

Deposition year	Incubation start			1st step of incubation			2nd step of incubation			3rd step of incubation		
	C/N	C/P	N/P	C/N	C/P	N/P	C/N	C/P	N/P	C/N	C/P	N/P
2008	9.2	–	–	9.5	–	–	9.6	–	–	9.2	–	–
2006	8.9	115.5	13.0	9.5	114.6	12.1	9.3	114.4	12.3	9.2	114.8	12.4
2003	9.7	113.4	11.7	9.4	117.3	12.5	9.3	118.8	12.7	9.4	117.8	12.6
1999	9.7	110.8	11.5	9.9	107.8	10.9	9.4	103.9	11.1	9.4	102.5	10.9
1995	9.8	103.5	10.6	10.2	97.2	9.5	10.0	99.0	9.9	9.9	100.1	10.1
1992	9.9	97.8	9.9	9.9	99.9	10.1	10.0	100.4	10.0	10.0	96.9	9.7
1989	10.0	99.4	9.9	9.9	101.8	10.3	9.8	97.8	9.9	10.0	97.0	9.7
1985	9.6	98.1	10.2	9.7	97.4	10.0	9.6	95.1	9.9	9.8	92.6	9.5
1982	9.7	95.9	9.8	10.0	97.9	9.8	9.9	96.3	9.8	10.3	96.5	9.3
1979	9.6	94.6	9.8	9.9	97.3	9.8	10.2	98.0	9.6	10.3	92.8	9.0
1975	9.7	91.6	9.4	10.0	92.8	9.3	10.4	91.8	8.8	10.7	93.3	8.7
1972	10.1	89.1	8.8	9.9	92.0	9.3	9.9	91.6	9.2	10.1	91.2	9.0
1969	9.1	84.7	9.4	9.7	85.3	8.8	9.5	86.5	9.1	9.9	86.6	8.8
1965	9.1	81.9	9.0	9.2	81.2	8.9	9.2	82.9	9.0	9.0	82.3	9.1
1962	8.9	83.6	9.4	9.8	85.0	8.7	9.5	85.7	9.0	9.8	86.9	8.9
1959	9.1	83.7	9.2	9.8	87.1	8.9	10.0	86.7	8.6	10.4	84.7	8.2
1956	9.3	85.2	9.2	10.0	81.5	8.2	10.3	85.2	8.2	10.3	86.5	8.4
1952	9.8	81.9	8.3	10.1	85.2	8.4	10.5	86.5	8.3	10.5	85.7	8.2
1949	9.9	78.6	7.9	10.0	80.9	8.1	10.1	81.4	8.0	–	–	–
1946	10.0	78.6	7.8	10.2	77.2	7.6	9.9	84.8	8.5	–	–	–
1943	10.1	80.6	8.0	9.8	78.3	8.0	10.9	86.9	8.0	–	–	–
1939	9.1	73.8	8.1	10.3	75.0	7.3	10.2	74.9	7.3	–	–	–
1936	10.0	73.9	7.4	10.3	77.3	7.5	–	–	–	–	–	–

4.4 Carbon Inflow to the Baltic with Precipitation

To illustrate the magnitude of carbon inflows and losses, Algesten et al. (2006) present comprehensive approach of organic carbon loads transported by different atmospheric deposition forms. With annual precipitation equal to 237 km^3 (Lass and Matthäus 2008), the total organic carbon reaching the Baltic Sea has been estimated at 0.45 Tg C $year^{-1}$. Aerosols are considered to be the main source of carbon in rainwater (Abril et al. 2002). For samples collected above the Baltic open water area, the organic carbon concentration has been estimated to be eight times higher than those recorded for the particulate carbon present mainly as soot (Kuśmierczyk-Michulec et al. 2001). Based on this conclusions, a similar ratio has been assumed for the rainwater, which gives a positive load of 0.06 Tg C reaching the Baltic each year.

For the purpose of assessing an inorganic carbon load carried with the rainwater, the aerosol fraction has not been included in calculations. It has been also

assumed that the aerosols emitted from the Baltic surface are compensated through the dry and wet re-deposition.

The atmospheric CO_2 dissolved in rainwater has been recognized as the Baltic Sea inorganic carbon source. The CO_2 dissolved in rainwater is assumed to be in equilibrium with the atmospheric CO_2 characterized by partial pressure of 385 ppm (value for 2009, NOAA records, www.esrl.noaa.gov).

Using Henry's law (Eq. 4.1) for a temperature of 10°C and atmospheric pressure of 1013 hPa, the CO_2 concentration in rainwater was calculated at 0.24 mg C dm^{-3} (Ibanez et al. 2007). When multiplied by the annual precipitation (237 km^3), the annual carbon load to the Baltic equal to 0.06 Tg C $year^{-1}$ is obtained. Henry's law equation reads:

$$C = K_H \cdot p \tag{4.1}$$

where: C—CO_2 concentration in a rainwater (mol dm^{-3})

K_H—Henry's law constant (mol dm^{-3} atm^{-1})
p—CO_2 partial pressure in the atmosphere (atm)

It is difficult to assess the annual load of organic carbon brought to the Baltic with precipitation, since no data regarding the DOC and/or POC concentration in the rainwater have been reported. Taking the value of TOC in the rainwater reported by Pempkowiak (1976), the annual load of organic carbon deposited to the Baltic amounts to 0.24 Tg C $year^{-1}$. This approximation should be taken with caution, since the assumed concentrations have not been confirmed by recent reports. Nevertheless, the figure approximates the magnitude of organic carbon delivered to the Baltic with rainwater. Both DIC and TOC loads deposited to the Baltic with rainwater are negligible as compared to other sinks and sources of carbon to the Baltic.

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