Biogeochemistry **51:** 141–160, 2000.

Origin and fate of dissolved inorganic carbon in interstitial waters of two freshwater intertidal areas: A case study of the Scheldt Estuary, Belgium

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Received 24 December 1999; accepted 26 January 2000

Key words: Belgium, DIC, intertidal sediments, methanogenesis, Scheldt Estuary, stable, carbon isotopes

Abstract. Processes affecting the concentration and isotopic composition of dissolved inorganic carbon (DIC) were investigated in pore waters of two freshwater intertidal areas of the Scheldt Estuary, Belgium. Pore water $\delta^{13}C_{DIC}$ values from marshes and mudflats varied from −27 to +13.4‰, these very large variations reflect the contribution of different carbon sources to the DIC pool.

In pore waters of the upper mudflat, river water DIC and dissolution of calcite contribute to a lesser extent (10% and 16% respectively) to the total DIC pool. Results indicate that inorganic carbon added to the pore water of the mudflats has a $\delta^{13}C$ value of +20.3‰ in May 1998. These strongly enriched $\delta^{13}C_{DIC}$ values suggest that the major contribution (up to three-quarters) to total DIC is CO_2 derived from methanogenesis.

In pore waters of the marshes, CO_2 derived from organic matter degradation (−27.5‰) and river DIC (−11.5 to −16.1‰) are the major sources of inorganic carbon contribution to the total DIC pool. In pore waters from a marsh site colonised by willow trees, the contribution from CO_2 derived from organic matter degradation is larger than in pore waters from an area with only reed vegetation. In the latter case river water DIC is the major source of pore water DIC.

Introduction

Diagenetic reactions in sediments can be at the origin of a significant exchange between sediments and the water column with a dominant impact on the biogeochemical cycle of carbon in riverine and estuarine environments (e.g. Ogrinc et al. 1997). The carbon cycle in aquatic systems is extremely dynamic because of the presence of carbon in chemical components having different reactivities: particulate organic and inorganic carbon (POC and

PIC), dissolved inorganic carbon (DIC = $[CO_{2aq}] + [HCO_3^-] + [CO_3^{2-}]$) and dissolved organic carbon (DOC). Carbon present as CO_2 in pore water can be derived from respiration on sedimented organic matter, dissolution of $CaCO_3$, and infiltration of river water into the sediments. $\delta^{13}C$ signatures present an efficient tracer to assess contribution of carbon from various sources, particularly that derived from organic matter. Since the isotopic composition of organic matter is very different (more depleted in ^{13}C) from other carbon sources, the $\delta^{13}C$ of pore water CO_2 is very sensitive to the fraction of CO_2 derived from organic matter.

Two general relationships between the concentration of total dissolved inorganic carbon (DIC) and its isotopic composition ($\delta^{13}C_{DIC}$) have been reported in literature (LaZerte 1981). In more oxidising sediments, the stable carbon isotope ratio of dissolved inorganic carbon declines with increasing DIC concentrations (Presley et al. 1968). Increasing DIC concentrations are derived from the respiration of organic material, which has a lighter stable carbon isotope ratio than the original DIC. The opposite relationship was observed in reducing sediments, with $\delta^{13}C_{DIC}$ increasing with increasing DIC concentrations. This $^{13}C_{DIC}$ enrichment has been related to the production of highly ^{13}C-depleted methane in these reducing sediments (e.g. Nissenbaum et al. 1972; Quay et al. 1988).

In the present study we coupled an investigation of the $\delta^{13}C$ of dissolved inorganic carbon in pore water with a study of pore water chemistry and sediment environment. The objective was to define processes affecting the production of dissolved inorganic carbon, and to understand the observed variations in $\delta^{13}C$ of the pore waters in two different freshwater intertidal areas of the Zeeschelde. This study was performed as part of a more general investigation on carbon fluxes in a tidally influenced riverine system under significant anthropogenic stress (e.g. Hellings et al. 1999; Hellings 2000).

Study area

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. The Dutch part of the Scheldt Estuary is called the Westerschelde, the Belgian part (from the Dutch-Belgian border to Gent) the Zeeschelde (Figure 1). The tidal amplitude varies between 4 m near Vlissingen, 6 m near the Durme, and to 2 m near Gent. From Gent to Rupelmonde the water is fresh (<0.7 ppt), between Rupelmonde and Hansweert brackish (0.7–10 ppt) and between Hansweert and Vlissingen salt (>10 ppt) (Meire et al. 1995; Baeyens et al. 1998).

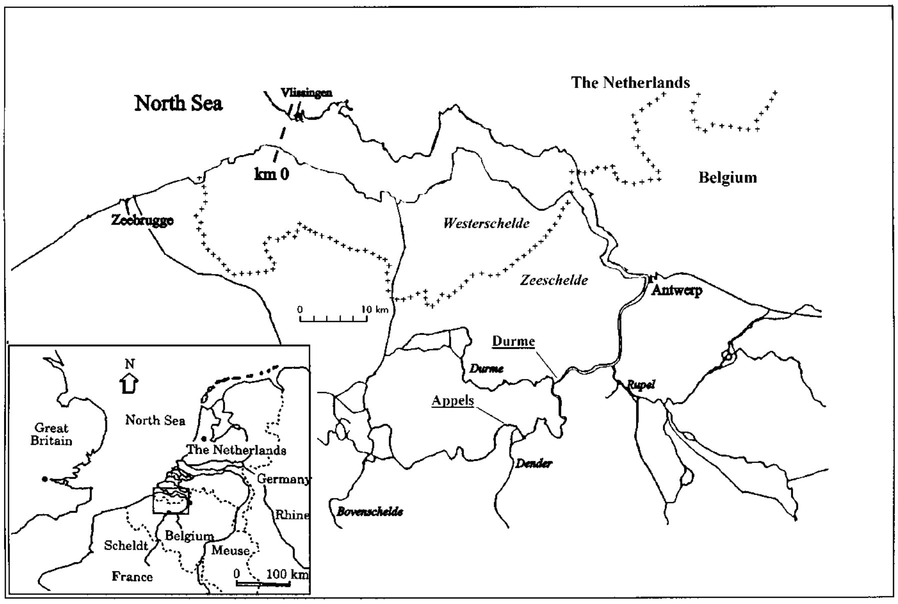

Figure 1. Map of the Zeeschelde, with the two investigated freshwater intertidal areas: Durme and Appels sites (underlined).

The Scheldt Estuary is subject to intense anthropogenic disturbance, reflected in elevated loadings of detrital organic matter which induce high respiration rates and the production of large quantities of CO_2 (Frankignoulle et al. 1998). The Scheldt Estuary shows a clear increase of pCO_2 within the upper estuary (low salinity), which is associated with a decrease in oxygen (Frankignoulle et al. 1998). pCO_2 values as high as 5700 μatm have recently been reported at the turbidity maximum in the Scheldt Estuary, which is about 16 times the pCO_2 of the present atmospheric equilibrium (360 μatm) (Frankignoulle et al. 1996).

The Zeeschelde is characterised by a single channel, bordered with relatively small mudflats and marshes (28% of the total surface). We selected two completely different freshwater intertidal sites: Durme and Appels (Figure 1). The Durme site, located at 101 km from Vlissingen (at the mouth of the estuary), was created by the destruction of the Scheldt dike. The old dike was opened at at least three sites, so that part of the nearby polder has become an intertidal area again. The Appels intertidal site, at 127 km from Vlissingen, is located in the outside bend of a river meander. It was created by the dumping of dredging sludge in the seventies.

According to flooding frequency and vegetation these two intertidal areas were divided in 4 subgroups (Table 1): lower (flooding frequency = 100%, no

Table 1. Characteristics of the wells and cores at the Appels and Durme sites.

Well core	Subgroup	Depth (cm)		Vegetation	Flooding frequency (%)	Infiltration capacity
		Range	Mean			
Appels						
A6	Upper marsh	50–150	100	Willow	39	1–8 mm/min
A11	Lower mudflat	30–130	80	No	100	nd
A13	Lower mudflat	20–120	70	No	100	nd
A8	Upper mudflat	170–200	185	Rush/reed	75	Almost 0
A9	Upper mudflat	130–160	145	Rush/reed	75	Almost 0
A10	Upper mudflat	80–110	95	Rush/reed	75	Almost 0
A15	Upper mudflat	20–120	70	Rush/reed	70	Almost 0
C1	Lower mudflat	0–75	–	No	100	nd
C2	Upper mudflat	0–55	–	Rush/reed	75	Almost 0
C3	Upper mudflat	0–35	–	Rush/reed	70	Almost 0
C4	Upper marsh	0–24	–	Willow	45	1–8 mm/min
Durme						
D1	Lower marsh	60–160	110	Reed	51	Almost 0
D2	Upper marsh	110–210	160	Reed	21	0–50 mm/min
D3	Upper marsh	59–159	109	Reed	35	5–50 mm/min
D4	Upper marsh	75–175	125	Willow; reed	28	Almost 0
D5	Upper marsh	85–185	135	Willow	34	2–10 mm/min

A = wells in Appels; D = wells in the Durme; C = cores in Appels; nd = not determined

vegetation) and upper mudflat (flooding frequency = 70–75%, rush/reed) and lower (flooding frequency = 50%, mainly reed) and upper marsh (flooding frequency = 20–40%, mainly reed and willow).

Materials and methods

Sampling. In Appels, 7 wells (Figure 2) were installed along an elevation gradient going from the river over a mudflat to the highest part of the marsh covered with mainly willow trees. Two wells were located close to the river in the lower mudflat (A11 and A13), 4 wells in the upper mudflat (A8, A9, A10 and A15) extending at different depths in the sediments and 1 well in the upper marsh between the willow trees (A6) (Figure 2; Table 1). At the Durme marsh (Figure 3; Table 1), all 5 wells were situated in a vegetation covered marsh. Four of the wells (D2, D3, D4 and D5) were located in the upper marsh and 1 well in the lower marsh (D1). In November 1997 and May 1998 pore water samples were taken from these wells with a handpump and a silicone hose. During every sampling the wells were completely emptied. The

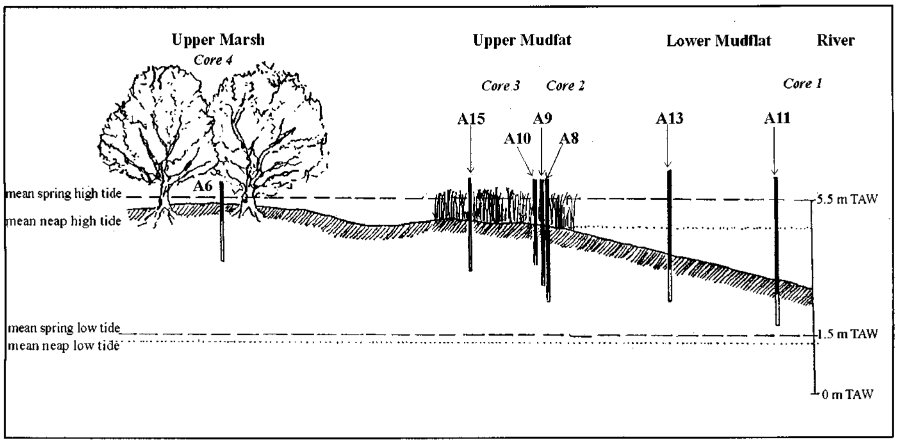

Figure 2. Vertical position of the wells (A6, A8, A9, A10, A15, A11 and A13) and the cores (core 1, 2, 3 and 4) in the Appels intertidal area. TAW (Tweede Algemene Waterpassing) is a reference level for water heights in Belgium.

high-density polyethylene wells have a diameter of 5 cm. Each well is made up of a perforated lower part, that is completely stuck in the sediment and an upper part, closed with a cap to prevent rain from seeping into the well. A bentonite collar prevents infiltration from river water during flooding. The perforated lower part was covered with a mesh to prevent seepage of sediment into the well. The length of the perforated section is 100 cm for all wells except wells A8, A9 and A10, for which it is only 30 cm. The water sampled is representative for the depth region corresponding with the perforated part of the well.

Samples for $\delta^{13}C_{DIC}$ analysis were collected by gently overfilling a glass 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 were collected in 50 ml PE bottles, poisoned with $HgCl_2$, stored in the refrigerator and analysed within 24 hours. Water samples for Ca^{2+} were filtered and acidified with 0.1% distilled concentrated HNO_3 prior to analysis.

Additionally, undisturbed sediment cores of different depths (varying from 24 to 75 cm) were collected in June 1998 at 4 different locations of the Appels intertidal area. Core 1 was situated in the lower mudflat close to the river, core 2 and 3 in the upper mudflat and core 4 in the upper marsh underneath the willow trees (Table 1, Figure 2). Sediment cores were transported within 2 hours from sampling to the laboratory and sectioned into 4 to 15 cm intervals in an N_2-filled glove box. Interstitial waters were extracted from the sediments using a modified Reeburgh squeezer (Reeburgh 1967) under nitrogen pressure, dental gum for homogenous

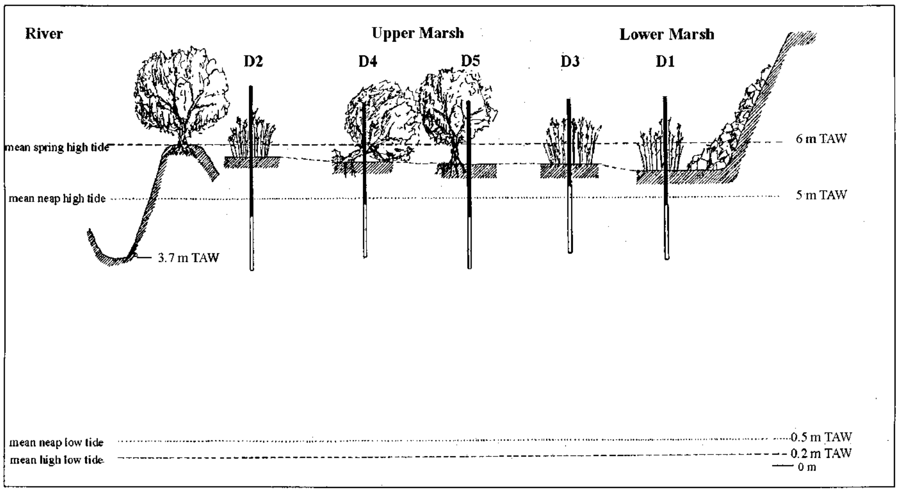

Figure 3. Vertical position of the wells (D1, D2, D3, D4 and D5) in the intertidal area of Durme. TAW (Tweede Algemene Waterpassing) is a reference level for heights in Belgium.

pressure repartition and a 0.45 μm pore size membrane filter for particle retention.

Chemical analysis. Total alkalinity was determined by end-point titration of 25 ml of the water samples with 0.01 M HCl (Merck) using an automatic titrator (Mettler-Toledo). pH was measured with a portable field pH-meter (Hanna instruments). DIC concentrations were calculated from total alkalinity and pH using dissociation constants of Mehrbach et al. (1973) refitted by Dickson and Millero (1987) (Program CO2SYS version 01.05 by Ernie Lewis). Ca^{2+} was determined using a flame atomic absorption spectroscopy in an air-acetylene flame with a Varian SpectrAA-10/20.

Isotopic analysis. The sediment was dried at 60 °C and homogenised using mortar and pestle. Sediment aliquots of approximately 4 mg were acidified with 1 mM HCl to remove the carbonates. The redried organic material was then combusted in an Elemental Analyser (Carlo Erba NA1500). 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 mass spectrometer (Hellings et al. 1999). A graphite reference material (USGS-24) was used as a reference for organic carbon isotopic ratio measurements.

The method for $\delta^{13}C$ determination of DIC has been described elsewhere (Hellings et al. 1999). Briefly, a flask with a septum, containing 3 ml pure *ortho*-phosphoric acid (99% crystal) and a magnetic stir bar was degassed and heated in a water bath at approximately 50 °C. Then 15 ml of sample was injected. 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 to remove water vapour.

For the $\delta^{13}C$ and $\delta^{18}O$ measurements of carbonate from the sediments a procedure modified from Craig (1957) was used. The carbonate was transformed into CO_2 by the reaction with anhydrous phosphoric acid at 25 °C under vacuum. CO_2 was then extracted from the reaction mixture and trapped into a glass tube cooled with liquid nitrogen after passing successively through liquid nitrogen and cooled iso-propanol traps. 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. Mass spectrometric measurements were performed using a Delta E, Finnigan Mat isotope ratio mass spectrometer. The normal working standard for carbon was CO_2 produced from Carrara marble. Values are expressed relative to the VPDB (Vienna Peedee Belimnite) standard (Coplen 1996). Stable isotopic ratios are expressed as δ-values:

$$\delta(‰) = [(X_{\text{sample}} - X_{\text{standard}})/X_{\text{standard}}] \times 10^3,$$

where

$$X = {}^{13}C/{}^{12}C \text{ or } {}^{18}O/{}^{16}O.$$

Reproducibility for analyses of different aliquots of the same sample was generally better than 0.1‰ for $\delta^{13}C_{\text{POC}}$, 0.04‰ for $\delta^{13}C_{\text{DIC}}$, 0.05‰ for $\delta^{13}C_{\text{CaCO}_3}$ and $\delta^{18}O_{\text{CaCO}_3}$.

The carbonate content was assessed from the collector signal (V) for a known quantity of sediment via an external calibration established using pure $CaCO_3$ standards, keeping the same instrumental conditions.

Results

Appels

We investigated pore waters from 7 wells, 2 in the lower mudflat (A11 and A13), 4 in the upper mudflat (A8, A9, A10 and A15) and 1 in the upper marsh (A6) (Figure 2). At each sampling exercise, river water was also sampled (Table 2).

$\delta^{13}C$ of dissolved inorganic carbon ($\delta^{13}C_{\text{DIC}}$)

River. In November 1997, early December the $\delta^{13}C_{\text{DIC}}$ of the river ranged from −12.9 to −15.8‰, with a mean value of −13.8‰ (Table 2). In May

Table 2. Appels intertidal site. Total alkalinity (TA) (mM), total dissolved inorganic carbon (DIC) (mM), $\delta^{13}C_{DIC}$ (‰) and Ca^{2+} (mM) of pore waters.

					Upper marsh				Lower mudflat							
	River water				A6 (100 cm)				A11 (80 cm)				A13 (70 cm)			
Date	TA	DIC	$\delta^{13}C$	Ca^{2+}	TA	DIC	$\delta^{13}C$	Ca^{2+}	TA	DIC	$\delta^{13}C$	Ca^{2+}	TA	DIC	$\delta^{13}C$	Ca^{2+}
29-10-97	4.77	5.50	−13.2	–	13.59	16.53	−17.5	–	–	–	−7.6	–	10.28	11.75	−8.3	–
04-11-97	5.32	5.70	−12.9	–	12.09	15.68	−16.5	–	–	–	−17.8	–	9.66	11.12	−9.2	–
13-11-97	6.29	6.79	−13.4	–	13.63	17.02	−17.5	–	6.15	6.53	−13.6	–	8.82	10.25	−10.2	–
17-11-97	5.82	6.13	−13.8	–	11.70	13.94	−23.0	–	7.98	9.02	−12.4	–	9.14	10.64	−9.8	–
25-11-97	5.74	6.19	−13.9	–	13.59	14.95	−21.2	–	7.65	8.32	−13.2	–	8.37	9.33	−12.5	–
07-12-97	4.38	4.75	−15.8	–	12.01	13.48	−21.9	–	7.69	8.87	−18.7	–	8.75	10.76	−10.5	–
11-05-98	5.22	5.66	−13.2	3.51	9.78	11.88	−19.4	4.51	12.98	13.98	−11.4	7.05	10.71	11.01	–	4.60
18-05-98	5.27	6.01	−12.7	3.45	10.69	12.66	−23.7	4.93	13.20	14.54	−12.2	4.89	10.97	12.46	−13.0	4.10
25-05-98	6.33	6.72	−12.2	3.42	6.07	7.88	−27.0	5.04	–	–	−12.5	3.45	11.70	13.24	−11.4	4.39
02-06-98	5.73	6.62	−11.5	3.71	9.25	11.95	−26.4	5.42	12.57	15.86	−11.6	5.89	12.17	15.13	−10.2	4.96

	Upper mudflat															
	A8 (185 cm)				A9 (145 cm)				A10 (95 cm)				A15 (70 cm)			
Date	TA	DIC	$\delta^{13}C$	Ca^{2+}	TA	DIC	$\delta^{13}C$	Ca^{2+}	TA	DIC	$\delta^{13}C$	Ca^{2+}	TA	DIC	$\delta^{13}C$	Ca^{2+}
29-10-97	30.65	31.33	+13.4	–	–	–	–	–	–	–	+6.4	–	15.38	17.19	–	–
04-11-97	31.62	34.94	+13.3	–	21.39	24.27	+11.0	–	–	–	+6.2	–	15.14	17.18	−0.7	–
13-11-97	30.25	33.69	+13.6	–	21.00	23.86	–	–	22.37	24.08	+6.2	–	15.73	16.33	−0.4	–
17-11-97	5.62	5.85	−13.0	–	10.13	10.96	−0.1	–	22.23	27.13	+5.6	–	17.96	21.03	+1.0	–
25-11-97	10.07	11.46	−1.4	–	28.83	34.72	+8.6	–	22.53	28.26	+5.3	–	19.37	22.85	+1.6	–
07-12-97	39.31	44.61	+9.8	–	36.67	40.68	+10.0	–	22.83	25.45	+5.8	–	14.35	14.78	−1.1	–
11-05-98	52.40	56.31	+12.3	12.65	28.03	30.27	+7.8	7.25	19.24	22.54	+3.7	6.20	24.26	26.51	+5.0	7.81
18-05-98	58.63	64.37	+12.3	13.60	34.60	39.97	+8.6	7.79	20.00	23.40	+3.9	5.37	25.81	29.10	+6.1	7.02
25-05-98	61.38	67.24	+12.7	13.13	34.26	38.29	+9.2	8.09	20.86	23.80	+4.9	5.80	19.94	23.02	+3.0	5.95
02-06-98	62.19	73.80	+12.8	16.54	33.64	42.70	+8.8	9.43	21.42	31.25	+7.2	6.25	17.39	22.23	+1.3	5.29

– = not determined

1998, early June the ^{13}C was slightly more enriched and $\delta^{13}C_{DIC}$ values ranged from −11.5 to −13.2‰, with a mean value of −12.4‰.

Wells. In November 1997, $\delta^{13}C_{DIC}$ from pore waters of the lower mudflat ranged from −7.6 to −18.7‰ (mean value −12‰) (Table 2). In May 1998, $\delta^{13}C_{DIC}$ values of the lower mudflat showed less spatial variability ranging from −10.2 to −13‰, with a mean value of −11.7‰. Pore waters from the upper mudflat were significantly enriched in ^{13}C (up to 27‰) relative to the $\delta^{13}C_{DIC}$ of the river. Furthermore, pore water DIC became more enriched with depth. The average $\delta^{13}C_{DIC}$ value of pore waters in the upper mudflat were +12.9‰ at A8 (185±15 cm), +9.1‰ at A9 (145±15 cm), +5.5‰ at A10 (95±15 cm) and +2.4‰ at A15 (70±50 cm). River water was able to seep into wells A8 and A9 due to a technical problem on November 17th 1997. At that time $\delta^{13}C_{DIC}$ (−13‰) of the pore water was similar to the $\delta^{13}C_{DIC}$ of the river (−13.8‰). However, within two weeks the pore water $\delta^{13}C_{DIC}$ increased again and reached the values initially observed in these wells (Table 2). Excluding the samples of November 17th and 25th for wells A8 and A9, we observed that average $\delta^{13}C_{DIC}$ values decreased with decreasing depth in the sediments.

Pore waters from the upper marsh (A6) had DIC that was more depleted in ^{13}C relative to the river. In May 1998 the $\delta^{13}C_{DIC}$ value of this pore water was even more negative (mean −24.1‰) than in November 1997 (mean −19.6‰).

Cores. In general, interstitial water DIC for cores from the lower and upper mudflat became isotopically heavier with depth (cores 1, 2 and 3; Figure 4A). For cores 1 and 2 respectively from lower and upper mudflat, $\delta^{13}C_{DIC}$ values in the upper 10 cm were similar to the value for river water. Below 10 cm $\delta^{13}C_{DIC}$ increased with depth (Figure 4A). In the upper mudflat (core 2 and 3), $\delta^{13}C_{DIC}$ values increased more strongly with depth (Figure 4A). $\delta^{13}C_{DIC}$ values for the upper marsh (core 4) first decreased (0–15 cm) from −13 to −16‰ then increased (15–25 cm) from −16 to −10.5‰, but overall values remained more negative than for the other sites.

Total dissolved inorganic carbon (DIC) in the wells

Average DIC concentration of the lower mudflat (mean 11.1 mM) was higher than the DIC concentration of the river (mean 6 mM; Table 2). We observed, furthermore, a seasonal variation of average DIC content for the lower mudflat. In May 1998 DIC concentration was higher (mean value 13.7 mM) than in November 1997 (mean value 9.7 mM). DIC contents in pore water from the upper mudflat were significantly higher than for river (Table 2), excepted for A8 and A9 on November 17th and 25th (see above).

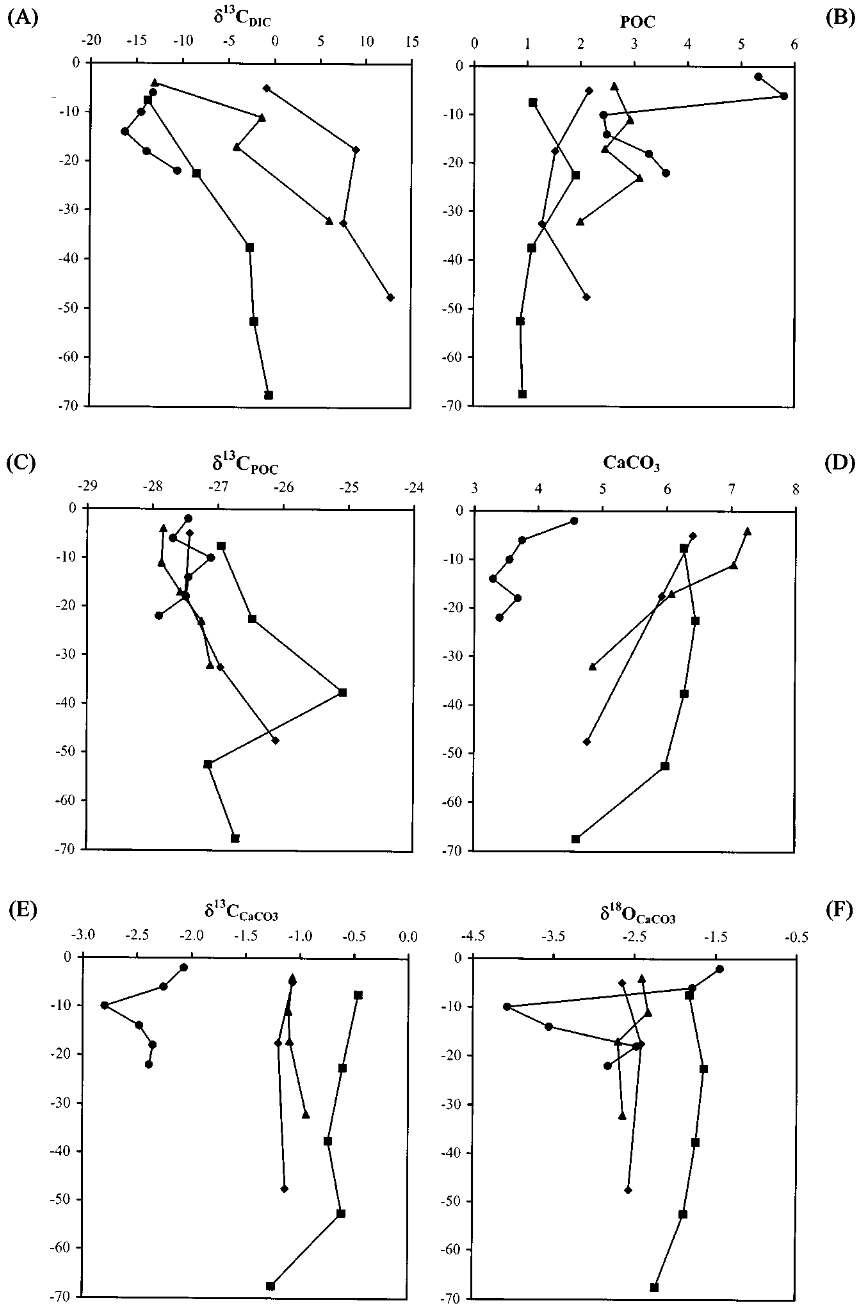

Figure 4. Profiles for sediment cores at Appels (June 1998) showing change with depth of (A) carbon isotopic composition of DIC ($\delta^{13}C_{DIC}$ (‰)), (B) POC concentration (%), (C) carbon isotopic composition of POC ($\delta^{13}C_{POC}$(‰)), (D) $CaCO_3$ concentration (%), (E) carbon isotopic composition of $CaCO_3$ ($\delta^{13}C_{CaCO_3}$(‰)) and (F) oxygen isotopic composition of $CaCO_3$ ($\delta^{18}O_{CaCO_3}$(‰)). Squares: core 1 in lower mudflat; triangles: core 2 in upper mudflat; diamonds: core 3 in upper mudflat and circles: core 4 in upper marsh.

Excluding these November 17th and 25th cases from the A8 and A9 series, it appears that DIC content also increased with depth as observed for $\delta^{13}C_{DIC}$ (mean values: A8(185±15 cm): 42.4 mM $>$ A9(145±15 cm): 31.8 mM $>$ A10(95±15 cm): 25.7 mM $>$ A15(70±50 cm): 21 mM). In May 1998, pore water DIC in well A8 (mean 65.4 mM) was almost twice as high as in November 1997 (mean: 36.1 mM, without the samples of November 17th and 25th).

Seasonal variability was also observed in the upper marsh, but here the situation was inverse: the pore waters had a higher DIC in November 1997 (mean value 15.3 mM) than in May 1998 (mean value 11.1 mM).

Carbon content and $\delta^{13}C$ of particulate organic carbon ($\delta^{13}C_{POC}$) from the cores

To provide a basis for estimating the contribution of dissolved inorganic carbon from organic carbon oxidation, the isotopic composition of the bulk organic carbon was determined (Figure 4(C)). The carbon content of core 1 from the lower mudflat stayed almost constant with depth (mean value 1.2%; Figure 4(B)). $\delta^{13}C_{POC}$ ranged from −25.1 to −27.1‰, with a mean value of −26.5‰ (Figure 4(C)). Sediments from the upper mudflat (core 2 and 3) were characterised by a higher organic carbon content, ranging from 1.3 to 3.1% (mean value 2.2%). The carbon content was slightly higher in core 2 than in core 3. $\delta^{13}C_{POC}$ values of these sediments (mean value −27.6‰) increased by approximately 1‰ over 50 cm. Surficial sediments of the upper marsh (core 4) were characterised by the highest carbon content (5.6%) and an average $\delta^{13}C_{POC}$ of −27.5‰. The C/N ratio of the sediments ranged from 11.1 to 16.3, with an average value of 14.2.

$CaCO_3$ and stable isotopes of $CaCO_3$ in the cores

Sediments of the lower mudflat (core 1) had an average $CaCO_3$ content of 5.9% (Figure 4(D)) and an average $\delta^{13}C_{CaCO_3}$ of −0.7‰ (Figure 4(E)). In the upper mudflat, the $CaCO_3$ content decreased with depth from 7.3% to 4.8% in core 2 and from 6.4% to 4.8% in core 3 (Figure 4(D)). In both cores, $\delta^{13}C_{CaCO_3}$ stayed almost constant with depth (mean value −1.1‰; Figure 4(E)). The sediment of the upper marsh (core 4) had the lowest $CaCO_3$ content (mean value 3.7%; Figure 4D) and the most depleted $\delta^{13}C_{CaCO_3}$ (mean value −2.4‰; Figure 4(E)). In cores 1, 2 and 3, $\delta^{18}O_{CaCO_3}$ ranged between −2.5 and −1.5‰, and was constant with depth. In the upper marsh (core 4) at 10 cm depth we observed a decrease of $\delta^{18}O_{CaCO_3}$ to −4‰.

Table 3. Durme intertidal site. Total alkalinity (TA) (mM), total dissolved inorganic carbon (DIC) (mM), δ^{13}C of dissolved inorganic carbon (‰) and Ca^{2+} (mM) of pore waters.

					Lower marsh				Upper march			
	River water				D1				D2			
Date	TA	DIC	δ^{13}C	Ca^{2+}	TA	DIC	δ^{13}C	Ca^{2+}	TA	DIC	δ^{13}C	Ca^{2+}
29-10-97	4.56	5.01	−12.9	–	–	–	−9.8	–	5.76	6.61	−16.3	–
13-11-97	5.07	5.43	−12.8	–	17.23	18.54	−9.1	–	5.84	6.73	−16.2	–
17-11-97	5.79	6.20	−13.9	–	17.73	22.26	−10.0	–	5.02	5.67	−15.1	–
25-11-97	5.76	6.08	−13.5	–	18.73	24.04	−9.1	–	5.27	5.97	−16.9	–
05-12-97	5.76	6.07	−14.9	–	17.22	21.69	−9.4	–	6.28	7.03	−15.8	–
11-05-98	5.51	5.70	−13.1	3.51	12.40	14.86	−10.8	5.78	5.70	6.43	−17.0	3.44
18-05-98	4.66	5.44	−16.1	3.33	17.13	22.21	−8.8	7.58	5.92	7.28	−16.6	3.39
25-05-98	5.30	5.65	−11.3	3.28	15.78	20.46	−9.6	7.24	5.36	6.23	−16.0	3.37
02-06-98	5.25	5.83	−11.9	3.94	16.18	22.97	−9.6	7.44	5.15	6.43	−15.4	3.95

	Upper march											
	D3				D4				D5			
Date	TA	DIC	δ^{13}C	Ca^{2+}	TA	DIC	δ^{13}C	Ca^{2+}	TA	DIC	δ^{13}C	Ca^{2+}
29-10-97	6.45	8.19	−17.2	–	5.07	6.01	−16.0	–	8.14	10.23	−14.7	–
13-11-97	4.79	5.96	−15.4	–	4.84	5.67	−15.3	–	5.73	7.24	−16.4	–
17-11-97	4.81	5.87	−15.1	–	4.69	5.65	−15.2	–	7.27	9.15	−15.5	–
25-11-97	5.69	7.02	−16.4	–	5.27	5.91	−15.9	–	8.22	10.03	−16.2	–
05-12-97	5.72	7.01	−16.3	–	5.35	6.32	−16.2	–	8.39	10.39	−14.5	–
11-05-98	6.92	8.33	−17.2	3.83	6.53	7.57	−17.2	3.63	6.06	7.07	−18.9	3.71
18-05-98	7.00	8.70	−17.4	3.59	6.34	8.44	−17.1	3.19	6.39	8.55	−18.8	3.47
25-05-98	4.93	5.83	−15.4	3.48	4.86	6.62	−15.5	3.45	5.77	7.45	−20.1	3.81
02-06-98	5.25	7.23	−16.2	4.20	5.10	7.03	−15.9	4.02	5.39	8.86	−18.4	4.19

– = not determined

Durme

We investigated pore water from 1 well in the lower marsh (D1) and 4 wells in the upper marsh (D2, D3, D4 and D5) (Table 3).

δ^{13}C of dissolved inorganic carbon ($\delta^{13}C_{DIC}$)

Pore waters from the lower marsh were more enriched in ^{13}C than river water (average −13.4‰) with $\delta^{13}C_{DIC}$ values ranging from −8.8 to −10.8‰ (mean value −9.6‰; Table 3).

On the contrary, pore waters from the upper marsh were more depleted in ^{13}C than river water. In November 1997, $\delta^{13}C_{DIC}$ values for the upper marsh ranged from −14.5‰ (D5; 05-12-1997) to −17.2‰ (D3; 29-10-1997) (mean value: −15.8‰). In May 1998, $\delta^{13}C_{DIC}$ values of the pore waters became even more depleted in ^{13}C, with the overall mean value decreasing to −17.1‰.

Total dissolved inorganic carbon (DIC)

The average DIC of the river at the Durme site was 5.7 mM. Pore water DIC contents for the lower marsh were higher by about 15 mM than river DIC content (Table 3).

Pore water DIC of the upper marsh ranged from 5.7 (D4; 17-11-1997) to 10.4 mM (D5; 05/12/1997). In November 1997, DIC from well D5 was slightly higher (mean 9.4 mM) than pore water DIC of the other wells (D2, D3 and D4: mean 6.4 mM).

Discussion

The marsh and the mudflats have completely different soil structures. The marsh is less frequently flooded (only at spring tide) and dry cracks occur in the top layer of the exposed sediments. Here soil-maturing processes create an internal soil structure and a moderate infiltration capacity (1–10 mm/min). To a depth of about 25 to 50 cm oxidising conditions prevail. The mudflats, on the other hand, are flooded twice a day. The top layer of these sediments is saturated with water, creating an impermeable top layer. The top 5 mm of these sediments has a brown colour, below 5 mm the sediments consist of black mud, indicative of anaerobic and strong reducing environments. We observed that in the strong reducing environments of the upper mudflat pore water DIC increased and became isotopically heavier with depth (Figure 5). In May, total DIC in well A8 (average 65.4 mM) was almost twice as high as in November (average 36.1 mM), while the $\delta^{13}C_{DIC}$ values of the interstitial dissolved inorganic carbon were similar (average +12.5‰ and +13.4‰ respectively) (Figure 5). High $\delta^{13}C_{DIC}$ values and high DIC concentrations are indicative of a supply of ^{13}C enriched CO_2. Grossman et al. (1989) have shown that the DIC reservoir and its isotopic composition can be closely linked to ground-water methane and methanogenesis in strong reducing environments. Methanogenesis produces isotopically lighter methane and a residual fraction of DIC significantly enriched in ^{13}C. For methanogenesis to be pervasive, sulphate concentrations must be low (e.g. Claypool & Kaplan 1974). Sulphate concentrations of the pore waters of Appels and the Durme were low, varying between 100 and 125 μM (W. Muylaert, Institute for Nature Conservation, pers. comm.). Furthermore, bacteria that decompose organic material into methane thrive in flooded, oxygen-depleted soils (e.g. Wang et al. 1996). Two methanogenic pathways exists: (1) acetate fermentation ($CH_3COOH \rightarrow CH_4 + CO_2$) and (2) CO_2-reduction (CO_2 +

$4H_2 \rightarrow 2H_2O + CH_4$). Both of these pathways can result in an increase in the concentration and $\delta^{13}C$ value of pore water DIC (Games & Hayes 1976; LaZerte 1981; Ogrinc et al. 1997). Methanogenesis can cause $\delta^{13}C_{DIC}$ values to increase to as high as +38‰ (Grossman 1997). Several studies have shown $\delta^{13}C_{DIC}$ values ranging from +16.8‰ to +26±7‰ (Nissenbaum et al. 1972; Barker & Fritz 1981; Ogrinc et al. 1997). Methane production was not measured in this study. However, from September until February 1997 methane emissions were measured in Appels by others (Siebens 1997). The emission rates in the upper mudflat varied strongly from 120 (January 1997) to 27,200 (August 1997) μg CH_4 m^{-2} h^{-1}, with an average emission of 6,600 μg CH_4 m^{-2} h^{-1} (Siebens 1997). Although the methane emissions are highly variable, the reported values indicate that the upper mudflat in the Appels intertidal area represents a significant source of CH_4. Temperature plays an important role in the magnitude of methane production (e.g. Zeikus & Winfrey 1979) and several studies showed that methane production rates from wetlands increase with increasing temperature (Crill et al. 1988; Williams & Crawford 1984). Methane often increases rapidly in concentration reaching saturation levels within several centimeters sediment depth (Whiticar et al. 1986). Interstitial waters saturated with respect to methane can lead to bubble formation. Furthermore, during summer months ebullition from sediments is triggered by low-tide hydrostatic pressure release (Kipphut et al. 1982) and this was only observed at the Appels site during the May field trip. Therefore we expect a higher methane production for May 1998 than for November 1997. This would explain the higher DIC values for May, but what about the $\delta^{13}C_{DIC}$ values which are similar in May and November? LaZerte (1981) presented a model explaining the evolution of $\delta^{13}C_{DIC}$ towards a limiting value in pore waters of lake sediments where methanogenic processes dominate. In his model LaZerte (1981) took into account the relative contribution of the two reaction pathways of methane formation (acetate fermentation vs. CO_2 reduction). The model shows that as methanogenesis proceeds, DIC increases continuously, whereas $\delta^{13}C_{DIC}$ approaches a limiting value. We observe a similar situation in the mudflat pore waters in the present study (Figure 5).

Pore waters of the upper marsh have a slightly higher DIC concentration and a more negative $\delta^{13}C_{DIC}$ relative to the river water (Figure 5). Because of the soil structure and the presence of an extensive root system, oxygen is able to diffuse down to 25 cm in the sediment as judged by colour change of the sediments. In the interstitial waters of the upper marsh, $\delta^{13}C_{DIC}$ is probably controlled mainly by the oxidation of terrestrial organic carbon. $\delta^{13}C_{POC}$ of the sediments underneath the willow trees varied between −27.1 and −27.9‰, with an average value of −27.6‰. These $\delta^{13}C_{POC}$ values

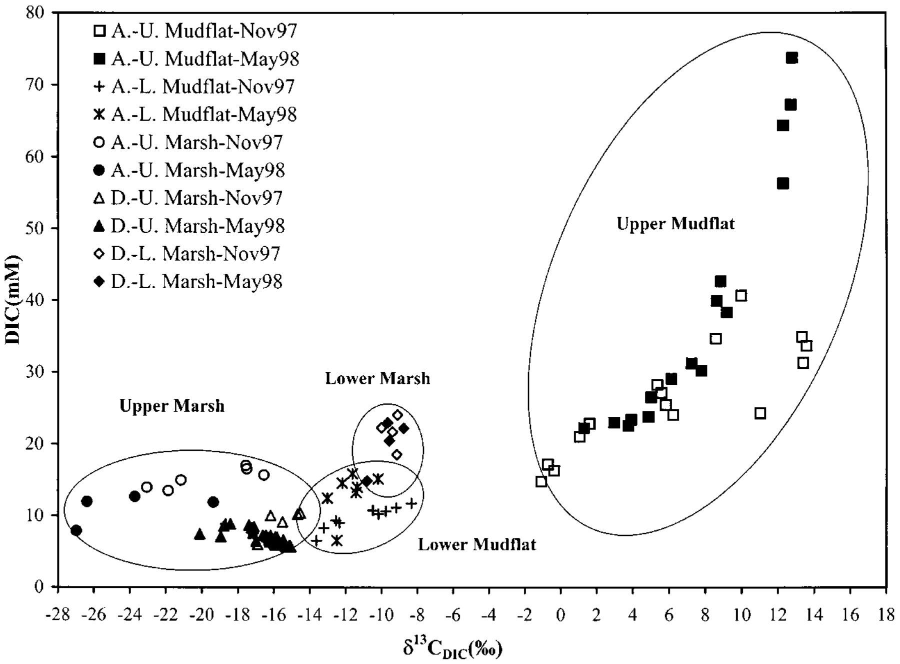

Figure 5. DIC concentration versus $\delta^{13}C_{DIC}$ for pore waters from the Lower Mudflat, Upper Mudflat, Lower Marsh and Upper Marsh. A. = Appels; D. = Durme; L. = Lower and U. = Upper.

are similar to values for C_3-vegetation. Aerobic decomposition of this ^{13}C-depleted terrestrial organic carbon results in dissolved inorganic carbon, which is isotopically lighter.

The huge variations of pore water $\delta^{13}C_{DIC}$ values for mudflat and marsh (−27‰ to +13.4‰) reflect the contribution of different DIC sources. In Figure 6 the $\delta^{13}C_{DIC}$ vs. DIC^{-1} plots for mudflats and marshes are shown. The trends are very different for pore waters from the mudflat and the marsh. It appears that the Appels mudflat data for November 1997 and May 1998 fit well to a linear regression (Table 4; R^2 = 0.90 and 0.96 respectively), suggesting a 2 end-member mixing situation (Faure 1986). The intercept of this linear regression on the y-axis provides an estimate of the $\delta^{13}C$ value of the DIC being added to the original (river) DIC pool (Grossman et al. 1989; Nascimento et al. 1997). Y-intercept values are +15.4‰ (range +12.8 to +18.1‰) and +20.3‰ (range +18.5 to +22.2‰) for November 1997 and May 1998, respectively (Table 4). In case there would be more than one DIC source other than river water, the y-intercept values in Figure 6 reflect the composite $\delta^{13}C_{DIC}$ value of this mixed source.

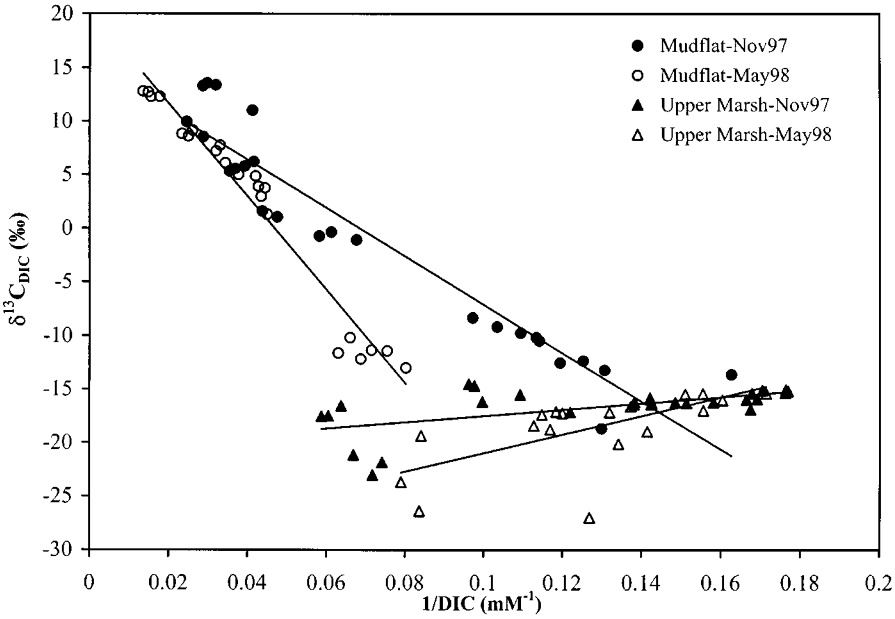

Figure 6. $\delta^{13}C_{DIC}$ versus DIC^{-1} for the mudflat (circles) and the upper marsh (triangles). Open symbols – May 1998; closed symbols – November 1997. Regression equations and statistics are given in Table 4.

Table 4. Linear regression equations (from Figure 6) for mudflat and upper marsh sediments.

	Regression equation	R^2	Intercept on $\delta^{13}C$ axis	
			Upper 95%	Lower 95%
Mudflat				
November	$\delta^{13}C_{DIC} = -225.2 \times DIC^{-1} + 15.4$	0.90	+18.1	+12.8
May	$\delta^{13}C_{DIC} = -434.2 \times DIC^{-1} + 20.3$	0.96	+22.2	+18.5
Upper marsh				
November	$\delta^{13}C_{DIC} = 29.4 \times DIC^{-1} - 20.4$	0.33	−18.1	−22.8
May	$\delta^{13}C_{DIC} = 86.9 \times DIC^{-1} - 29.7$	0.43	−23.1	−36.3

Grossman et al. (1986) concluded that addition of DIC with $\delta^{13}C$ values of +10‰ or greater is strong evidence for methanogenesis by CO_2 reduction, and evidence that this reaction, along with CO_2-producing fermentation and anaerobic oxidation reactions is responsible for the high carbonate content in pore waters. If we assume that only methanogenesis is responsible for the enrichment of $\delta^{13}C_{DIC}$ values relative to river water, the $\delta^{13}C$ value of DIC derived from methanogenesis in May 1998 would be +20.3‰.

However, high Ca^{2+} contents in the pore waters of the mudflat compared to river water (Table 2), are indicative that calcite dissolution occurs as well. Because of the paleo-marine nature of the signature of $CaCO_3$ (mean value of all cores (1 to 4) are: $\delta^{18}O_{CaCO_3} = -2.4$‰ and $\delta^{13}C_{CaCO_3} = -1.4$‰); it is clear that the carbonates are exogenous to the sampling site. If calcite precipitated in equilibrium with recent river water, we would expect a more negative $\delta^{18}O$ and $\delta^{13}C$ (river water: $\delta^{18}O_{SMOW} = -6.5$‰ and $\delta^{13}C_{DIC} = -11.5$ to -16.1‰). For example in May 1998 the increase in calcium content of the pore water from well A8 (upper mudflat) relative to river water could account for 15 to 17% of the observed DIC increase. If we assume that 15 to 17% of the DIC being added to the original DIC comes from calcite dissolution, the $\delta^{13}C$ value of DIC derived from methanogenesis would be even more enriched in ^{13}C, with values reaching +23.9 to +24.8‰. Using simple mass-balance equations we calculated the contribution of the different DIC sources to the total DIC pool in each well. For example in well A8, about three-quarters of total DIC is derived from methanogenesis, while less than one-quarter is from calcite dissolution and only one-tenth is from river water. In general, the contribution of DIC derived from methanogenesis and calcite dissolution to the total DIC pool will decrease with decreasing depth, while on the other hand the contribution from river water DIC to the total DIC pool will increase.

The marsh pore waters show a gentle slope on the $\delta^{13}C_{DIC}$ vs. DIC^{-1} plot (Figure 6). The y-intercept suggests an input of DIC with a $\delta^{13}C_{DIC}$ value ranging between -20.4 and -29.7‰ (Table 4). This indicates that aerobic decomposition of terrestrial organic matter (mean value of the marsh sediment: -27.5‰) represents the main source of the dissolved inorganic carbon in the marsh pore water. Mass balance calculations were used to determine the proportion of DIC added by respiration. If we assume that the total DIC pool in the marsh pore waters only consists of DIC from organic matter degradation and river water DIC, we calculated that about forty to ninety percent of the total DIC in the marsh pore waters from well A6 (May 1998, Appels) is derived from organic matter degradation and ten to sixty percent from river DIC. In pore waters from wells at the Durme site the relative contribution from river DIC is higher. For wells D2, D3 and D4 about seventy to ninety-five percent of the total DIC has a river source while five to thirty percent is derived from organic matter degradation. For well D5 between fifty and eighty percent of the total DIC is from river DIC and between twenty and fifty percent from organic matter degradation. Wells A6 (Appels site) and D5 (Durme site) are both located underneath willow trees. The presence of an extensive root system enables oxygen to diffuse in the top layer of the sediments. This might explain the higher contribution of the oxidation of terrestrial organic matter in both wells (A6 en D5) compared to the other wells in the upper marsh (D2, D3 and D5).

Conclusions

DIC concentrations and $\delta^{13}C_{DIC}$ values of the pore waters from the mudflat and the marsh are significantly different. In the strong reducing environment of the mudflat DIC concentrations are high and $\delta^{13}C_{DIC}$ values are enriched compared to river water. Calculations indicate that the DIC added to the pore water of the mudflat has a $\delta^{13}C_{DIC}$ value of +20.3‰ in May and +15.4‰ in November. We calculate that methanogenesis is a major contributor of ^{13}C enriched DIC to the interstitial water (up to three-quarters) in the upper mudflat. The contribution of DIC derived from methanogenesis and calcite dissolution to the total DIC pool will decrease with decreasing depth in the sediment, while the river DIC contribution to the total DIC pool will increase.

In the pore waters of the marsh DIC concentrations are slightly higher and $\delta^{13}C_{DIC}$ values are more depleted compared to river water. For the Appels marsh about 70% of the pore water DIC is derived from organic matter degradation, while the remaining 30% is from river water. For the Durme marsh the contribution of CO_2 from organic matter degradation to the total pore water DIC is smaller (20–40%). Here river water DIC is the major component of the pore water DIC (60–80%).

Acknowledgements

This research was conducted in the framework of OMES (Onderzoek Milieu-Effecten Sigmaplan), a project financed by the Ministry of the Flemish Community and co-ordinated by Patrick Meire (Institute of Nature Conservation, Brussels). We would also like to thank M. Frankignoulle for helping us with the total carbon calculations. F. Dehairs is Senior Research Associate at the Fund for Scientific Research-Flanders, Belgium.

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