Tidal exchange between a freshwater tidal marsh and an impacted estuary: the Scheldt estuary, Belgium

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ABSTRACT

Tidal marsh exchange studies are relatively simple tools to investigate the interaction between tidal marshes and estuaries. They have mostly been confined to only a few elements and to saltwater or brackish systems. This study presents mass-balance results of an integrated one year campaign in a freshwater tidal marsh along the Scheldt estuary (Belgium), covering oxygen, nutrients (N, P and Si), carbon, chlorophyll, suspended matter, chloride and sulfate. The role of seepage from the marsh was also investigated. A ranking between the parameters revealed that oxygenation was the strongest effect of the marsh on the estuarine water. Particulate parameters showed overall import. Export of dissolved silica (DSi) was more important than exchange of any other nutrient form. Export of DSi and import of total dissolved nitrogen (DIN) nevertheless contributed about equally to the increase of the Si:N ratio in the seepage water. The marsh had a counteracting effect on the long term trend of nutrient ratios in the estuary.

1. Introduction

It is generally thought that fringing marshes act as a filter for the estuarine water by removing inorganic and organic substances from the floodwaters or by changing the substance speciation (e.g. Cai et al., 2000; Tobias et al., 2001; Gribsholt et al., 2005). The marsh basically provides a large increase in reactive surface and enhances sedimentation. In the past, the interaction between tidal marshes and estuaries or coastal zones received much attention through numerous exchange studies (e.g. Valiela et al., 1978; Spurrier and Kjerfve, 1988; Whiting et al., 1989; Jordan and Corell, 1991; Childers et al., 1993). In these 'classic' interaction studies, fluxes were determined through the construction of mass balances. Dominant questions were whether marshes were importing or exporting substances, such as N, P, C or particulate matter (C and sediment), often testing the 'outwelling' hypothesis (e.g. Dame et al., 1986). Recently these studies have shifted their focus towards the underlying processes, using more refined techniques such as isotope labeling (e.g. Gribsholt et al., 2005, 2006). However, there are several reasons why exchange studies within the frame of the eutrophication problem in estuaries and coastal seas are still important.

Firstly, while certain aspects such as P and N retention (e.g. Valiela et al., 1978; Dame et al., 1986; Whiting et al., 1989; Jordan and Corell, 1991; Troccaz et al., 1994) have been studied in detail, others such as Si have been covered less frequently (e.g. Dankers et al., 1984; Struyf et al., 2005a,b).The high input of N and P in estuaries can lead to potential Si limitation in diatom communities, which are then less available to the higher trophic levels than dominating non-diatom species (Schelske et al., 1983; Smayda, 1997). Silica has only exceptionally been incorporated in mass-balance studies (e.g. Dankers et al., 1984; Struyf et al., 2005a). Furthermore, while tidal salt marshes are relatively well studied (e.g. Troccaz et al., 1994) only few mass-balance studies have focused on freshwater tidal marshes (e.g. Simpson et al., 1983; Childers and Day, 1988; Bowden et al., 1991; Gribsholt et al., 2005, 2006; Struyf et al., 2005a,b, 2006).With their botanical properties resembling inland freshwater wetlands, and as they interact more

with river hydrology and the corresponding water quality than saline marshes, freshwater tidal marshes are very specific process interfaces. Within these potentially strongly reactive areas, it has been shown through process studies that the seepage water, that usually contributes a minor part of the tidal water balance of the marsh, nevertheless can play a very important role in the processing capacity of a marsh. Yet the characterization of the seepage water has in the classic mass-balance studies only seldom been emphasized (e.g. Whiting and Childers, 1989).

Secondly, most tidal marsh exchange studies were performed in the 1970s and 1980s. For many estuaries, this period was characterized by peaking eutrophication problems. This is notably true for e.g. the Seine (Billen and Garnier, 1999), the Elbe (ARGE – Elbe, written communication) and the Scheldt estuary (Soetaert et al., 2006). In the 1990s, measures were generally taken to improve the water quality and, as a consequence, river scientists are now often studying "oligotrophication" (decreasing N and P loads) rather than eutrophication. Thus, potential nutrient limitation in estuaries has changed, especially in the Scheldt estuary, where the N:P Redfield ratio, charcterising the need for growth of diatoms, shifted from less than 20 in the seventies to over 50 in 2000 (Billen et al., 2005; Van Damme et al., 2005; Soetaert et al., 2006). In the Seine, a similar phenomenon was documented (Billen et al., 2001). It is interesting to investigate if such a trend in estuarine systems interacts with the processing potential of marshes. Therefore a reassessment of tidal marsh exchange is required, illustrating the use of old unpublished data.

Nutrient regulation, oxygenation, sediment accretion, carbon production and processing and water storage are all directly or indirectly linked with ecological functions or goods and services of estuarine systems, as defined e.g. by De Groot et al. (2002). The use of ecosystem functions in estuarine restoration has the major advantage that it is not a static approach, as is much of the protective legislation. The aim of this study was to assess the interaction of a freshwater tidal marsh and the water column by means of mass balances, including a comparison between nutrients, carbon, suspended matter and other parameters. This comparison is a basic essential step in the quantification and decision making of priorities in estuarine restoration. Also, the difference between the bulk tidal exchange and seepage is scoped.

In this study fluxes of nutrients (N, P and Si), carbon and particulate matter were determined in a freshwater tidal marsh, together with the ambient estuarine conditions. Also the oxygenating potential, the fluxes of chloride and sulfate, and other supporting parameters were determined simultaneously. To our knowledge, this is a tidal marsh exchange study with the most comprising parameter list so far.

2. Material and methods

Four mass-balance studies were conducted in a freshwater tidal marsh of the Scheldt estuary: on 1 July 1997, 7 October 1997, 27 January 1998 and 29 April 1998. Each tidal cycle was monitored at the entrance of the main creek as well as in the river upstream of the marsh. The cycles were monitored from the point of low tide in the river to the next low tide. All 13 h measurement campaigns started between 12:30 and 16:00.

2.1. Site description

The Scheldt estuary extends from the mouth in the North Sea at Vlissingen (km 0) till Gent (km 160), where sluices and weirs stop the tidal wave in the Upper Scheldt (Fig. 1). The tidal wave also enters the major tributaries Rupel and Durme, providing the estuary with approximately 235 km of tidal river. The Zeeschelde

(105 km long) is characterized by a single ebb/flood channel, bordered by relatively small mudflats and marshes (28% of total surface). The basic features of the Scheldt estuary are described in more detail elsewhere (Meire et al., 2005).

The selected area is a freshwater tidal marsh (surface approximately 92.000 m^2), situated at Tielrode near the mouth of the Durme tributary which is silted up in a high degree (Fig. 1). The marsh is surrounded by dikes. At the landside a winter dike is elevated 8 m above average low water level; at the riverside a summer dike is 2 m lower than the winter dike. At present, the vegetation of the marsh is dominated by a patchy pattern of osier thicket (dominated by *Salix sp.*), reed (*Phragmites australis*) and tall herb vegetation (characterized by *Urtica dioica*, *Epilobium hirsutum* and *Impatiens glandulifera*). A single creek has developed, from a breach in the winter dike, as the major access from the river to the marsh. The creeks and lower parts of the marsh are flooded by a semidiurnal tide while the highest parts are only flooded by spring tides. A bridge was installed over the main creek at the riverside, from which all sampling took place. The geometry of the cross-section of the creek, coated with stone rubble, was measured twice consecutively by means of a theodolite (Fig. 2).

2.2. Water balances

Discharged volumes were calculated by multiplying flow velocity measured every 2 min and cross-section area during the bulk tidal phase and every half hour during the seepage water phase. The bulk tidal phase is here defined as the period during which large amounts of water flow in and out (flood and ebb) the marsh through the main creek. The bulk tidal phase started when the rising tide entered the creek through the sampling transect (Fig. 2). The seepage phase started per definition when the water height in the creek dropped below approximately 30 cm depth at the deepest point of the creek transect.

During the bulk phase, water flow velocity was measured continuously over the cross-surface (about 30 m^2) at 2 m width and 0.5 m depth intervals (Fig. 2), using 4 'OTT'-mill flow velocity meters which could rotate on a vertical axis to determine the angle of the water flow relative to the banks. Thus, temporal, vertical and horizontal flow variations were covered. The 'seepage' flow was measured chronographically in 30-min intervals by following floating coarse particulate debris that flowed over a known distance in a straight stretch. Water height was recorded in the centre of the creek approximately every 2 minutes in the bulk tidal phase and every half hour during the seepage phase.

The water balances were corrected for precipitation which fell during the tidal cycle when relevant, using the data of the nearby weather station of Bornem of the Belgian Royal Meteorological Institute. The correction of the water balance was done by adding the precipitation mass over the marsh area to the mass of the flood phase.

Data interpolations were performed using a simple model, as in Struyf et al. (2006).

2.3. Sampling and analysis

Water samples were collected at 0.5 m depth intervals along the vertical gridline in the centre of the creek (Fig. 2) using a handpump that was connected to sampling pipes. The sampling pipes were attached in a vertical tube and reached out through openings at the depth intervals. Samples were collected every half hour during the bulk tidal phase at each depth (when flooded).

Water samples (250 ml) for Cl$^-$ (included in the study as a tracer), NH$_4^+$-N, NO$_3^-$-N, NO$_2^-$-N, Kjeldahl-N, dissolved inorganic phosphorous (DIP), total phosphorous (Tot P), dissolved silica (DSi)
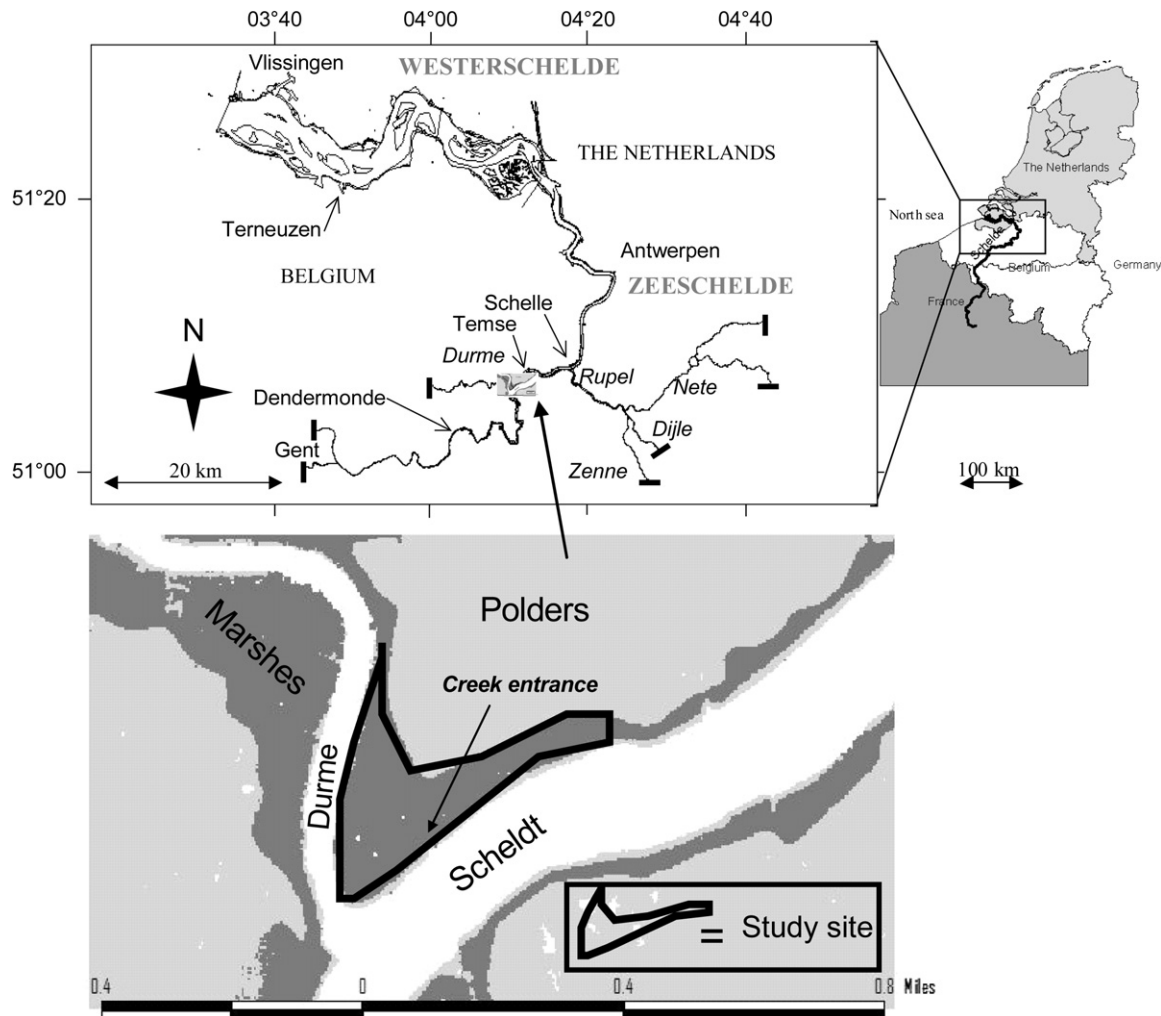
Fig. 1. Map of the Scheldt estuary, with the investigated study site.

and SO_4^{2-}-S were stored at 4 °C and were analyzed within 24 h after sampling. Analysis of Cl^-, NO_3^--N, NO_2^--N, NH_4^+-N, SO_4^{2-}-S, DIP, Kjeldahl-N (after oxidation in H_2SO_4) and Tot P (after oxidation in H_2SO_4 and $K_2S_2O_8$) was done using a SKALAR SA 5100 segmented flow analyzer. Organic N was calculated by subtracting NH_4^+-N from

Fig. 2. Geometry of the cross-section of the main creek (two profiles). At the crossing of horizontal and vertical grid lines, current velocity was measured (sampling tube = location where water samples were taken; datasonde = location of the datasonde; Bidge = level of the walking board over the creek).

Kjeldahl-N. Total dissolved inorganic nitrogen (DIN) is the sum of NO_3^--N, NO_2^--N and NH_4^+-N, while total nitrogen (tot N) is the sum of DIN and organic N. Dissolved silica (DSi) was analyzed by ICP-OES (Iris®).

Samples for dissolved organic carbon (DOC) were filtered (25 ml) on Gelman glassfiber filters (0.45 μm nominal porosity). For DOC determination, a preliminary treatment with H_2SO_4 acidification and flushing with nitrogen gas to remove background CO_2 concentration was performed. DOC was then set free by further oxidation to CO_2 and analysis was done using a SKALAR (phenolphthalein 550 nm detection).

Suspended particulate matter (SPM) was determined gravimetrically after filtration (25 ml) on pre-combusted Whatman GF/F 0.7 μM filters, previously dried at 60 °C. Particulate organic carbon (POC) and particulate nitrogen (PN) were determined after filtration on pre-combusted Whatman GF/F 0.7 μM filters, using a Carlo Erba CN analyzer NA 1500 after Cr_2O_3 and $AgCo_3O_4$ catalyzed oxidation and segregation on a Haysep-Q-column.

Particulate total carbon (PTC) and particulate inorganic carbon (PIC) were analyzed by use of carbon analyser Ströheim Model Coulomat 70I LI, using heating at 900 °C and an acid medium (i.e., 85% orthophosphoric acid, ortho-H_3PO_4 plus 15% silver nitrate, $AgNO_3$) to convert respectively PTC and PIC to CO_2 which was quantified by automatic coulometric titration of alkaline barium perchlorate (Ba(ClO$_4$))$_2$ solution. The Coulomat was standardised
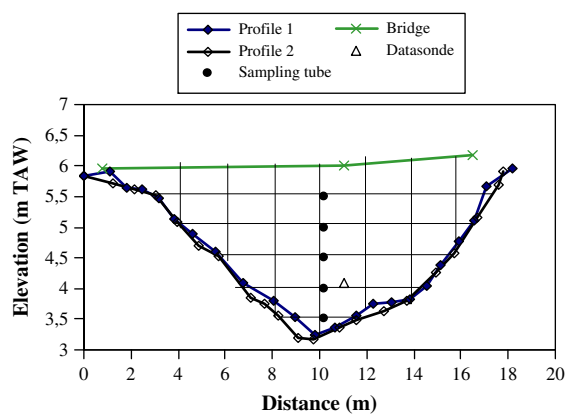
with $CaCO_3$. The particulate organic carbon (POC) content in the samples was obtained by subtracting the values for PIC from those of respective PTC.

Water samples for chlorophyll (100 ml) were filtered on pre-combusted 45 μ Sartorius filters and frozen at −20 °C immediately afterwards. Pigments were extracted in 90% acetone and quantified using high pressure liquid chromatography according to Wright et al. (1991).

A Water Quality Multiprobe Hydrolab H20®, measuring oxygen saturation every 5 min, was installed in the center of the creek (Fig. 2) under the water surface during the bulk tidal phase. In the seepage phase, samples were collected with the cup of the multiprobe and immediately fixed on it for measurement.

River water was collected from a boat with a 15 L Niskin bottle for analysis of the same parameters as mentioned above (incl. handling and analysis). The boat was positioned in the middle of the river before the marsh entrance. Temperature and oxygen content of the river were measured in situ with a 'WTW OXI 91' oxygen-meter.

Statistics were performed using S-Plus 2000.

2.4. Balances of dissolved and particulate matter

Transport of dissolved and particulate material was calculated by multiplying discharge with measured concentrations throughout the tidal cycles. Weighted average concentrations per tidal cycle phase (bulk inflowing, bulk out flowing and seepage phase) were calculated as the ratio of the total amount of transported matter and the amount of water discharged during a particular tidal phase.

Nutrient balances were rendered conservative by correcting for the import or export of water (by subtracting percentage import/export of water from percentage matter exchange). In a conservative mass-balance, it is assumed that there was no net import or export of water (Dankers et al., 1984). This correction was necessary to allow comparison between tidal cycles, which differ in the ratio of imported and exported water volumes (Fig. 3).

3. Results

3.1. Water balances

The discharge profiles of the four monitored cycles showed a similar pattern (Fig. 3). It took a few hours before the rising tide
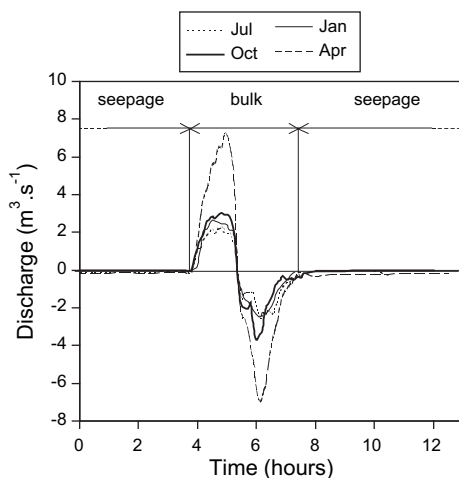
Fig. 3. Water discharge through the main creek for each measured tidal cycle (Jul = July 1997, Oct = October 1997, Jan = January 1998, Apr = April 1998).

reached the level of the breach where the creek starts. During this period, water from the previous tide still seeped out of the marsh. During flood the discharge increased to a maximum after which it slowed down till slack tide. Superimposed on the tidal discharge asymmetry pattern, as described by Postma (1967), the out flowing water showed an additional discharge peak when the level of the river surface dropped below the level of the creek. Only in April were the two peak discharge patterns smoothed out by the high discharge values. The vertical distribution of the inflow was less homogenous than of the outflow; the lateral distribution of the stream velocity showed an asymmetrical pattern (data not shown).

Inflowing and out flowing water volumes were nearly equal during 3 out of the 4 studies (Table 1). The exported water volume greatly exceeded the inflowing volume in April. Here the exchanged water volume was more than double than that of October, although the water level reached was only 8 cm higher. A possible reason is that water that entered the marsh during the previous tidal cycle had not completely flowed out of the marsh yet. This is more likely to occur at higher tides (Dankers et al., 1984), which was the case for the April 1998 cycle (Table 1). It was also noticed that at this higher tide the river water was at some locations flowing over the worn out crown of the summer dike. It is also likely that the marsh, while still not fully flooded through the main access channel, was flooded by water that in a diffuse way flowed over the dike, and that the subsequent drainage occurred predominantly through the main channel, thus creating strong ebb current. This phenomenon also often occurs in coastal zones and is known as 'rip currents'.

Precipitation was only recorded during the July campaign, where 4 mm of rain fell just after high tide. In January, air temperature dropped below zero, so that an unknown mass of water froze onto the marsh surface. This amount was probably very limited as the flood level was then quite low.

The exchanged water volumes were small compared to the long term averaged discharge of 100 $m^3 s^{-1}$ of the Scheldt estuary at Schelle, situated 10 km downstream of the sampling site (Fig. 1). The yearly average of 1997 and 1998 was 84 and 135 $m^3 s^{-1}$ respectively.

3.2. Concentrations and mass balances

Some features of the Scheldt estuary can readily be recognized in the data. The tidal marsh of Tielrode is situated in the oligohaline zone (0.5–5 PSU) of the Scheldt estuary, which is reflected in the tidal maxima of chloride and sulfate (Table 2). The marsh is furthermore situated upstream the Rupel tributary, discharging untreated wastewater from the city of Brussels. The tidal action dissipates this load up till and even far upstream the sampling site. This is reflected in the water quality patterns of the Scheldt estuary (Van Damme et al., 2005): at high tide, minimal concentrations were observed in the river for DO and NO_3^--N, and maxima for NH_4^+-N.

Over all months, consistent import or export was noted for 13 of the 17 independent (in the sense of not calculated from others) parameters (Fig. 4). Dissolved oxygen, DSi and chloride were exported in all cases, while SO_4^{2-}-S showed mostly export with only slight import in April. Import was observed in all cases for NH_4^+-N, NO_3^--N, hence also for DIN. Parameters from the particulate phase (SPM, Chl a and b, PN, PIC, POC, PTC) and also organic N, Tot N and Tot P showed import in all cases.

Of all campaigns, the results of the winter were distinct. In January, export in general was marginal (Fig. 4). The marsh surface was then frozen, which was apparently blocking most seepage (Table 1). Import however was noted for SPM, PN, PIC, Tot P, POC

Table 1
Water balances for all tidal cycles conducted, with separate indication of seepage, bulk inflowing and bulk out flowing water. The net balance is also indicated in percent of the inflow (% of In) Maximal water height is expressed in cm TAW, the Belgian national tidal reference (indicating a historic low tide average at Antwerpen). The average discharge of the decade preceding each tidal cycle is given for Schelle; precipitation data provided by the Belgian Royal Meteorological Institute.

Date	Max. height (cm)	Bulk water mass		Seepage		Precipitation (m³)	Balance Out–In[a]	
		Incoming (m³)	Out going (m³)	(m³)	(% of total out going)		(m³)	(% of In)
01/07/97	541	9834	9601	750	7.5	368	149	2
07/10/97	562	12649	11415	1090	8.7	0	−144	−1
27/01/98	533	10221	9843	99	1.0	0	−279	−3
29/04/98	570	26221	23501	5845	19.9	0	3125	12

[a] Positive value = export, negative value = import.

and organic N, as the frost did not prevent deposition of particulate matter (Fig. 4).

The export of DO was the clearest observed phenomenon. In April, a sevenfold export amount was recorded, while in the other seasons except winter, oxygen also showed top export rates of well over 100% (Fig. 4). For DO, the seepage phase contributed more to the mass balance than for any other parameter, except in January (Fig. 5) when the river concentrations were high.

Chloride concentrations in the river were much higher in October than in any other month, despite the fact that the water level was higher at high tide in April (Table 2). This can be explained by the discharge in October, which was almost three times lower than in April (Table 1). The salinity gradient along the estuary showed in October 1997 an intrusion of about 20 km more upstream as compared with April 1998 (Van Damme et al., 2005). Sulfate showed similar patterns.

Parameters from the particulate phase (SPM, Chl a and b, PN, PIC, POC, PTC) and also organic N, Tot N and Tot P showed similarity in the concentration pattern: At the end of the bulk out flowing phase and the beginning of the seepage phase, concentrations peaked to reach the maximal value of the whole profile (Table 2, detail pattern not shown). Despite this peak there was always a net import, because the high concentrations in the bulk out flowing phase were linked with lower discharges than the bulk inflowing phase (Fig. 3; Table 1). Also, without exception, the seepage phase of these parameters showed clear decreasing profiles, so that the seepage phase showed always depletion relative to the bulk out flowing phase, except for PIC and Tot P in July, and for some parameters in January, when the marsh was frozen and the seepage water showed only minor difference with the bulk out flowing phase (Fig. 5). There was no consistent ranking between the parameters of the particulate phase concerning shifts in SPM composition from bulk water to seepage water: POC accounted for 2.1–26.5% of SPM (8.3 ± 2.7%), and for 73–98% of PTC (88 ± 3%).

The components of Tot N (NH_4^+-N, NO_3^--N, NO_2^--N and org N) behaved differently. In terms of percentage the import of NO_3^--N was maximal (Fig. 4) when the concentration in the river was lowest, i.e. in July (Table 2). On the contrary, in January, when NO_3^--N concentrations in the river were highest, the net import was relatively low, despite the high amounts that were exchanged. NH_4^+-N on the other hand showed largest import when the concentrations in the river were high, and lowest import at the lowest concentrations, i.e. in October. The seepage phase was, relative to the bulk out flowing phase, in all cases enriched with NO_3^--N and depleted of NH_4^+-N. The concentration profile of the seepage phase was for nitrate and ammonium always decreasing, except in October, when an increase of ammonium was recorded (Table 2). The import of NO_3^--N was thus due to the bulk phase, the seepage phase even somewhat counteracting the import (Fig. 5), while for NH_4^+-N the seepage phase played a more important role. Org N accounted for 16.8–37.8% of Tot N. The exchanged PN amounted between half and completely the corresponding amount of org N (Table 2).

Of all N-parameters, only NO_2^--N showed both export and import (Fig. 4). The export/import ratio for nitrite was predominantly determined by changes in the bulk tidal phase (Table 2). The seepage phase was, compared with the bulk out flowing phase, consistently depleted of nitrite. However, the fact that nitrite showed both export and import is made less important in view of that constituents consistently low concentrations.

DIP was one of the four elements not showing consistent import or export in the four measured tidal cycles. Import occurred in July and export in the three other months (Fig. 4). In three of four cases, the seepage phase showed highest concentrations of DIP. Lowest concentrations were measured at high tide in the river (Table 2).

DSi concentrations were highest in the seepage phase, showing strong increase (Table 2). In July, October and April the DSi enriched seepage water contributed more to the overall out flowing DSi budget than any other parameter but DO (Fig. 5). The export in these months could be attributed to these high amounts of DSi in the seepage phase (Table 2). Clearly the winter situation was totally different from the other seasons (Table 2; Fig. 4), showing some import and a constant concentration level throughout the tidal cycle. DSi was the only parameter to show this particular behaviour, which was with these data for the first time observed for tidal marshes. The concentration profiles and balances of DSi are therefore presented in more detail and extent elsewhere, pointing at the concentration increase in the seepage phase in comparison with patterns in a saline marsh (Struyf et al., 2005a). Here, the focus is pointed at the relation with the other nutrients.

3.3. Nutrient ratios

The molar ratios of N:P (Fig. 6) and Si:N (Fig. 7) delivered by the marsh are important because they show how the marsh influences the elements that control estuarine and eventually marine phytoplankton. In all cases, the N:P ratio of the seepage phase dropped below the values of the river, reaching the lowest values in July and October (Fig. 6). In these months the seepage phase nutrient ratios showed potential N limitation.

The Si:N ratio (optimal 1:1) of the river water was confined between 0.2 and 0.4, except in January, when a maximum of 0.57 was reached (Fig. 7). In July, October and April the Si:N ratio increased strongly in the seepage phase, exceeding the river values clearly, and lifting the ratio beyond potential Si limitation. In January the increase of Si:N in the seepage phase was very moderate, hardly exceeding the river values, and the N:P ratio in the seepage phase was then relatively high, compared to the other months.

3.4. Contribution of the changes in the seepage phase to the balance

In July and October, the strongest positive influence of the seepage phase on the net balance was found for parameters of the dissolved phase: DO, DSi, ammonium and DIN (Fig. 8). In October

Table 2
Concentrations and mass balances (+ = export, − = import) for all parameters and for each studied tidal cycle. Shown concentration values include river values, averaged for low tide (LT) and high tide (HT), and minimal and maximal values of the seepage phase. If a homoscedastic single T-test, comparing the chronological first half with the second half of the seepage phase samples ($n \geq 8$), was significant ($p \leq 0.05$), then an arrow indicates if the concentration pattern of the seepage phase goes from maximum to minimum or vice versa. The mass balances are shown with separate indication of seepage, bulk inflowing and bulk out flowing water. The net balance (Out–In) is also given per marsh area unit and in percent versus the inflow (% of In) (Cons. = conservative net balance (in% according to the inflow), i.e. corrected for import or export of water, DO = Dissolved oxygen, SPM = suspended matter, DIN = total dissolved nitrogen, org N = organic nitrogen, PN = particulate nitrogen, tot N = total nitrogen, tot P = total phosphorous, DSi = dissolved silica, DOC = dissolved organic carbon, POC = particulate organic carbon, PIC = particulate inorganic carbon, PTC = particulate total carbon, Chl a = chlorophyll a, Chl b = chlorophyll b).

Par.	Month	Concentrations					Mass balance						Cons. Out-In
		River		Seepage			Incoming	Outgoing		Out–In			
		LT[a]	HT[a]	Min[a]		Max[a]	Bulk[b]	Bulk[b]	Seepage[b]	b	c	% of In	% of In
Cl⁻	Jul	2.7	4.7	3.5	→	4.1	1119	1252	105	238	2.58	21	20
	Oct	16	37	22	←	24	13200	13011	906	717	7.80	5.4	6.6
	Jan	2.0	3.2	2.5	→	3.0	915	938	9.6	33	0.36	3.6	6.4
	Apr	2.5	3.1	2.3	→	2.6	2217	2414	528	725	7.89	33	21
SO4²⁻	Jul	1.0	0.88	1.1	→	1.1	918	881	77	40	0.44	4.4	2.8
	Oct	1.6	2.2	1.9	←	2.2	2505	2430	209	134	1.46	5.3	6.5
	Jan	1.2	1.1	1.2		1.2	1119	1079	11	−28	−0.31	−2.5	0.2
	Apr	1.2	0.93	1.1	→	1.1	2618	2236	529	147	1.60	5.6	−6.3
DO	Jul	0.03	0.02	0.13		0.17	7.0	13	3.6	10	0.11	143	141
	Oct	0.16	0.01	0.17		0.18	7.7	14	6.1	12	0.13	154	155
	Jan	0.23	0.18	0.37	→	0.43	80	83	1.3	4.6	0.05	5.7	8.4
	Apr	0.07	0.01	0.13		0.16	8.8	45	28	64	0.69	723	712
SPM	Jul	63	28	34	←	128	1214	956	82	−176	−1.91	−14	−16
	Oct	97	66	42	←	200	4277	3272	260	−745	−8.10	−17	−16
	Jan	192	22	28	←	214	1554	985	14	−555	−6.03	−36	−33
	Apr	179	18	14	←	104	3781	3363	313	−105	−1.14	−2.8	−15
NH4⁺-N	Jul	0.29	0.34	0.11	←	0.14	48	44	1.2	−2.7	−0.03	−5.6	−7.1
	Oct	0.00	0.15	0.03	→	0.05	23	22	0.5	−0.3	0.00	−1.1	0.0
	Jan	0.19	0.24	0.08	←	0.11	30	28	0.1	−1.6	−0.02	−5.3	−2.5
	Apr	0.15	0.20	0.02	←	0.05	55	55	1.7	1.8	0.02	3.3	−8.6
NO3⁻-N	Jul	0.15	0.08	0.12	←	0.20	20	16	1.5	−2.1	−0.02	−10	−12
	Oct	0.37	0.18	0.16	←	0.26	37	32	3.3	−2.1	−0.02	−5.8	−4.6
	Jan	0.54	0.42	0.50	←	0.57	70	66	0.8	−2.5	−0.03	−3.6	−0.9
	Apr	0.40	0.31	0.37	←	0.43	139	114	33	8.6	0.09	6.2	−5.7
NO2⁻-N	Jul	0.01	0.03	0.01	←	0.01	1.3	2.2	0.1	0.9	0.01	65	63
	Oct	0.01	0.02	0.00	←	0.00	3.0	2.7	0.1	−0.2	0.00	−8.2	−7.1
	Jan	0.01	0.01	0.01	→	0.02	5.9	4.1	0.0	−1.8	−0.02	−30	−28
	Apr	0.02	0.03	0.00	←	0.01	9.4	8.7	0.3	−0.4	0.00	−4.5	−16
DIN	Jul	0.46	0.44	0.24	←	0.34	69	63	2.8	−3.9	−0.04	−5.6	−7.1
	Oct	0.39	0.35	0.19	←	0.31	63	56	3.9	−2.7	−0.03	−4.2	−3.1
	Jan	0.75	0.67	0.59	←	0.70	106	99	0.9	−5.9	−0.06	−5.6	−2.9
	Apr	0.57	0.53	0.40	←	0.49	202	177	35	10	0.11	4.9	−7.0
Org N	Jul	0.17	0.11	0.13	←	0.26	27	22	1.7	−2.7	−0.03	−10	−12
	Oct	0.11	0.00	0.10	←	0.17	27	22	1.7	−3.3	−0.04	−12	−11
	Jan	0.09	0.04	0.06	←	0.19	21	16	0.2	−5.4	−0.06	−25	−23
	Apr	0.14	0.09	0.06	←	0.09	48	42	6.7	1.1	0.01	2.3	−9.6
PN	Jul	0.05	0.04	0.00		0.00					0.00		
	Oct	0.07	0.04	0.08	←	0.16	27	21	1.4	−4.2	−0.05	−16	−15
	Jan	0.09	0.03	0.02	←	0.09	9.5	7.0	0.1	−2.4	−0.03	−25	−23
	Apr	0.06	0.02	0.01	←	0.05	36	22	2.1	−12	−0.13	−32	−44
Tot N	Jul	0.63	0.55	0.37	←	0.60	96	85	4.5	−6.6	−0.07	−6.9	−8.4
	Oct	0.50	0.36	0.29	←	0.48	89	78	5.5	−6.0	−0.06	−6.7	−5.5
	Jan	0.84	0.71	0.64	←	0.88	127	115	1.1	−11	−0.12	−8.9	−6.2
	Apr	0.71	0.62	0.46	←	0.58	250	220	42	11	0.12	4.4	−7.5
PO4³⁻–P	Jul	0.04	0.02	0.04	→	0.05	5.0	4.2	0.5	−0.2	0.00	−4.9	−6.5
	Oct	0.04	0.03	0.03	→	0.04	6.7	6.3	0.6	0.2	0.00	2.3	3.4
	Jan	0.03	0.02	0.03	→	0.04	3.2	3.1	0.0	−0.1	0.00	−1.6	1.1
	Apr	0.02	0.02	0.03		0.04	7.6	6.3	3.0	1.7	0.02	22	10
Tot P	Jul	0.07	0.04	0.09	←	0.23	14	9.8	1.3	−3.1	−0.03	−22	−23
	Oct	0.07	0.03	0.08	←	0.15	28	21	1.5	−5.3	−0.06	−19	−18
	Jan	0.05	0.03	0.05	←	0.13	12	8.4	0.1	−3.4	−0.04	−28	−26
	Apr	0.06	0.03	0.04	←	0.07	28	25	3.9	0.5	0.01	1.8	−10
DSi	Jul	0.15	0.15	0.24	→	0.28	50	50	6.5	5.7	0.06	11	9.8
	Oct	0.10	0.11	0.24	→	0.28	52	51	9.1	8.0	0.09	15	17
	Jan	0.20	0.20	0.21	→	0.24	65	63	0.7	−1.4	−0.02	−2.1	0.6
	Apr	0.16	0.17	0.22	→	0.28	138	127	50	39	0.42	28	16
DOC	Jul	0.29	0.28	0.16	→	0.20	33	37	1.6	5.6	0.06	17	16
	Oct	0.41	0.31	0.18	→	0.30	49	41	2.7	−5.7	−0.06	−12	−10
	Jan	0.04	0.12	0.16	→	0.24	23	24	0.2	1.8	0.02	8.0	11
	Apr	0.18	0.71	0.58		0.69	302	214	47	−41	−0.45	−14	−25

Table 2 (*continued*)

Par.	Month	Concentrations						Mass balance						Cons. Out-In	
		River		Seepage				Incoming	Outgoing		Out–In				
		LT[a]	HT[a]	Min[a]			Max[a]	Bulk[b]	Bulk[b]	Seepage[b]	[b]	[c]	% of In	% of In
POC	Jul	0.43	0.33	0.83	←		3.0	113	83	5.2	−25	−0.27	−22	−24
	Oct	0.66	0.43	0.58	←		0.87	219	167	13	−39	−0.42	−18	−17
	Jan	1.0	0.19	0.12	←		0.98	82	60	0.8	−21	−0.23	−26	−23
	Apr	0.89	0.17	0.18	←		0.65	283	197	19	−66	−0.72	−23	−35
PIC	Jul	0.03	0.02	0.07	←		0.47	11	9.2	0.8	−1.2	−0.01	−11	−13
	Oct	0.08	0.06	0.08	←		0.22	39	30	3.7	−5.4	−0.06	−14	−13
	Jan	0.14	0.02	0.02	←		0.13	16	11	0.2	−5.0	−0.05	−31	−28
	Apr	0.15	0.05	0.02	←		0.07	71	43	3.9	−24	−0.26	−34	−46
PTC	Jul	0.47	0.36	0.90	←		3.5	124	92	6.0	−26	−0.28	−21	−23
	Oct	0.74	0.49	0.67	←		1.1	258	197	16	−44	−0.48	−17	−16
	Jan	1.2	0.21	0.13	←		1.1	98	71	0.9	−26	−0.29	−27	−24
	Apr	1.0	0.22	0.20	←		0.72	354	240	23	−90	−0.98	−26	−37
Chl a	Jul	63	63	63			63	1209	968	17	−224	−2.43	−19	−20
	Oct	63	63	63			63							
	Jan	4.3	1.1					32	19					
	Apr	63	63	4.0	←		63	931	837	50	−44	−0.48	−4.8	−17
Chl b	Jul	6.3	6.0	4.6			7.3	64	56	0.6	−7.8	−0.08	−12	−14
	Oct	6.9	2.6											
	Jan	0.30	0.02					3.4	0.4					
	Apr	1.7	0.80	0.10	←		1.3	47	42	1.7	−3.7	−0.04	−7.8	−20

[a] Concentration unit: mM except for SPM (mg L^{-1}) Chl a and Chl b (μg L^{-1}).
[b] Mass unit: kg except for Chl a and Chl b (g).
[c] Unit: g m^{-2} except for Chl a and Chl b (mg m^{-2}).

larger contributions were found than in July. Parameters of the particulate phase added less than 1% to the net balance or counteracted it maximum 2%. For DIP the enrichment of the seepage phase counteracted the net (non conservative) balance, except in April. In January, limited contribution was noted, as the seepage was hardly differentiated from the bulk phase (Fig. 5), and the balances were relatively conservative compared to the other months (Fig. 4). In April, strong effects on the net balance took place, 34% of the SPM import was due to depletion of SPM in the seepage phase, while the counteracting effects mounted up to over 50% for Tot P. For chloride, only a relative strong effect was seen in October, when the tidal variation was high.
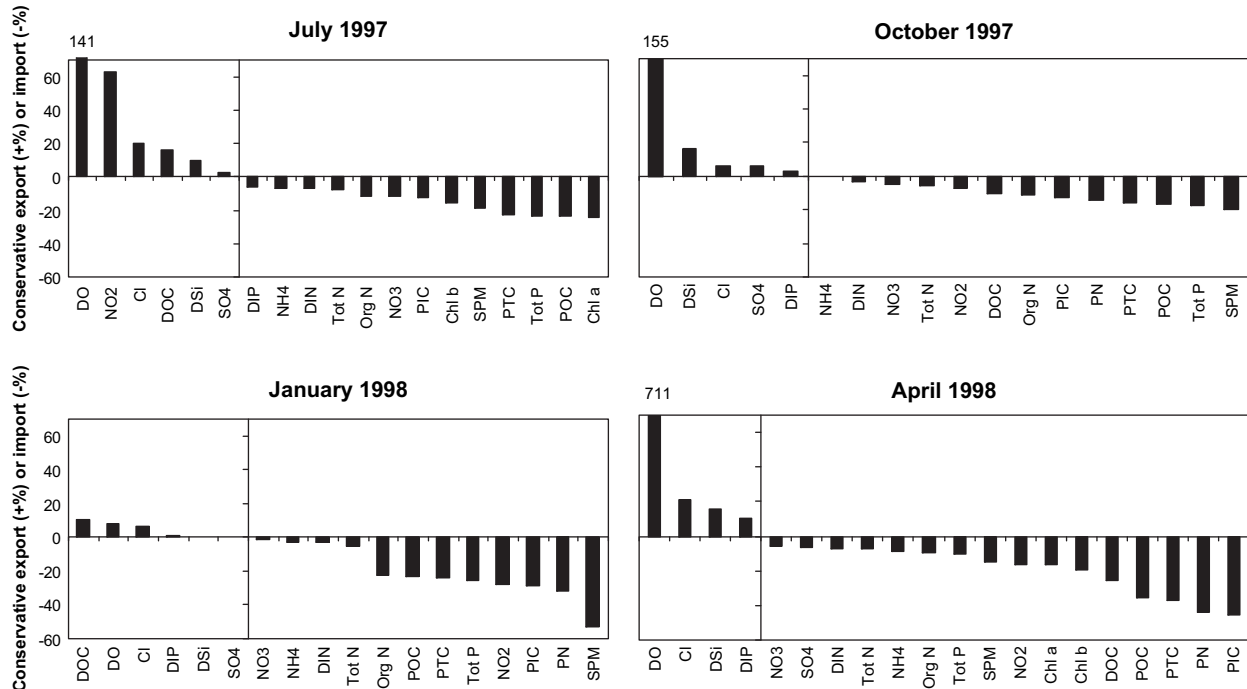

Fig. 4. Conservative import (negative value) or export (positive value), i.e. corrected for import or export of water, for all measured parameters and for each tidal cycle (DO = dissolved oxygen, Cl = chloride, DOC = dissolved organic carbon, DSi = dissolved silica, SO$_4$ = sulfate, DIP = dissolved inorganic phosphorous, tot P = total phosphorous, NH$_4$ = ammonium-N, NO$_3$ = nitrate N, NO$_2$ = nitrite-N, DIN = total dissolved nitrogen, tot N = total nitrogen, org N = organic nitrogen, PIC = particulate inorganic carbon, POC = particulate organic carbon, PTC = particulate total carbon, SPM = suspended matter, chl a = chlorophyll a, chl b = chlorophyll b).
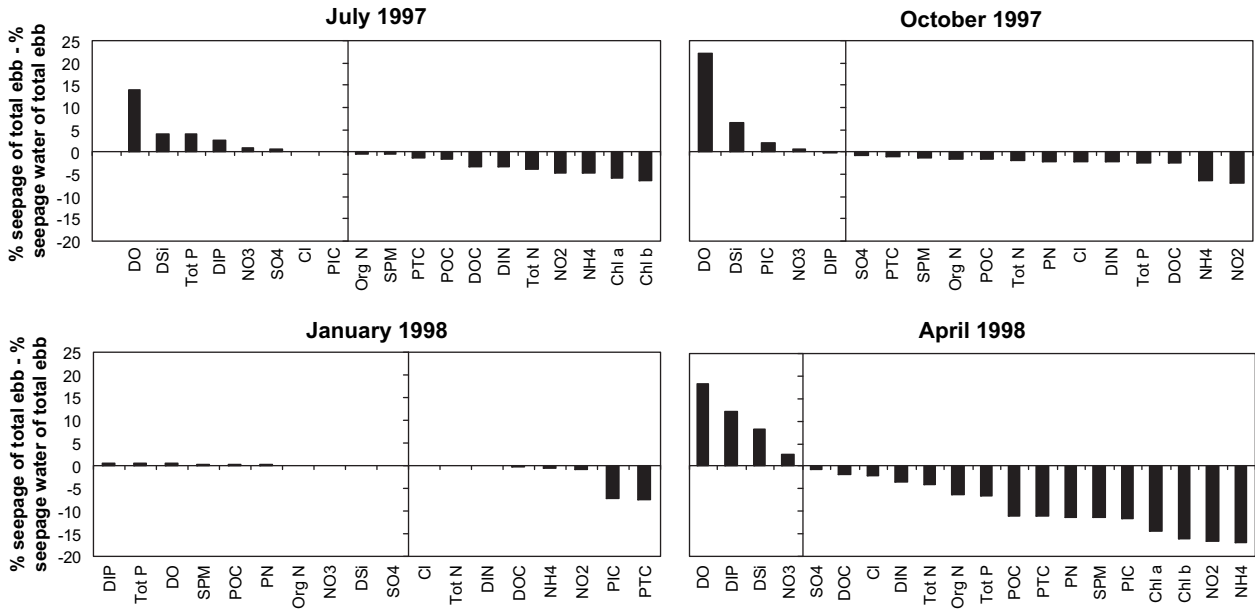
Fig. 5. Difference (in%) between export in the seepage phase of any measured physicochemical parameter and export of water in the seepage phase (DO = dissolved oxygen, Cl = chloride, DOC = dissolved organic carbon, DSi = dissolved silica, SO₄ = sulfate, DIP = dissolved inorganic phosphorous, tot P = total phosphorous, NH₄ = ammonium-N, NO₃ = nitrate N, NO₂ = nitrite-N, DIN = total dissolved nitrogen, tot N = total nitrogen, org N = organic nitrogen, PIC = particulate inorganic carbon, POC = particulate organic carbon, PTC = particulate total carbon, SPM = suspended matter, chl a = chlorophyll a, chl b = chlorophyll b).

4. Discussion

Before addressing the aims of this study (the effect of the marsh, the comparison between parameters and the difference between the seepage and bulk phase) the quality of the data must be assessed. Indeed, the water vs. the chloride balances showed differences that could indicate error. However, the concentration profiles indicate that the marsh can to some degree load and unload salt. Sediment physical properties, evapotranspiration and elevation are important determinants of salinity variation in pore water (Morris, 1995). This confirms that it is unsuitable to use chloride as a conservative tracer in single tidal exchange studies. Spurrier and Kjerfve (1988) calculated that at least 34 cycles need to be measured in order to quantify the error of tidal exchange balances.
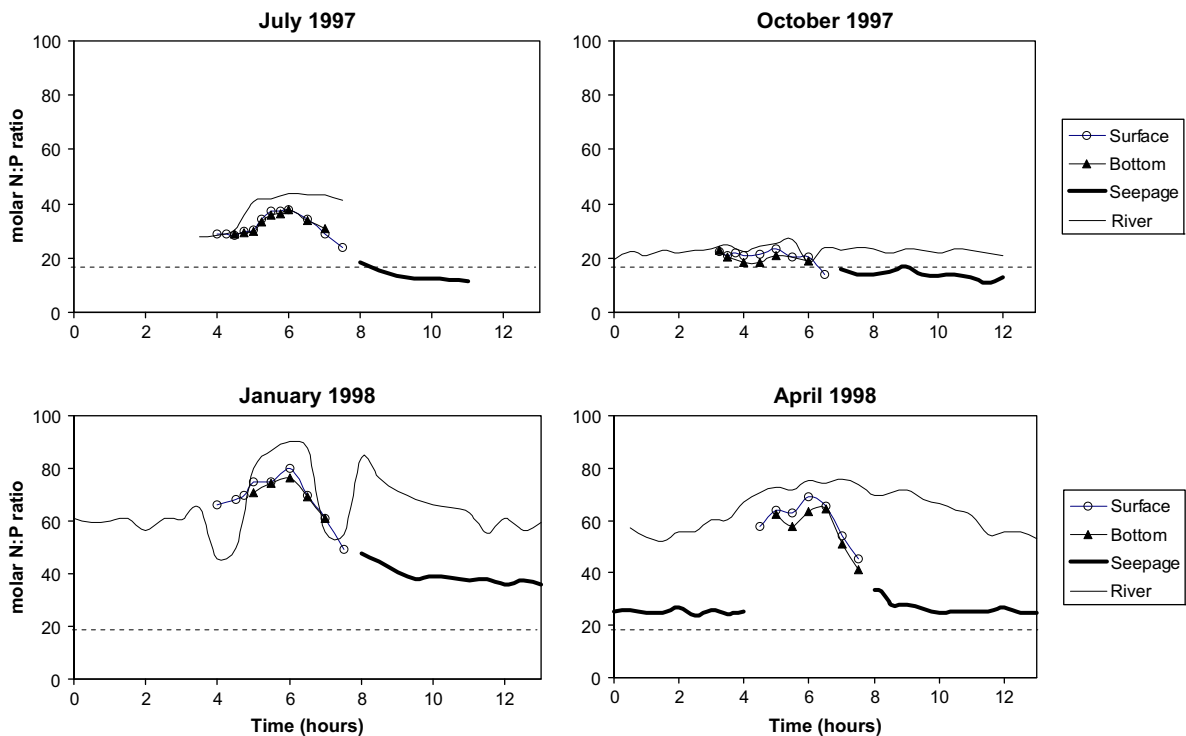
Fig. 6. Variations of the N:P ratio during the conducted tidal cycles. The Redfield ratio characterising the need for diatom growth is indicated in the dashed line.
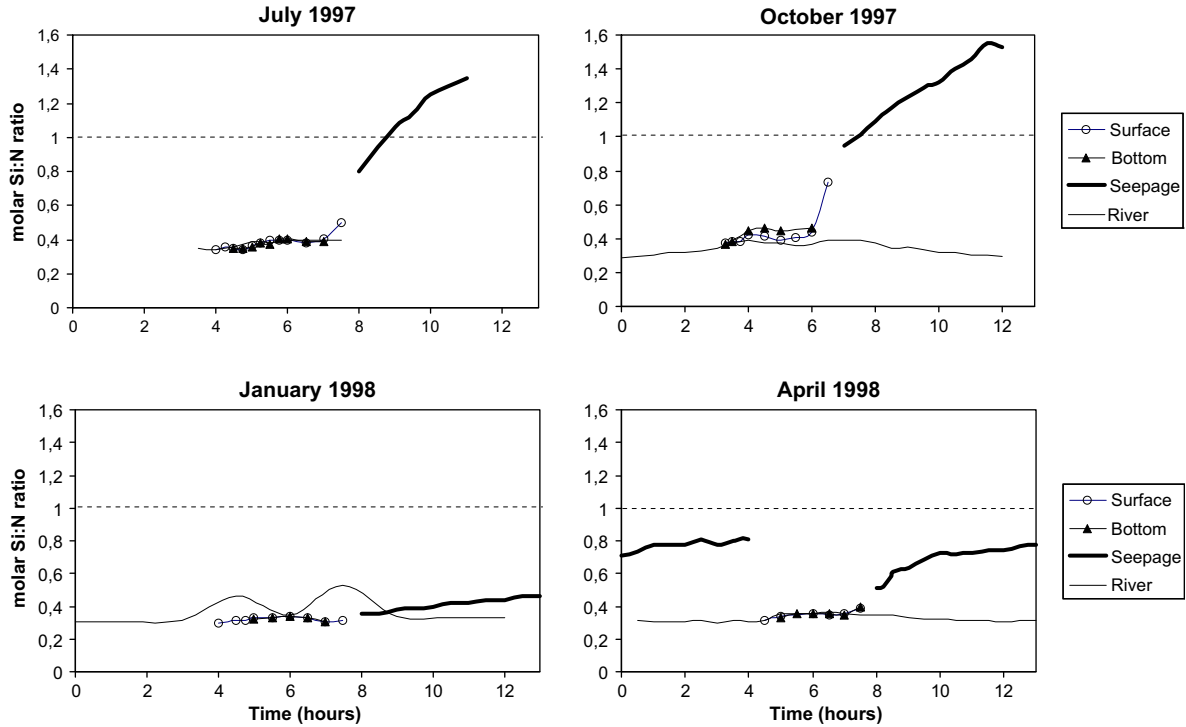
Fig. 7. Variations of the Si:N ratio during the conducted tidal cycles. The Redfield ratio characterising the need for diatom growth is indicated in the dashed line.

This implies that the error of the presented 4 balances remains unclear. The mass balances in April were probably biased by a rip current. In the three other cases the water balances showed less than 3% imbalance, which is a very good fit for traditional mass-balance studies, if compared with other studies (e.g. Dankers et al., 1984; Gribsholt et al., 2005).

The oxygenating effect was the most conspicuous impact of the marsh on the flood water. In the river, the main source of aeration is input from the atmosphere (Soetaert and Herman, 1995). On the marsh, this is different, since in a shallow layer of flooding water, primary production is not hampered by light limitation as it is in the river. The residence time of the water on the marsh surface is too low
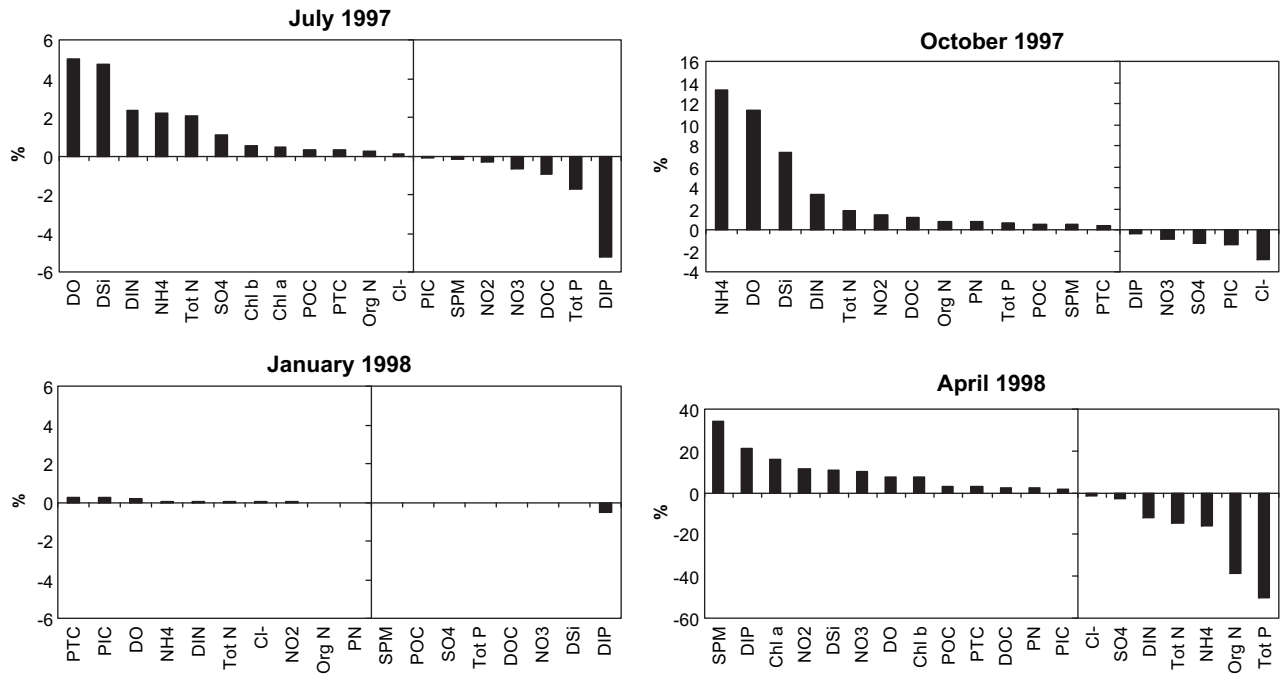

Fig. 8. Contribution (in%) of the seepage phase to the net (non conservative) balance, determined through comparing the net total balance with a conservative and a non-conservative seepage phase. Positive values mean that the seepage added up to the net import or export. Negative values mean that the seepage counteracted the net import or export (DO = dissolved oxygen, Cl = chloride, DOC = dissolved organic carbon, DSi = dissolved silica, SO_4 = sulfate, DIP = dissolved inorganic phosphorous, tot P = total phosphorous, NH_4 = ammonium-N, NO_3 = nitrate N, NO_2 = nitrite-N, DIN = total dissolved nitrogen, tot N = total nitrogen, org N = organic nitrogen, PIC = particulate inorganic carbon, POC = particulate organic carbon, PTC = particulate total carbon, SPM = suspended matter, chl a = chlorophyll a, chl b = chlorophyll b).

to allow much local pelagic or benthic primary production that could explain the oxygenation. Besides, during all campaigns except in July, the seepage phase was predominantly sampled overnight. The oxygenation is due to the physical process of gas exchange with the atmosphere, as the oxygen poor water extends over the marsh surface in a shallow layer. As such, freshwater tidal marshes provide oxygen to the estuary, especially when the oxygen demand is high. This pattern was also observed by Gribsholt et al. (2006).

Import of nitrate and ammonium was per square meter of the same order of magnitude than in other in freshwater tidal areas (Simpson et al., 1983; Childers and Day, 1988; Bowden et al., 1991). In a 3477 m^2 corner of the Tielrode marsh, the fate and transport of ammonium was quantified in two whole-ecosystem ^{15}N-NH$_4^+$ labeling experiments in May 2002 and September 2003, showing that nitrification was one of the most important transformation processes, accounting for 17–32% of the transformed label (Gribsholt et al., 2006). This confirms our findings that the seepage water was somewhat enriched in nitrate and depleted of ammonium. Only a small amount of denitrification was found by Gribsholt et al. (2005), which seems in discordance with the import of DIN. It could be that in the labeling studies, denitrification was underestimated, as some 14% of the label was not found back, and the denitrification appeared more important when the label was added in a higher degree (Gribsholt et al., 2006).

The high chlorinity in October can explain the increase of ammonium during the seepage phase, which was recorded only then. It has been shown that salinity increases from 0 to 10 PSU, corresponding with the observed chloride increase, can markedly decrease the ammonium adsorption capacity of sediment, thus releasing it in the seepage water (Rysgaard et al., 1999).

The results indicated export for carbon. Although the sampling method was probably not adequate to collect all of the coarse vegetation debris that was floating around, especially during the high flooding in April, the seepage phase was depleted of particulate carbon. DOC on the other hand showed export. The role of primary production on the marsh is ambiguous. Carbon is produced by marsh plants, and storm events can have a drastic effect on the export of this production (e.g. Roman and Daiber, 1989), but vegetation also stimulates sedimentation of particulate matter (Rooth et al., 2003). The import rates of SPM correspond with sedimentation rates between 0.84 kg m^{-2} a^{-1} in April and 5.91 kg m^{-2} a^{-1} in October. These relatively low values are typical for old, elevated marshes (Temmerman et al., 2005), such as the Tielrode marsh.

Silica plays a key role in the symptoms of eutrophication of coastal waters (Smayda, 1997). In the lowest reaches of the Scheldt estuary silica can be limiting for diatom blooms (Van Spaendonk et al., 1993). Therefore the observed export of the marsh needs attention. Clearly the winter situation was totally different from the other seasons (Figs. 4 and 5), showing some import and a constant concentration level throughout the tidal cycle. The export values of the other seasons (Table 2) correspond with 4–27 mM Si m^{-2} d^{-1}, taking into account a marsh surface of 10 ha. These values are much higher than the modeled mass transfer between muddy sediment and water (1.7 mM Si m^{-2} d^{-1}) in the adjacent coastal zone (Vanderborght et al., 1977). Increasing salinity is associated with higher silica dissolution (Yamada and d'Elia, 1984), so the salinity gradient is unlikely to explain the higher fluxes in the marsh. Efflux of silicic acid from sediments has been shown to be dependent on biogenic (i.e. diatom) deposition (Yamada and d'Elia, 1984). Drying creeks at low tide may well act as a trap for diatoms. The high export rates are probably related to regeneration of deposited biogenic matter. The fact that no export was noted in winter, when diatoms are nearly absent (Muylaert et al., 2000), sustains this hypothesis.

The export of DSi is only one aspect of the silica processing of the marsh. Struyf et al. (2006) revealed that the strong export of DSi is a result of the recycling of imported biogenic silica in the marsh. The import that was found for chlorophyll is in accordance with these findings, as this suggests that diatoms are imported to the marsh. The processing of Si in the marsh is however not at all restricted to diatom recycling; vegetation, especially reed (Phragmites australis) plays a major role in transforming BSi to DSi (Struyf et al., 2005b).

Tidal input/output studies are a relatively simple tool to combine several aspects of ecological functioning of marshes, offering possibilities not only to compare them, but also to rank them in order of importance regarding their effect. This can only be achieved if standards for comparison are available, for instance in the form of ecological objectives. These are in the process of construction, but already the nutrient ratios provide opportunities to assess the relative importance of estuarine immissions.

A modeled reconstruction of the water quality history showed that in the seventies, when the water quality was very deteriorated, yearly values of N:P near the marsh (Temse) were below 16 (Billen et al., 2005). Since then the ratio showed an increase to more than 60 at the end of the nineties. The Si:N ratio decreased from more than 1 in the beginning of the fifties to less than 0.4 at the end of the nineties. These results are confirmed by the observed trends in the downstream part of the estuary: the Western Scheldt. Here the N:P ratios more than doubled from 1980 to 2002, due to the differences in the reduction rate of DSi (1.2% yr^{-1}), DIN (1.7% yr^{-1}), and DIP (5.4% yr^{-1}), while the Si:N ratio varied from 0.2 to 0.4 (Soetaert et al., 2006). These trends were attributed to more DSi retention in the drainage network as its quality gradually improved, and the human effort to restore water quality by water treatment plants, resulting in higher efficiency in reducing the P load, as it originates mainly from point sources (Billen et al., 2005). The studied marsh had a decreasing effect on the N:P ratio, counteracting in fact the increasing trend in the estuary. This is because the marsh is relatively more efficient in transforming N than P, when compared with the human effort, thus providing a measure to restore water quality that is complementary to the effect of water treatment plants. Also the negative Si:N trend in the estuary was countered by the marsh, even in a stronger way, as DSi and DIN contributed both and about equally to the increase of the ratio in the seepage water.

The nutrient ratios in the Scheldt showed seasonal variation: in the estuary, near the marsh, the N:P ratio ranged in 1997–1998 between roughly 100 in winter and 20 in summer and Si:N between 0.5 in winter and 0.2 in summer (Van Damme, unpublished results). The results of the river profiles reflect these variations, meaning that in summer, nitrogen limitation can still occur, and that potential DSi limitation is prominent year round and is maximal in summer. The marsh had its most prominent effect on the Si:N ratio (Table ratio) when the concentrations of both DIN and DSi in the river were low (Table 2).

Primary production in the Scheldt estuary is however not primarily limited by nutrients, but by light (Soetaert et al., 1994). Although it is known that nearly all the sediment input from the watershed results from anthropogenic activities such as tillage (Van Oost et al., 2000; Van Rompaey et al., 2001), the relation between estuarine hydrology and SPM concentration is not yet fully understood. Therefore it is not possible to assess the importance of marshes in trapping sediment.

Acknowledgements

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