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Origin and fate of organic carbon in the freshwater part of the Scheldt Estuary as traced by stable carbon isotope composition

L. HELLINGS[1], F. DEHAIRS[1], M. TACKX[2], E. KEPPENS[3] & W. BAEYENS[1]
[1]*Department of Analytical Chemistry, Vrije Universiteit Brussel, Pleinlaan 2, B-1050 Brussels, Belgium;* [2]*Department of Ecology and Systematics, Vrije Universiteit Brussel, Pleinlaan 2, B-1050 Brussels, Belgium;* [3]*Department of Geology, Vrije Universiteit Brussel, Pleinlaan 2, B-1050 Brussels, Belgium*

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Abstract. We investigated the seasonal and geographical variation in the stable carbon isotope ratios of total dissolved inorganic carbon ($\delta^{13}C_{DIC}$) and suspended matter ($\delta^{13}C_{POC}$) in the freshwater part of the River Scheldt. Two major sources of particulate organic matter (POM) occur in this riverine system: riverine phytoplankton and terrestrial detritus. In winter the lowest $\delta^{13}C_{DIC}$ values are observed due to enhanced input of CO_2 from decomposition of ^{13}C-depleted terrestrial plant detritus (average $\delta^{13}C_{DIC} = -14.3‰$). During summer, when litter input from terrestrial flora is the lowest, water column respiration on POM of terrestrial origin is also the lowest as evidenced by less negative $\delta^{13}C_{DIC}$ values (average $\delta^{13}C_{DIC} = -9.9‰$). In winter the phytoplankton biomass is low, as indicated by low chlorophyll a concentrations (Chl a $< 4.5\ \mu g l^{-1}$), compared to summer when chlorophyll a concentrations can rise to a maximum of 54 $\mu g l^{-1}$. Furthermore, in winter the very narrow range of $\delta^{13}C_{POC}$ (from −26.5 to −27.6‰) is associated with relatively high C/N ratios (C/N > 9) suggesting that in winter a major fraction of POC is derived from allochthonous matter. In summer $\delta^{13}C_{POC}$ exhibits a very wide range of values, with the most negative values coinciding with high Chl a concentrations and low C/N ratios (C/N < 8). This suggests predominance of phytoplankton carbon in the total particulate carbon pool, utilising a dissolved inorganic carbon reservoir, which is already significantly depleted in ^{13}C. Using a simple two source mixing approach a reconstruction of the relative importance of phytoplankton to the total POC pool and of $^{13}C/^{12}C$ fractionation by phytoplankton is attempted.

Introduction

In estuaries huge amounts of organic matter originating from *in situ* primary production, litterfall from riparian vegetation and anthropogenic inputs can be respired and can enter the foodweb when transiting towards the ocean. This is especially the case for the River Scheldt. This river is characterised by large tidal prisms and low river discharge resulting in long residence times of freshwater masses, and flows through one of the most industrialised and populated areas of North West Europe (Figure 1). In the Scheldt Estuary tidal exchange (about 100 000 m^3 s^{-1}) is much more important than freshwater discharge. During winter, the average river discharge rate amounts to 180 m^3 s^{-1} with exceptional values up to 600 m^3 s^{-1}. Average summer values decrease to 60 m^3 s^{-1} with minimal values down to 20 m^3 s^{-1} (Baeyens et al. 1998). In the estuary, which is 160 km long, it takes a water parcel 50 to 70 days to reach the sea (Ronday 1976; Wollast et al. 1982; Soetaert & Herman 1994a). This slow journey favours chemical and biological transformation of the components carried by the river. The long residence time of the water and intense bacterial respiration lead to oxygen depletion and a large efflux of CO_2 to the atmosphere in the central and upper parts of the estuary (Goosen et al. 1995; Frankignoulle et al. 1996).

To elucidate the origin and the fate of organic matter in an estuary it is crucial to utilise natural tracers as source indicators. There are multiple possible sources of particulate organic carbon, and major ones have been identified on the basis of their carbon isotopic composition (Coffin et al. 1994). For instance, the carbon isotope ratio ($\delta^{13}C$) of terrestrial plants and marine algae is significantly different (Fry et al. 1984). Because of the large differences in isotopic compositions of different potential carbon sources in rivers, estuaries and coastal waters, stable carbon isotopic composition has been used extensively to examine diverse aspects of carbon cycling in such environments (e.g. Cai et al. 1988; Quay et al. 1992). The use of stable isotopes to trace organic matter is based on the assumption that isotopic ratios are conservative and that physical mixing of endmembers determines the isotopic distributions of organic matter in natural systems (Cifuentes et al. 1988). However, on certain time scales biogeochemical processes will change the isotopic composition of organic matter. An understanding of these processes is possible via knowledge of (1) the isotopic composition of the source(s) and (2) the direction and magnitude of isotopic alteration during microbial or phytoplankton mediated processes. However, studies of biogeochemical reactions in natural environments are complicated since numerous reactions and processes may cause isotopic variation. For example, stable carbon isotope compositions can be altered by fractionations that occur during photosynthesis, biosynthesis and catabolic reactions during respiration, decomposition, and remineralisation (Ostrom et al. 1997).

The objectives of this study are (1) to assess spatio-temporal variability of the carbon isotopic composition of total dissolved inorganic carbon (DIC

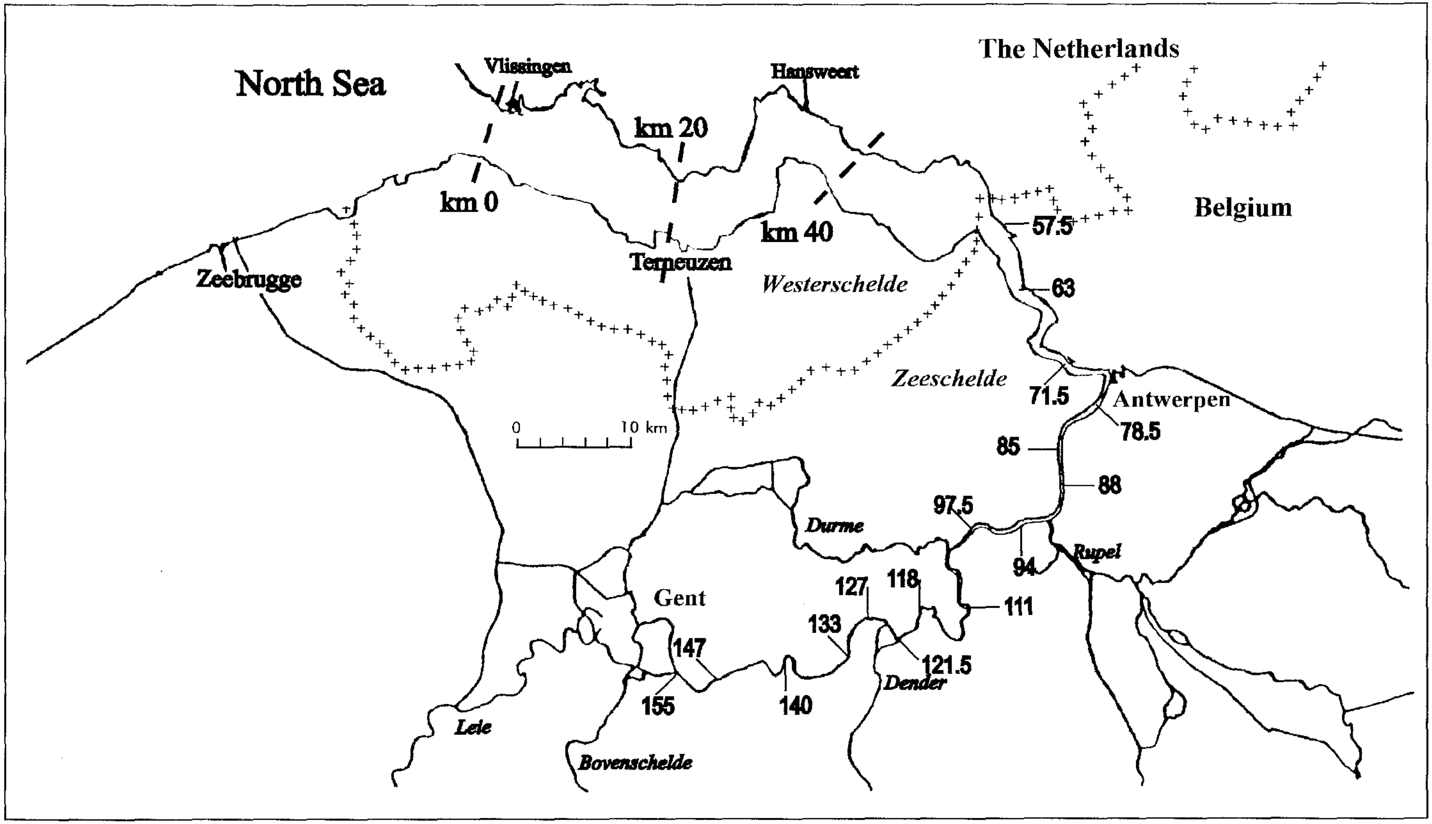

Figure 1. Map of the Zeeschelde with 16 sampling stations and 4 tributaries (Rupel (Ru), Durme (Du), Dender (De) and Bovenschelde (BS)). Numbers on the map refer to distance in km of the sampling stations relative to Vlissingen.

= $[CO_{2(aq)}] + [HCO_3^-] + [CO_3^{2-}]$) and of suspended organic matter; (2) to identify the mechanisms controlling this spatio-temporal variability and (3) to identify the relative importance of major sources of organic carbon in the Zeeschelde.

Study area

With a total length of 330 km, the River Scheldt flows through France, Belgium and The Netherlands before it discharges into the North Sea. The Scheldt Estuary is that part of the river that is subject to tidal exchange. The Scheldt Estuary has a total length of 160 km and it flows from Gent (Belgium) to Vlissingen (The Netherlands) where it opens into the North Sea (Figure 1). The Dutch part of the Scheldt Estuary is called Westerschelde; the Belgian part (from the Dutch-Belgian border located 57.5 km from Vlissingen, to Gent located 155 km from Vlissingen) is called Zeeschelde. The tidal amplitude varies between 4 m near Vlissingen, 5.2 m near Antwerpen, and to 2 m near Gent. Vertical salinity stratification is either absent (downstream) or minor (upstream), but there is a pronounced horizontal salinity gradient which is subject to tidal and seasonal variations (Middelburg et al. 1995). From Gent to Rupelmonde the water is fresh (<0.7), between Rupelmonde and Hansweert brackish (0.7–10) and between Hansweert and Vlissingen salt (>10) (Meire et al. 1995).

Along its course the river is heavily polluted by discharge from large cities, active industrial areas and intensive stock farming. The estuary receives about 100×10^3 ton of mainly anthropogenic organic C per year, of which a large fraction is respired in the estuarine zone (Wollast 1988). Due to the hydrodynamic conditions imposed by the strong tidal regime and the relatively low water discharge, this organic matter accumulates preferentially in the upper estuary, between salinities of 2 and 10 (Wollast 1983). The high load of organic matter in this zone induces a high microbial activity, which causes a serious depletion of oxygen in the water column in summer (Billen et al. 1988; Heip 1988). The high load of organic carbon and the associated intensive bacterial activity results also in high nutrient concentrations. For the period covered by the present study concentrations of ammonium, nitrate and nitrite range from 4 to 1400, 40 to 500 and 1 to 60 μM, respectively (J. Piraux, pers. comm.), while phosphate concentrations range from 5 to 70 μM (S. Van Damme, pers. comm.).

Methods

Water sampling. During 1996, surface water from 16 stations in the Zeeschelde (Figure 1) were sampled once a month. All stations are indicated by their distance in km from Vlissingen located at the mouth of the Scheldt Estuary. Within two days all stations were sampled as well as four major tributaries: Rupel, Durme, Dender and Bovenschelde (Figure 1). Surface water samples were collected with a Niskin sampling bottle of 30 litre. Temperature and pH were measured with a portable field pH-meter (Hanna instruments). Oxygen concentration and salinity were measured *in situ* with a Datasonde®3 Multiprobe logger (S. Van Damme, pers. comm.). DIC samples for ^{13}C analysis were collected by gently overfilling a glass bottle from the Niskin bottle, poisoning with $HgCl_2$, gas tight capping with a rubber plug and an aluminium cap, and storing at ambient temperature. Water samples for total alkalinity, POC, $\delta^{13}C_{POC}$ and suspended solids were collected in 500 ml PE bottles, poisoned with $HgCl_2$, stored in the refrigerator and analysed within a week.

Chemical analysis. 25 ml of the water samples were filtered on 25-mm diameter pre-weighed glass fibre filters (Whatman, GF/F, 0.7 μm pore size) which were precombusted overnight at 450 °C. After filtration, filters were dried at 60 °C during 2 hours. The concentration of total suspended solids (SS) was deduced from the weight of the filtered particles (typically 3–4 mg/25 ml). These filters were then used for analysis of particulate organic carbon (POC) and particulate nitrogen (PN). Filters were left in an acid (HCl) atmosphere for at least 2 hours to remove inorganic carbonate.

POC and PN were then measured by combustion in a Carlo Erba NA 1500 elemental analyser. Standardisation of analysis was done using acetanilide (C = 71.03%, N = 10.36%).

For the measurement of chlorophyll a (Chl a) content, 100 ml water was filtered on glass fibre filters (Whatman, GF/F) and stored at −20 °C. Chl a was extracted in 5 ml of 90% acetone and quantified by HPLC (Waters).

Total alkalinity was determined on 25 ml samples by an end-point titration with 0.01M HCl (Merck, Titrisol) using an automatic titrator (Mettler-Toledo).

Isotopic analysis. Determination of δ^{13}C in POC ($\delta^{13}C_{POC}$) has been described by Marguillier et al. (1997). Briefly, the organic material was combusted in an Elemental Analyser (Carlo Erba NA1500), and the CO_2 generated during the combustion was automatically trapped in an on-line Finnigan Mat CT-NT trapping-box for cryopurification before injection into the isotope ratio mass spectrometer (Finnigan Mat Delta E). The normal working standard was CO_2 produced from Carrara marble, calibrated against NBS-19 and NBS-18 (IAEA). Graphite reference material (USGS-24) was used as reference standard.

The $\delta^{13}C$ value of DIC ($\delta^{13}C_{DIC}$) was measured using a method similar to that described by Kroopnick (1974). A flask with a septum, containing 3 ml of pure *ortho*-phosphoric acid (99% cryst.) and a magnetic stir bar was degassed and heated in a water bath at approximately 50 °C. Then 15 ml of sample was injected with a syringe through the septum of the flask. Evolved CO_2 was extracted in the evacuated system and was quantitatively trapped in a liquid nitrogen cooled trap after passing through 4 traps with cooled iso-propanol (−80 °C) to remove water vapour. The glass tubes with trapped CO_2 were sealed using a torch. They were then connected manually to the mass spectrometer inlet port via a tube cracker.

Values are expressed relative to the VPDB (Vienna Peedee Belemnite) standard (Coplen 1996). Stable carbon isotopic ratios are expressed as δ values:

$$\delta^{13}C\ (‰) = [(X_{sample} - X_{standard})/X_{standard}] \times 10^3,\ \text{where } X = {}^{13}C/{}^{12}C.$$

Reproducibility for the analysis of different aliquots of the same water sample was generally better than 0.1‰ for $\delta^{13}C_{POC}$ and 0.04‰ for $\delta^{13}C_{DIC}$.

Results

Physical and chemical parameters

Physical and chemical parameters (pH, Temp, Sal, Tot Alk, O_2, SS, POC, PN and C/N) showed considerable seasonal variation in 1996. Table 1 shows the monthly (16 sampling stations) and seasonal averages of these parameters. Salinity, total alkalinity and dissolved O_2 also showed a longitudinal gradient in the Zeeschelde. Water temperature reached a mean value of 20 °C in summer (during the warmest month, August, water temperature raised to 21 °C) and it declined to 4 °C in winter (February was the coldest month with 2.2 °C). The geographical variation of water temperature was rather small. The annual average salinity in the Zeeschelde varied between 14.1 at 57.5 km from Vlissingen (the Dutch–Belgian border) and 0.1 at km 155. The salinity of the first five sampling points (km 57.5 to km 85) varied between 15.2 and 0.3. From km 88 to km 155 the salinity was close to 0. The pH of the Zeeschelde ranged between 7.00 and 7.92, with an annual average of 7.60. For total alkalinity, there was a gradual increase from km 57.5 (the Dutch–Belgian border) to km 155. For example, in spring total alkalinity increased

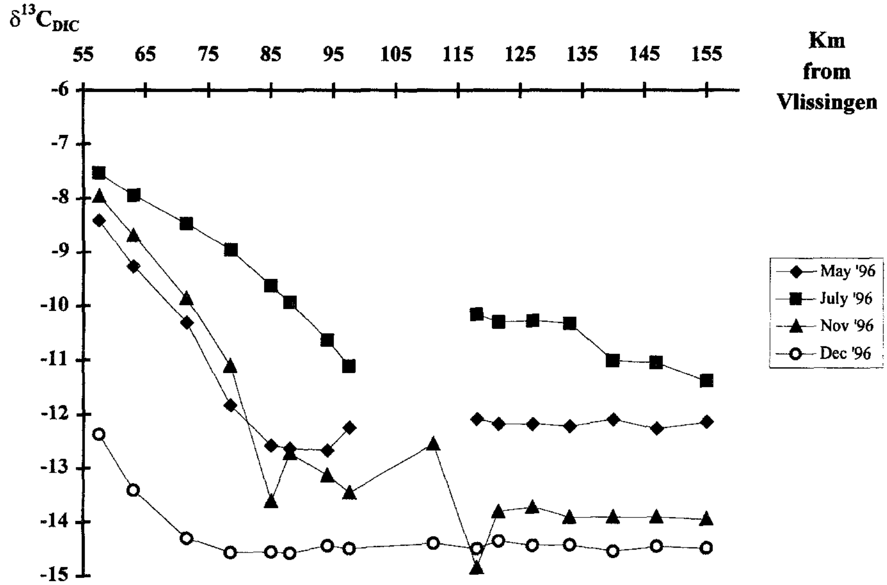

Figure 2. Seasonal variation of the $\delta^{13}C$ in dissolved inorganic carbon ($\delta^{13}C_{DIC}$). Diamonds: May '96; squares: July '96; triangles: November '96 and circles: December '96.

from 3.80 to 7.08 mM. Total alkalinity did not show a clear seasonal variation. The winter of 1995–1996 was characterised by the highest amount of suspended solids (average of 147 mgl^{-1}), the highest POC concentration (average: 847 μM) and the highest C/N atomic ratio (average: 11.1). The summer, on the other hand, had the lowest amount of suspended solids (average: 92 mgl^{-1}), a lower POC concentration (average: 557 μM) and the lowest C/N ratio (average: 7.5).

Seasonal and geographical variations in $\delta^{13}C$ of DIC

The $\delta^{13}C$ pattern of total dissolved inorganic carbon had a clear seasonal variation (Figure 2, Table 2). In spring (May) the $\delta^{13}C_{DIC}$ of the Zeeschelde ranged from −8.4 to −12.7‰, with a mean value of −11.7±1.3‰. During summer (July) the isotopic ratios of DIC were enriched in ^{13}C. $\delta^{13}C_{DIC}$ values ranged from −7.5 to −11.4‰, with a mean value of −9.9±1.2‰. More negative $\delta^{13}C_{DIC}$ values were measured in fall (November) with $\delta^{13}C_{DIC}$ ranging from −8.0 to −14.8‰ (mean value −12.6±2.0‰). In winter (December) the $\delta^{13}C_{DIC}$ signal of the Zeeschelde was characterised by the most negative values ranging from −12.4 to −14.6‰ (mean value −14.3±0.6‰).

During all seasons, the $\delta^{13}C_{DIC}$ showed a significant decrease from km 57.5 (the Dutch–Belgian border) to km 78.5 (Antwerp). From km 111 up

Table 1. Monthly and seasonal averages and ranges of the physical and chemical parameters of Zeeschelde water in 1996. SD – Standard Deviation; Sal – Salinity; TA – Total Alkalinity; SS – Suspended Soilds; POC – Particulate Organic Carbon; and PN – Particulate Nitrogen. Sal and O_2 data are from S. Van Damme (pers. comm.).

	March '96		April '96		May '96		Spring '96	
	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range
pH	7.67 ± 0.09	7.57–7.80	7.62 ± 0.07	7.50–7.80	7.77 ± 0.10	7.58–7.90	7.69 ± 0.11	7.50–7.90
T (°C)	5.7 ± 0.3	5.0–6.3	11.1 ± 1.7	8.9–14.4	14.1 ± 0.9	12.5–15.1	10.6 ± 3.6	5.0–15.1
Sal (ppt)	1.3 ± 2.7	0.1–10.1	2.1 ± 3.8	0.2–12.4	2.1 ± 3.8	0.1–12.2	1.9 ± 3.5	0.1–12
TA (mM)	5.40 ± 0.71	4.10–6.10	5.76 ± 0.94	3.92–7.08	5.59 ± 0.94	3.80–6.54	5.60 ± 0.88	3.80–7.08
O_2 (μM)	176 ± 64	63–270	7 ± 68	3–216	53 ± 61	6–204	102 ± 82	3–270
SS (mg/l)	187 ± 63	108–324	102 ± 52	16–184	106 ± 63	32–244	128 ± 69	16–324
POC (μM)	529 ± 314	132–1547	405 ± 219	46–785	425 ± 225	102–771	450 ± 256	46–1547
PN (μM)	53 ± 20	11–85	58 ± 32	5–108	45 ± 22	11–81	53 ± 26	5–108
C/N	10.0 ± 2.8	7.1–18.8	7.4 ± 1.9	3.4–10.6	9.4 ± 1.5	6.8–12.1	8.7 ± 2.4	3.7–18.8
	June '96		July '96		August '96		Summer '96	
	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range
pH	7.47 ± 0.07	7.37–7.62	7.66 ± 0.12	7.46–7.89	7.53 ± 0.10	7.35–7.75	7.56 ± 0.13	7.35–7.89
T (°C)	19.9 ± 1.3	17.8–22.5	19.3 ± 0.7	18.5–20.8	21.1 ± 0.3	20.8–21.8	20.2 ± 1.2	17.8–22.5
Sal (ppt)	1.4 ± 2.8	0.1–10.3	3.4 ± 5.0	0.2–14.2	2.4 ± 4.3	0.2–15.2	2.4 ± 4.2	0.1–12.0
TA (mM)	5.13 ± 0.56	3.78–5.98	5.01 ± 1.15	3.20–6.88	5.35 ± 0.77	3.70–6.74	5.17 ± 0.85	3.20–6.88
O_2 (μM)	26 ± 23	3375–6.00	834 ± 72	10–228	35 ± 36	7–144	48 ± 53	6–228
SS (mg/l)	80 ± 47	20–168	86 ± 36	20–168	109 ± 69	44–308	92 ± 54	20–308
POC (μM)	451 ± 244	217–912	485 ± 320	72–1205	725 ± 477	122–2073	557 ± 377	72–2073
PN (μM)	57 ± 27	28–110	71 ± 49	10–175	97 ± 56	14–229	75 ± 48	10–229
C/N	7.8 ± 0.9	6.4–9.5	7.3 ± 1.0	6.3–9.8	7.5 ± 1.0	6.0–10.0	7.5 ± 1.0	6.0–10.0
	September '96		October '96		November '96		Fall '96	
	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range
pH	7.24 ± 0.16	7.00–7.57	7.60 ± 0.16	7.31–7.92	7.64 ± 0.12	7.40–7.90	7.51 ± 0.23	7.00–7.92
T (°C)	18.3 ± 1.1	17.4–20.4	15.5 ± 0.9	12.7–16.7	12.4 ± 0.7	10.7–13.5	15.0 ± 2.5	10.7–20.4
Sal (ppt)	1.6 ± 3.5	0.1–12.2	2.2 ± 3.9	0.2–12.5	2.5 ± 4.6	0.2–15.0	2.1 ± 4.0	0.1–15.0
TA (mM)	3.29 ± 0.41	2.70–4.16	5.09 ± 1.16	3.42–6.72	5.45 ± 1.38	3.50–6.96	4.63 ± 1.42	2.70–6.96
O_2 (μM)	42 ± 37	13–112	38 ± 39	7–155	86 ± 72	30–266	56 ± 56	7–266
SS (mg/l)	147 ± 85	34–350	89 ± 36	26–176	98 ± 51	28–192	110 ± 64	26–350
POC (μM)	748 ± 408	157–1689	438 ± 237	97–999	488 ± 266	125–970	555 ± 334	97–1689
PN (μM)	79 ± 42	18–166	56 ± 27	11–112	57 ± 29	12–107	64 ± 34	11–166
C/N	9.5 ± 1.0	7.6–10.8	7.9 ± 0.9	5.1–8.9	8.6 ± 1.2	7.0–10.8	8.6 ± 1.2	5.1–10.8
	December '95		January '96		February '96		Winter '96	
	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range
pH	7.62 ± 0.09	7.40–7.80	7.56 ± 0.09	7.40–7.68	7.66 ± 0.12	7.40–7.83	7.61 ± 0.11	7.40–7.83
T (°C)	5.4 ± 1.3	3.8–7.6	4.4 ± 1.0	3.3–6.5	2.2 ± 1.3	0.6–5.6	4.0 ± 1.8	0.6–7.6
Sal (ppt)	2.1 ± 4.0	0.2–13.0	1.4 ± 2.9	0.1–9.8	1.9 ± 4.0	0.2–14.5	1.8 ± 3.6	0.1–14.5
TA (mM)			5.05 ± 0.60	4.14–5.84	6.04 ± 0.89	4.37–6.94	5.54 ± 0.90	4.14–6.94
O_2 (μM)	98 ± 61	14–260	139 ± 52	51–264	160 ± 60	70–303	132 ± 62	14–303
SS (mg/l)	117 ± 89	30–340	142 ± 74	30–310	183 ± 99	36–388	147 ± 91	30–388
POC (μM)	861 ± 529	310–2048	1083 ± 561	318–2189	597 ± 321	154–1368	847 ± 513	154–2189
PN (μM)	78 ± 45	17–172	94 ± 48	30–181	58 ± 31	16–134	77 ± 44	16–181
C/N	11.4 ± 2.8	7.8–18.5	11.7 ± 2.0	9.2–16.4	10.2 ± 0.9	8.9–12.5	11.1 ± 2.1	7.8–18.5

to km 155 $\delta^{13}C_{DIC}$ values stayed almost constant. It is interesting to note that, except for winter (December), the $\delta^{13}C_{DIC}$ for the most seaward-located station (km 57.5) showed only a small seasonal variation (−7.5 to −8.4‰).

Table 2. Seasonal variation of the $\delta^{13}C_{DIC}$, the $\delta^{13}C_{POC}$ and the chlorophyll a concentration in the Zeeschelde.

	δ^{13}C-DIC(‰)		δ^{13}C-POC(‰)		Chl a (μg l^{-1})	
	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range
May '96	−11.7 ± 1.3	−8.4 to −12.7	−29.4 ± 1.7	−26.9 to −31.9	18.0 ± 12.6	3.2–41.6
July '96	−9.9 ± 1.2	−7.5 to −11.4				
August '96			−29.4 ± 1.2	−26.7 to −31.2	28.9 ± 17.1	2.4–54.0
November '96	−12.6 ± 2.1	−7.6 to −14.8	−27.8 ± 0.7	−26.3 to −29.2	4.9 ± 3.3	1.0–9.9
December '96	−14.3 ± 0.6	−12.4 to −14.6	−27.2 ± 0.3	−26.5 to −27.6	2.4 ± 1.3	0.7–4.5

Seasonal and geographical variations in $\delta^{13}C$ of POC

The pattern of δ^{13}C in suspended matter in the Zeeschelde changed seasonally (Figure 3, Table 2). In winter (December), $\delta^{13}C_{POC}$ showed little spatial variation (−26.5 to −27.6‰; mean value −27.2±0.3‰), irrespective of the salinity gradient. During spring (May) some of the most negative values (−26.9 to −31.9‰; mean value −29.4±1.7‰) were recorded throughout the Zeeschelde. In summer (August) the spatial distribution was similar to that in spring. $\delta^{13}C_{POC}$ varied within a wide range from −26.7 to −31.2‰, with a mean value of −29.4±1.2‰. During fall (November) the particulate organic carbon was again more enriched in ^{13}C with $\delta^{13}C_{POC}$ values ranging from −26.3 to −29.2‰ (mean of −27.8±0.7‰).

For all seasons, except winter, $\delta^{13}C_{POC}$ showed a geographical variation with most negative values upstream of km 100 and progressively less negative values downstream towards km 57.5. The $\delta^{13}C_{POC}$ values of the two most seaward stations (km 57.5 and km 63) showed very little seasonal variation. The same pattern (except for winter) was observed for $\delta^{13}C_{DIC}$.

Discussion

The annual cycle of the $\delta^{13}C_{DIC}$ is a sensitive indicator of the changes resulting from biological carbon fixation and subsequent degradation because of the large isotope fractionation during photosynthesis (Quay et al. 1986). Inorganic carbon, derived autochthonously from respiration and decomposition of aquatic flora and fauna, or allochthonously through heterothropic decomposition of terrestrial litter entering the system, can markedly lower the δ^{13}C value of the inorganic carbon pool (Keeley & Sandquist 1992). Quay et al. (1986) demonstrated that the $\delta^{13}C_{DIC}$ in surface water of Lake Washington is set by a balance between photosynthetic uptake and respiratory production. Unusu-

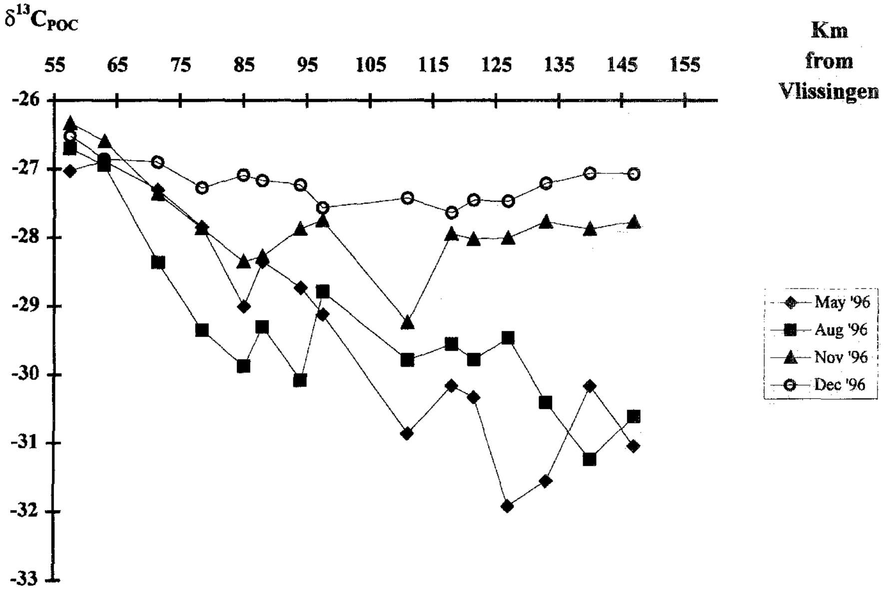

Figure 3. Seasonal variation of the δ^{13}C in suspended organic matter ($\delta^{13}C_{POC}$). Diamonds: May ’96; squares: August ’96; triangles: November ’96 and circles: December ’96.

ally light or heavy isotopic ratios of DIC may result from net-heterothropic or net-autotrophic processes, respectively (Coffin et al. 1994). Mook and Tan (1991) also reported seasonal variability of $\delta^{13}C_{DIC}$ in Dutch rivers. They concluded that the higher δ^{13}C values of the HCO_3^- fraction in summer are the result of the photosynthetic activity and isotopic exchange with atmospheric CO_2. Furthermore during fall, lower temperatures, heavy rainfall and increased groundwater discharge cause δ^{13}C to decrease. $\delta^{13}C_{DIC}$ can vary substantially and will depend upon: (i) the extent to which atmospheric CO_2 is in equilibrium with the water mass, although the contribution of atmospheric CO_2 to DIC in rivers is negligibly small (Mook et al. 1991); (ii) groundwater discharge; (iii) respiration on particulate organic carbon of natural terrestrial and domestic sewage origin and (iv) *in situ* photosynthesis.

The $\delta^{13}C_{DIC}$ in the Zeeschelde varied seasonally. In summer (July) the isotopic ratio of DIC showed enrichment in ^{13}C. Since in summer *in situ* photosynthesis is high and respiration on particulate organic matter of terrestrial origin is low, the reduced input of CO_2 from decomposition of ^{13}C-depleted terrestrial detritus and the discrimination against ^{13}C during biological carbon fixation induce less negative $\delta^{13}C_{DIC}$ values (Figure 2). In fall (November) and winter (December) more negative $\delta^{13}C_{DIC}$ values were measured. In this period respiration is the dominant process and production of respired CO_2 from ^{13}C-depleted terrestrial organic matter resulted in dissolved inorganic carbon with a light $\delta^{13}C$ value (Figure 2).

The $\delta^{13}C_{DIC}$ in the Zeeschelde varied also geographically. The question arises whether this spatial variability reflects conservative mixing for $\delta^{13}C_{DIC}$ or not. To test this, information is needed on $\delta^{13}C_{DIC}$ values over the whole salinity range in the estuary. Our sampling stations did normally not include typically estuarine and marine conditions which are encountered further downstream of the Dutch-Belgian border (km 57.5). However, for February 1997 we have $\delta^{13}C_{DIC}$ values for the section of the estuary between Vlissingen and Antwerpen (L. Hellings, unpublished results). We tested whether our data for that section (km 0 to km 78.5) obeyed conservative mixing. Conservative mixing requires the $\delta^{13}C_{DIC}$ to obey the ^{13}C mass balance equation (Mook et al. 1991):

$$\delta^{13}C = \frac{\mathrm{Sal}(\mathrm{DIC_F}\delta^{13}C_F - \mathrm{DIC_M}\delta^{13}C_M) + \mathrm{Sal_F DIC_M}\delta^{13}C_M - \mathrm{Sal_M DIC_F}\delta^{13}C_F}{\mathrm{Sal}(\mathrm{DIC_F} - \mathrm{DIC_M}) + \mathrm{Sal_F DIC_M} - \mathrm{Sal_M DIC_F}}. \quad (1)$$

Where Sal, Sal_F and Sal_M refer to the salinities of the actual sample, the freshwater and the seawater components, respectively. DIC concentrations were calculated from experimental determinations of pH and total alkalinity; again subscripts F and M refer to river water and seawater, respectively. Observed endmember values were, for the marine condition: $DIC_M = 2.8$ mM, $\delta^{13}C_M = -0.3$‰ and $Sal_M = 34$ and for the freshwater condition: $DIC_F = 4$ mM, $\delta^{13}C_F = -13.8$‰ and $Sal_F = 0.5$.

Figure 4 shows the regression between the observed $\delta^{13}C_{DIC}$ values and the values calculated assuming conservative mixing. It appears that for February the variation of $\delta^{13}C_{DIC}$ throughout the estuary can be explained by conservative mixing. For other seasons we have no sufficient data in the downstream estuary, but it is clear that riverine and marine endmembers will change seasonally as discussed before.

As observed for $\delta^{13}C_{DIC}$, $\delta^{13}C_{POC}$ values showed a considerable seasonal and spatial variability. $\delta^{13}C_{POC}$ values were almost constant in winter (-27.2 ± 0.3‰, Table 2), irrespective of the salinity gradient in the Zeeschelde. This uniformity $\delta^{13}C_{POC}$ values suggests that the dominant sources of organic matter have similar $\delta^{13}C_{POC}$ values. In winter the contribution of phytoplankton to the total POC pool is unlikely to be large as confirmed by the low chlorophyll a concentrations (Chl a < 4.5 μgl^{-1}; Figure 5), relative to summer when chlorophyll a concentrations can rise to a maximum of 54 μgl^{-1}. Furthermore, the very narrow range of $\delta^{13}C_{POC}$ (-26.5 to -27.6‰) was associated with relatively high C/N ratios (C/N > 9; Figure 6). In winter differences between $\delta^{13}C_{DIC}$ and $\delta^{13}C_{POC}$ ($\Delta\delta^{13}C$) ranged from 12.4 to 14.1‰. Such $\Delta\delta^{13}C$ values are smaller than expected in case the

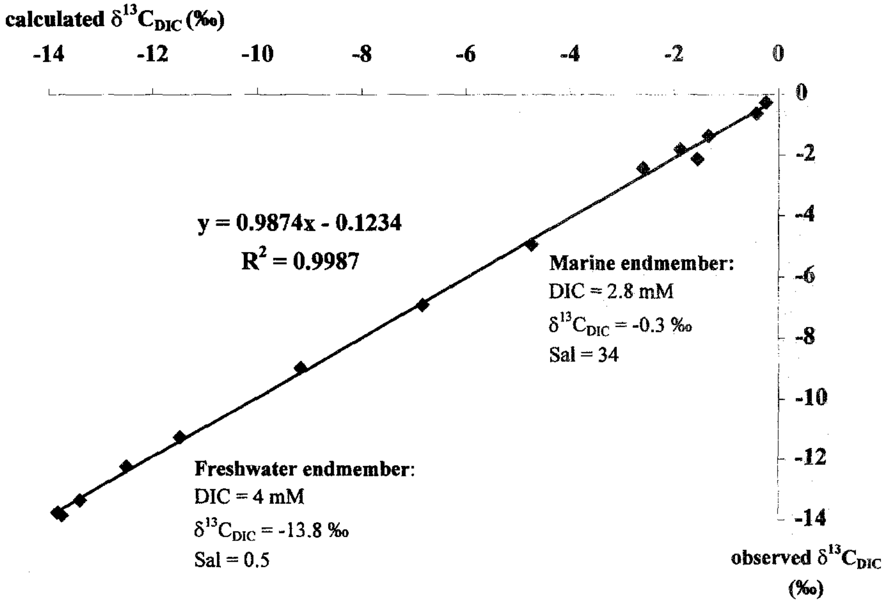

Figure 4. Calculated $\delta^{13}C_{DIC}$ (‰) versus the observed $\delta^{13}C_{DIC}$ (‰) for the section between Vlissingen and Antwerpen for February 1997.

particulate organic carbon is predominantly of autochthonous origin, suggesting that in winter almost all riverine POC is derived from allochthonous terrestrial matter of natural, anthropogenic and industrial-domestic origin. Most terrestrial plant species are C_3 plants. Plants with the C_3 pathway of photosynthesis reduce CO_2 to phosphoglycerate, a 3-C compound, via the enzyme RuBP (RUBISCO) carboxylase oxygenase. This enzyme discriminates against $^{13}CO_2$, resulting in relatively low $\delta^{13}C$ values for C_3 plants. Plants with the C_3 pathway have $\delta^{13}C$ values ranging between −32 to −20‰, with a mean of −27‰ (e.g. Boutton 1991). Willow trees are the most common vegetation type along the freshwater part of the Zeeschelde (46.4% of the total vegetation; Meire et al. 1994). Leaves from 16 willow trees, chosen at random, were collected in September 1996, and revealed a $\delta^{13}C$ range from −26.2 to −31.5‰.

During summer we recorded some of the most negative $\delta^{13}C$ values for suspended organic carbon. The $\delta^{13}C_{POC}$ exhibited a wide range of values from −26.7 to −31.2‰ (Table 2). These values are largely consistent with observations for the Scheldt Estuary reported in literature. Laane et al. (1990) reported $\delta^{13}C$ values for suspended matter in the upper estuary ranging from −27.2 to −31‰. For August 1994 Middelburg et al. (1997) reported a value of −28.9±1.1‰ for the fresh-water POM endmember. For summer,

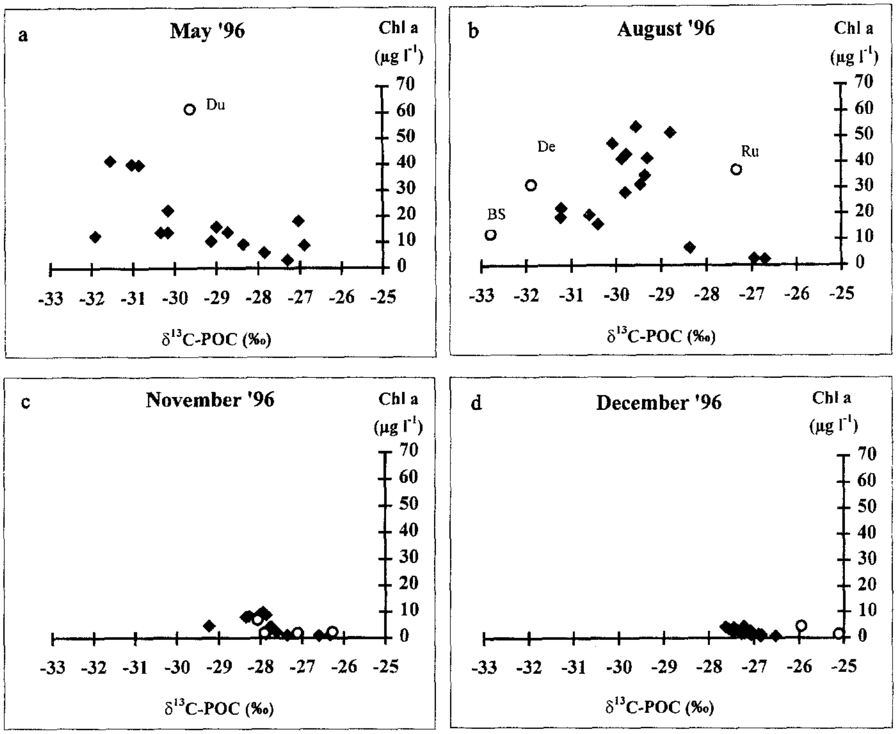

Figure 5. Chlorophyll a concentrations versus $\delta^{13}C_{POC}$ for a typical spring(a), summer(b), fall(c) and winter(d) month. Ru, Du and De confluences of Rupel, Durme and Dender respectively; BS = Bovenschelde.

our most negative $\delta^{13}C_{POC}$ values coincide with high Chl a concentrations (Figure 5) and low C/N ratios (C/N $<$ 8; Figure 6). This suggests predominance of suspended POM by phytoplankton (C/N ratio = 6.5; Redfield et al. 1963). Middelburg et al. (1997) reported a similar situation for August 1994. They identified a riverine endmember having a $\delta^{13}C_{POC}$ value of −30‰ and a C/N ratio of 7.5, indicating that riverine algae and their detritus, rather than terrestrial organic matter, dominated suspended organic matter. On the contrary, least negative $\delta^{13}C_{POC}$ values (approximating −27‰) were associated with higher C/N ratios (C/N $>$ 8) and lower Chl a contents, suggesting that for these situations the POC pool contained a larger fraction of terrestrial origin.

In the following we evaluate the relative importance of major sources of organic carbon to the Zeeschelde. Two potential major sources can contribute to the total particulate organic carbon pool in the river: (1) allochthonous matter consisting of terrestrial organic carbon of natural (vegetation) and of anthropogenic (domestic and industrial wastes) origin; (2) autochthonous

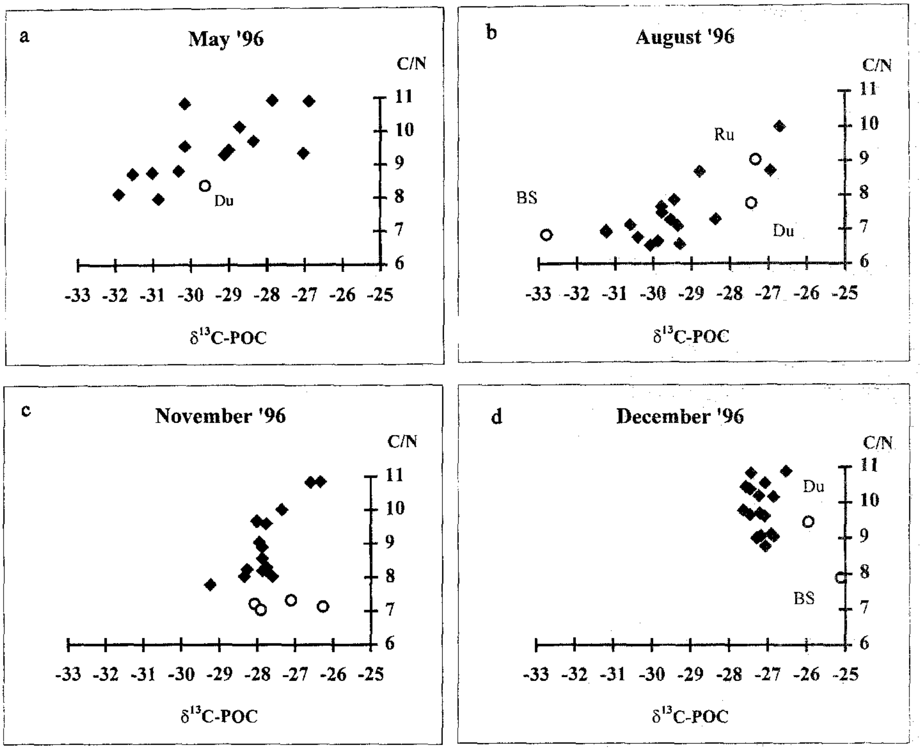

Figure 6. C/N ratio versus $\delta^{13}C_{POC}$ for a typical spring (a), summer (b), fall (c) and winter (d) month. Ru, Du and De confluences of Rupel, Durme and Dender respectively; BS = Bovenschelde.

matter consisting of living plankton and detrital organic matter of planktonic origin.

The $\delta^{13}C$ value of phytoplankton is difficult to assess because of the impossibility to separate it from other suspended matter components. The isotope ratio of phytoplankton is a function of the enzymatic fractionation of $^{13}CO_2$ and $^{12}CO_2$ during carbon fixation, the $\delta^{13}C$ signal of the inorganic carbon substrate, the substrate concentration and the rate of carbon fixation (Farquhar et al. 1989). Using the measured isotopic composition of DIC and estimates for isotopic fractionation between riverine phytoplankton and dissolved inorganic carbon, we attempted to calculate $\delta^{13}C$ composition of the Zeeschelde phytoplankton. Tan and Strain (1983) reported the carbon isotopic fractionation between plankton and total dissolved inorganic CO_2 ($\Delta\delta^{13}C$) for a riverine and estuarine environment (St. Lawrence Estuary, Canada) to range between 21.2 and 24.3‰ (mean 22.3‰). Similar values have been recorded for other environments. For example for a Dutch lake Mook (1970) measured an isotope fractionation between dissolved inorganic carbon and plankton of 23‰. Such values are equivalent to a fractionation of 14‰ between $CO_{2(aq)}$ and plankton, since $CO_{2(aq)}$ is about 9‰ more negative in $\delta^{13}C$ than HCO_3^- at a temperature of 25 °C (Mook et al. 1974). Although $\Delta\delta^{13}C$ values may differ from expected fractionation factors and may vary unpredictably within a single estuary (Tan & Strain 1983), we assumed a similar and constant fractionation to apply in our study, as was also done by Cai et al. (1988) in their study on the Amazon River.

We limit this discussion to the riverine section (Salinity 0) of the Zeeschelde (from km 85 to km 155), where the POC sources are likely to be limited to terrestrial POC and *in situ* autotrophic POC. Since for spring (May) our observed $\delta^{13}C_{DIC}$ values in this section of the river range between −12.1 and −12.7‰ (mean −12.3‰; Table 3), the expected $\delta^{13}C$ of the phytoplankton ($\delta^{13}C_{Phyto1}$) is estimated to range between −34.4 and −35.0‰ (mean −34.6‰; Table 3). Mook et al. (1991) reported $\delta^{13}C$ values for freshwater phytoplankton ranging between −32‰ for high HCO_3^- water at moderate temperatures and −44‰ for high CO_2 water at low temperatures. Our calculated $\delta^{13}C$ values of phytoplankton ($\delta^{13}C_{Phyto1}$) fall within these ranges. Using our calculated values of phytoplankton $\delta^{13}C$ we now estimate the relative contribution of phytoplankton carbon to the total POC pool. For the $\delta^{13}C$ value of allochtonous material ($\delta^{13}C_{POCallocht}$) we chose a value of −27‰. This value is the typical value for C_3 plant material reported in literature and it is also very close to the average value for Zeeschelde POC in winter when phytoplankton contribution is lowest and the river POC pool is essentially composed of allochthonous material. The relative importance of allochthonous versus autochthonous organic carbon can be estimated (Table 3) by applying a two source-mixing model:

$$\begin{aligned}\delta^{13}C_{POC} &= \delta^{13}C_{POCallocht} \times \text{Terrestrial fraction} + \delta^{13}C_{POCautocht} \times \\ &\quad \times \text{Phytoplankton fraction.} \qquad (1)\end{aligned}$$

If we assume that $\delta^{13}C_{POCallocht} = -27‰$ and $\delta^{13}C_{POCautocht} = \delta^{13}C_{phyto}$

$$\begin{aligned}\delta^{13}C_{POC} &= -27‰ \times (1 - \text{Phytoplankton fraction}) + \delta^{13}C_{phyto} \times \\ &\quad \times \text{Phytoplankton fraction.} \qquad (2)\end{aligned}$$

We calculate phytoplankton (Phytoplankton fraction 1; Table 3) to contribute from 17 to 65% to the total POC pool.

In order to verify whether the assumption of a constant fractionation is realistic we also calculated the fraction of total POC pool carried by phytoplankton in a different way (Phytoplankton fraction 2; Table 3) assuming that a healthy phytoplankton community is characterised by C/Chl a weight ratio of 50 (e.g. Geider 1987). We then applied the two end member mixing model (Equation 3) to estimate the $\delta^{13}C$ values of phytoplankton ($\delta^{13}C_{phyto2}$;

Table 3. Estimated phytoplankton fraction in total suspended particulate matter (May 1996) using two approaches.

km	$\delta^{13}C_{DIC}$ ‰	$\delta^{13}C_{POC}$ ‰	POC_{total} μM	Chla $\mu g l^{-1}$	$\delta^{13}C_{phyto1}$ ‰(1)	Phytoplankton fraction 1(2)	Phyto C μM(3)	Phytoplankton fraction 2(4)	$\delta^{13}C_{phyto2}$ ‰(5)	Fractionation ‰(6)
85.0	−12.6	−29.0	404.3	15.99	−34.9	0.25	66.6	0.16	−39.1	26.5
88.0	−12.6	−28.4	582.2	9.20	−34.9	0.17	38.3	0.07	−47.5	34.9
94.0	−12.7	−28.7	771.2	13.95	−34.0	0.22	58.1	0.08	−49.9	37.2
97.5	−12.2	−29.1	752.4	10.45	−34.5	0.28	43.5	0.06	−63.6	51.4
118.0	−12.1	−30.9	169.8	39.92	−34.4	0.52	166.3	0.98	−30.9	18.9
121.5	−12.2	−30.2	272.3	22.44	−34.5	0.42	93.5	0.34	−36.2	24.0
127.0	−12.2	−30.3	208.4	13.78	−34.5	0.45	57.4	0.28	−39.1	26.9
133.0	−12.2	−31.9	148.4	12.53	−34.5	0.65	52.2	0.35	−41.0	28.8
140.0	−12.1	−31.5	207.0	41.59	−34.4	0.62	173.3	0.84	−32.4	20.3
147.0	−12.2	−30.2	295.3	13.89	−34.5	0.42	57.9	0.20	−43.1	30.8
155.0	−12.1	−31.0	194.9	40.15	−34.4	0.54	167.3	0.86	−31.7	19.6

(1) $\delta^{13}C_{DIC}$ - constant fractionation of 22.3‰

(2) Calculated from Equation 3

(3) (50/12) * Chla

(4) Phyto C/POC_{total}

(5) Calculated from Equation 3

(6) $\delta^{13}C_{DIC} - \delta^{13}C_{phyto2}$

Table 3). The calculated $\delta^{13}C_{phyto2}$ now range between: −31.7 to −63.6‰ (mean −41.3‰). The very negative values are not realistic. However, when considering only the section upstream of the Rupel (from km 118 to km 155) we notice that phytoplankton $\delta^{13}C$ values ($\delta^{13}C_{phyto}$) as well as phytoplankton fractions compare well with the values obtained using the constant fractionation approach. Indeed, for the constant fractionation approach we obtain an average $\delta^{13}C_{phyto1}$ of −34.4‰ and an average phytoplankton fraction of 0.52, while for the fixed C/Chl a ratio approach we obtain an average $\delta^{13}C_{phyto2}$ of −34.5‰, and an average phytoplankton fraction of 0.51. It ensues that for the fixed C/Chl a ratio approach the average fractionation between DIC and the calculated $\delta^{13}C_{phyto2}$ was 22.4‰, similar to the one reported by Tan and Strain (1983). Since for the section upstream of the Rupel, both approaches converge, we can conclude that a $\delta^{13}C$ value for phytoplankton of −34.4 ‰ and a fractionation of 22.3‰ seem realistic for spring in the Zeeschelde (km 118 to km 155). However, the deduced phytoplankton biomass representing about half of the total POC pool is higher than reported phytoplankton biomass values obtained for the Zeeschelde from cell counting and sizing (Muylaert K. et al. 1997; Billiones R. 1998). To understand this discrepancy further investigation is needed.

For the section between km 85 and km 97.5 calculated $\delta^{13}C$ values and phytoplankton fractions are different for both approaches. In this section the stations were characterised by high total POC and low Chl a concentrations. Using a C/Chl a ratio of 50, we calculate low phytoplankton fractions. These result in phytoplankton $\delta^{13}C$ ($\delta^{13}C_{phyto2}$) which are very negative (unrealistic) and in too high fractionations. Larger values for phytoplankton fractions would require larger C/Chl a ratios. It is unlikely that the chosen C/Chl a value of 50 is too low since the area between km 85 and km 97.5 was characterised by a high turbidity and thus limited light penetration, a situation which would favor low C/Chl a ratios (Geider 1987). However, this section is strongly influenced by the Rupel, a tributary that carries the untreated sewage load from the city of Brussels. Therefore, it is likely that the high POC pool in the section downstream of the Rupel was significantly affected by a third POC source with a different $\delta^{13}C$ value. In this case the two-source mixing model no longer applies.

Summary and conclusions

A seasonal and geographical variation was observed in the stable carbon isotope ratios of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) and suspended particulate matter ($\delta^{13}C_{POC}$) in the Zeeschelde. During fall (November) and winter (December) significant CO_2-production during decomposition of terrestrial organic matter resulted in DIC with low $\delta^{13}C$ values. Furthermore, the very narrow range of $\delta^{13}C_{POC}$ (mean −27.2‰) was associated with relatively high C/N ratios (C/N > 9) and relatively low Chl a concentrations. It is therefore concluded that in winter almost all riverine POC is derived from allochthonous terrestrial matter either of anthropogenic or natural origin. In spring and summer the reduced input of CO_2 from decomposition of ^{13}C-depleted terrestrial detritus and the discrimination against ^{13}C during biological carbon fixation induced less negative $\delta^{13}C_{DIC}$ values. During the summer period, on the contrary for suspended POC some of the most negative isotopic ratios were recorded. These very negative $\delta^{13}C_{POC}$ values were accompanied by high Chl a concentrations and low C/N ratios, suggesting phytoplankton accounted for a significant fraction of POM. Indeed, we observed for the river section upstream of the Rupel (km 118 to km 155) in spring (May) that phytoplankton contributes on average about 50% to the total POC pool. This phytoplankton has an average $\delta^{13}C$ value of −34.4‰, reflecting an average fractionation between total dissolved inorganic carbon and phytoplankton of 22.3‰.

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