Fluxes and major transport routes of Arsenic in the Scheldt estuary

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Abstract

The estuary of the Scheldt was monitored for As during seven seasonally spread sampling campaigns. The resulting data indicated that As did not behave conservatively in the estuary; an important mobilisation of As was observed from the river up to halfway the estuary. Both input flux (from river to estuary) and output flux (from estuary to coastal zone) of dissolved As (As_d) were calculated from statistical interpretations of the longitudinal profiles. The size of the input flux changed equally to the river discharge, being at its highest in winter, during flood period, and at its lowest in summer, during dry period. The same could not be said for the output fluxes; in fact, as a consequence of the mobilisation, there was a large discrepancy between input and output fluxes and these differences appeared to depend largely on the season. In summer and early autumn, the estuary exported three times more dissolved As to the sea than it received from the river. In winter and spring, this amount was barely double. The additions in dissolved As during each sampling period were quantified spatially by applying an estuarine analogue of 21 sequential tanks assumed to be homogeneous, as well as by statistical estimates and calculations of dilution in each tank. A second model was used to model particulate As (As_p), dividing the estuary into four characteristic zones, in each of which the movements of suspended particulate matter (spm) were well defined. Since particulate particles are mainly transported as associated to suspended matter, the major routes of particulate As transport in each box could be determined from the knowledge of this spm transport. They appeared to be longitudinal, in downstream direction, together with a large flux of sedimentation of continental material in the 2–10 salinity zone. Such sedimentation greatly reduced the flux of particulate As to the coastal zone; the flux to the sea was only 16% of the initial particulate As flux from the river. By combining the findings of both models, literature data on As biogeochemistry and seasonal observations, some transport routes additional to the spm transport were suggested.

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Keywords: Arsenic; Mobilisation; Estuary; Input and output; Fluxes; Mass balance; Processes

1. Introduction

In 1980, a report of the German Council of Environmental Advisors concluded that knowledge...
on the effects of pollution by certain harmful substances was limited. These substances could cause long-term and perhaps irreversible damage as a result of their chronic toxicity. The Council also concluded that: (1) a successful environmental protection policy for the North Sea had to be based on the "precautionary principle" and (2) that protection of the North Sea was only possible through international co-operation. In 1984, in Bremen, the first International Conference on the Protection of the North Sea was held. Its aim was to ensure more efficient and effective implementation of the existing international rules on the reduction of both direct and indirect emission loads to the North Sea—agreed on at the Treaties for the Protection of the Marine Environment (OSPARCOM—Oslo 1971, Paris 1974). On the 2nd North Sea Conference (London 1987), it was agreed that conclusions about the state of the North Sea should be science based and that the preparatory work should produce comprehensive quality status reports (QSRs) of the North Sea environment. Meanwhile, policies have expanded into instruments such as the Water Framework Directive, 2000/60/EC and the Sixth Environment Action Programme of the European Community (2002), needed to effectively set environmental objectives and priorities for sustainable development, and to give strategic direction to the European Commission’s environmental plans over the next decade.

Even though the North Sea Conference QSRs are valuable documents in the sense that they describe the state of the art of most of the dangerous contaminants in the sea, they hardly include information on arsenic (North Sea Quality Status Report, 1993, 2000); data on dissolved As are limited to observations in the Strait of Dover, the Southern Bight and off the Dutch coast, data on the element in sediments are limited to the northern and eastern areas of the North Sea. Although the observed concentrations are similar to the background concentrations in the Atlantic waters, the OSPAR Strategy with regard to Hazardous Substances (OSPAR, 1998) classified arsenic in the list of candidate substances, with prioritisation for revision of the List of Chemicals for Priority Action. In this publication we aimed at making a sketch of the transport of As through the Scheldt estuary. Our goal was to (1) estimate the fluxes of the element to the Southern Bight of the North Sea and (2) elucidate the cycling routes that dominate the As transport in the estuary.

2. Study location

The North Sea is situated on the continental shelf of northwest Europe. It opens both to the north and to the south into the Atlantic Ocean. Its coastline has undergone considerable changes due to human intervention, such as the development of towns and harbours, building of ports, industries and coastal protection structures. Still, it mainly consists of sandy beaches and dunes with numerous estuaries (e.g., Scheldt, Rhine, Meuse, Humber and Thames). Next to atmospheric deposition, it is these estuaries that represent the most important transport routes of anthropogenic compounds to the sea.

While in terms of water discharge, the Scheldt river is not of primary importance to the North Sea, the river and its tributaries drain a total of 21,600 km², with approximately 7 million people and large industrial areas in the river basin. In other words, the Scheldt River and its tributaries are used as major drains for both industrial and domestic waste, a substantial part of which has not been purified in a wastewater treatment plant before discharge. Among other things, this leads to high nutrient and pollutant loads in the river as well as in part of the estuary. A significant effect from the Scheldt on the pollutant load in the North Sea is therefore anything but unlikely (Baeyens et al., 1998a).

3. Materials and methods

3.1. Sampling and analysis

Seven sampling cruises on board of the RV Belgica or the RV Zeeleeuw were organised in the time period 1997–2001. The cruises were seasonally planned, so as to be able to account for processes induced by differences in biological and hydrological conditions. Sampling was realised on 11 stations on the estuary itself and on one station 10 km outside the estuary, under the direct influence of the Scheldt’s outflow (Fig. 1). These points were sampled during one and the same tidal cycle, from
Vlissingen at high tide to Antwerp at low tide. Sampling dates and prevailing hydrodynamic conditions during the cruises are summarised in Table 1. Fresh water flows were provided by the Ministry of the Flemish Community (Ministerie van de Vlaamse Gemeenschap–Departement Maritieme Schelde) and were measured at Schelle.

Since the Scheldt estuary is a well-mixed estuary, with only limited vertical stratification (Baeyens et al., 1998a), only surface samples were collected. This was done either by hand from a rubber boat, or using 10-l go-flow bottles when weather conditions were bad. One-liter acid-cleaned HDPE bottles were thoroughly rinsed and filled with the estuarine water. Immediately upon collection, the samples were transferred to PTFE filter devices on board of the ship and filtered under N₂ pressure on 0.4-μm polycarbonate filters (Nuclepore), to separate the dissolved from the particulate. Samples of the dissolved phase were acidified to 1% HCl suprapur and refrigerated, while those of the particulate phase were stored at −20°C. A l lm a t e r i lu s e df o r collection or processing of samples had been thoroughly cleaned with detergent and acid before use. Contamination and sample preservation were checked at every sampling occasion by adding controls in the form of blanks and spiked samples to every sampling batch. Contamination or degradation problems were never encountered.

Analysis of dissolved As (Asₐ) was performed by Hydride Generation–Atomic Fluorescence Spectrometry (PS Analytical Excalibur 10.003), after 30 min of reacting with a mixture of KI and ascorbic acid (PS Analytical, 1997). Filters were dried in a laminar flow, weighed to determine the suspended particulate matter load and acid-digested overnight in a mixture of H₂O₂ p.a. and subboiled HNO₃, at

<table>
<thead>
<tr>
<th>Cruise</th>
<th>Date</th>
<th>Qₘ (m³ s⁻¹)</th>
<th>Mean T (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B9716</td>
<td>14 Jul 1997</td>
<td>88</td>
<td>20.2</td>
</tr>
<tr>
<td>B9809</td>
<td>27 Apr 1998</td>
<td>123</td>
<td>12.0</td>
</tr>
<tr>
<td>B9820</td>
<td>22 Sep 1998</td>
<td>138</td>
<td>16.2</td>
</tr>
<tr>
<td>B9905</td>
<td>23 Feb 1999</td>
<td>307</td>
<td>5.4</td>
</tr>
<tr>
<td>B9910</td>
<td>14 Apr 1999</td>
<td>148</td>
<td>11.2</td>
</tr>
<tr>
<td>ZL0105</td>
<td>15 May 2001</td>
<td>140</td>
<td>15.3</td>
</tr>
<tr>
<td>ZL0107</td>
<td>26 Jul 2001</td>
<td>109</td>
<td>20.4</td>
</tr>
</tbody>
</table>
105 °C. Analysis for particulate As (As\textsubscript{p}) was performed by Inductively Coupled Plasma Mass Spectrometry (VG PlasmaQuad II). A choice of CRMs was added to every sample batch, both for particulate as for dissolved As (seawater CRMs NASS-4, SPS-SW1 and SPS-SW2 and marine sediments BCSS-1 and MESS-2 from the National Research Council of Canada; estuarine sediments CRM277 and 1646a and plankton CRM414 from the Standard, Measurement and Testing programme of the European Commission). Accuracy of the HG-AFS analysis was regularly checked and validated through participation in Quasimeme (Quality Assurance of Information for Marine Environmental Monitoring in Europe) laboratory performance/intercomparison exercises.

3.2. Dissolved flux calculations

The degree of mixing between river and sea water in estuaries is generally evaluated by use of a tracer, i.e., often a dissolved constituent of known or assumed conservative behaviour. In practice it is convenient to use salinity as a tracer. Assuming that the concentration of the compound of interest and the freshwater flow at the riverine-end-member remain constant within the time scale of mixing in the estuary, and according to the model of Boyle et al. (1974), the flux \( R_X \) of a dissolved constituent \( X \) across an isohaline \( S \) can be defined as

\[
R_X = Q_w \left[ C_X (S - S_r) \frac{dC_X}{dS} \right]
\]

(1)

with \( Q_w \) as the initial river water discharge, and \( S_r \) as the salinity at the riverine end-member and \( C_X \) the concentration of compound \( X \). The variation of this flux with salinity then becomes

\[
\frac{dR_X}{dS} = - Q_w (S - S_r) \frac{d^2C_X}{dS^2}
\]

(2)

When constituent \( X \) behaves conservatively, i.e., when variations in concentration of the compound are only a consequence of hydrodynamic mixing processes, this variation of the flux with salinity equals zero; \( C_X(S) \) is linear over the mixing range. In this case, for any salinity belonging to the curve of \( C_X(S) \), the term in Eq. (1) in brackets is constant and equal to the intercept \( (C_{X,0}) \) of the straight line extrapolated from this curve, with the \( y \)-axis at \( S = S_r \). The flux \( R_X \) can thus be calculated as the product of the river discharge \( Q_w \) and this concentration \( C_{X,0} \).

When a substance \( X \) behaves conservatively, its input flux from the river to the estuary, will equal its output flux from the estuary to the sea. However, when the compound does not behave conservatively, the realistic output flux will be different from the one calculated. A more exact calculation would then require a hypothetical dilution line that would explain \( X \)’s concentration at the mouth of the estuary, if only conservative mixing were occurring. Officer (1979) proposed to calculate this theoretical riverine end-member concentration as the so-called ‘effective zero salinity end-member concentration’ \( (C_{Cezem}) \), by extrapolating to salinity 0, from a linear regression line that is fitted through data points in the high salinity range of the estuary. It should, however, be noted that this approach is again based on the steady state assumption of river discharge and concentration of \( X \) at the fresh water end-member remaining constant over the time scale of mixing. Non-conservative behaviour can then be demonstrated from the difference between input and output flux not being equal to zero, and from deviations from the linear mixing curve.

3.3. Particulate flux calculations

Since particulate constituents are transported through the river and estuary while associated with suspended particulate matter (spm), the fluxes of those particulate constituents are logically directly linked to those of the spm. The main point of departure to the calculation of the Scheldt estuarine As\textsubscript{p} fluxes in this study was the box-model of Baeyens et al. (1998b). This model divides the estuary into four physicochemical zones:

- **Zone I:** salinities from 0 to 2, clay bottom sediments, low sedimentation rates and oxygen depletion throughout most of the year.
- **Zone II:** salinities of 2 to 10, turbidity maximum arising from convergence of the downstream oriented freshwater current and the upstream oriented bottom current from tidal action, high sedimentation rates, fine grain sediments and oxygen undersaturation in summer.
- **Zones III and IV:** characterised by coarse bottom sediments, further subdivided into...
– 10 to 20 salinity zone, where oxygen gradually increases due to re-aeration;
– 20 to 27.5 salinity zone, the mouth of the estuary, always aerated.

Estimates of spm flows through each of these zones, sedimentation and resuspension fluxes in each and lateral input in zone I, have been reported by several authors (D’Hondt and Jacques, 1982; Baeyens et al., 1998a; Van Eck, 1991) and are summarised in Fig. 7. Sedimentation is represented by two separate fluxes: one related to continentally derived spm that settles right after entering the considered box and a second one for the sedimentation of upstream transported spm, settling down after mixing with residual particles. The boxes are regarded upon as homogeneous and it is assumed that the sediment mass balance has not changed substantially over the last decade.

4. Results and discussion

4.1. Daily dissolved As output flux

In contrast with several reports of As behaving conservatively in estuaries, e.g., in Charlotte Harbour (Froelich et al., 1985) and in the Tejo estuary (Andreae et al., 1983), the longitudinal dissolved As (Asd) profiles from this study revealed at first glance that this was not the case in the Scheldt estuary. On the contrary, the profiles showed an important positive deviation from the theoretical values.

![Fig. 2. Profiles of Asd (μg l⁻¹) versus salinity. Filled diamonds (●) represent the data points that were used for the calculation of the C_{ezsem} (effective zero salinity end-member concentration), the theoretical riverine end-member concentration that would have explained the As concentration at the mouth of the estuary, when only dilution processes would have been of importance. This concentration was obtained from extrapolating to salinity 0, from a linear regression line that was fitted through data points in only the high salinity range of the estuary; open diamonds (○) correspond to data points that deviated from theoretical mixing.](image-url)
mixing/dilution curve for every studied period. Concentrations gradually increased from the river up to about halfway the estuary, then decreased again further on to the mouth. Therefore, it was obvious that fitting a linear relationship to the As data over the entire estuary, would not have been meaningful for any of the cruises. Linearity was however proven significant at the 95% confidence level, over a limited salinity range at the marine end-member (Fig. 2). This salinity range was determined as the series with the lowest residual variance in regression analysis (Table 2). Despite differences in hydrodynamic conditions between sampling dates, we observed that geographically, As started behaving conservatively from station S07 onwards, at 35 km from the mouth. Using the approach of Officer (1979), this linear trendline could then be regarded upon as the theoretical riverine dilution that would result in concentrations at the mouth of the estuary equal to the concentrations observed. As such, the effective zero salinity end-member concentration ($C_{ezsem}$) and the associated As$_d$ fluxes—out of the estuary—could be calculated from this trendline for each time period.

4.2. Daily dissolved input flux

While the fluxes calculated from the $C_{ezsem}$’s provided estimates of the amounts of As$_d$ that were actually transported from the estuary to the sea, the measured/realistic riverine As concentrations were much lower than these $C_{ezsem}$’s. Thus, the fluxes of As out of the estuary did not match the amounts of As$_d$ that were supplied to the estuary by the river. Such riverine As$_d$ fluxes could have been deduced from the effective concentrations at the riverine end-member, but while the most upstream sampling point in our study was Antwerp and although the salinity at this station was only around 0.5 in all periods except for one, this sampling point should be considered as a part of the estuarine mixing zone. Therefore, we opted for estimating the effective riverine As concentrations from a function that described the separate longitudinal profiles; all optimal fitted curves were of the quadratic polynomial kind and were proven statistically significant at the 95% confidence level (Fig. 3). From these polynomial curves, the intercept with the Y-axis at salinity 0 was regarded as the effective riverine As concentration, $C_{As,0}$ (Table 3). Note that extrapolating from curvilinear relationships should be performed with extreme caution. As a check for these extrapolations, and because the fitted curves were second-order polynomials, a second set of assessments was made by fitting a linear relationship through only the low salinity data points, i.e., salinities lower than 10. Five out of seven of these linear relationships were statistically significant. For the B9910 cruise, the correlation was rather poor, the regression coefficient was only 0.4977 and $P$ was therefore large. Nevertheless, all riverine concentrations calculated from both the linear and the polynomial fits were compared and matched satisfactory (paired $t$-test), which confirmed that the estimates could readily be used for calculation of the riverine fluxes. Since the polynomial fits in general were slightly more accurate judging from the regression coefficients, and since they included more data points, the riverine As concentrations estimated from the polynomials were used for further calculations. As an additional reliance, the estimated riverine concentra-

<table>
<thead>
<tr>
<th>Cruise</th>
<th>Date</th>
<th>Salinity range</th>
<th>$C_{ezsem}$ (µg l$^{-1}$ As)</th>
<th>$F$</th>
<th>$P$ [z$F_{crit}$, 95%]</th>
<th>Daily output flux (kg day$^{-1}$ As)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B9716</td>
<td>Jul 1997</td>
<td>22.5–31.9</td>
<td>8.70±0.42</td>
<td>251.4</td>
<td>0.0040</td>
<td>66±7</td>
</tr>
<tr>
<td>B9809</td>
<td>Apr 1998</td>
<td>18.3–32.8</td>
<td>4.97±0.19</td>
<td>296.0</td>
<td>0.0004</td>
<td>53±6</td>
</tr>
<tr>
<td>B9820</td>
<td>Sep 1998</td>
<td>19.8–33.5</td>
<td>7.10±0.57</td>
<td>54.36</td>
<td>0.018</td>
<td>85±11</td>
</tr>
<tr>
<td>B9905</td>
<td>Feb 1999</td>
<td>19.8–30.1</td>
<td>3.74±0.096</td>
<td>420.0</td>
<td>0.0024</td>
<td>99±10</td>
</tr>
<tr>
<td>B9910</td>
<td>Apr 1999</td>
<td>15.8–28.6</td>
<td>2.92±0.064</td>
<td>333.2</td>
<td>0.0030</td>
<td>37±4</td>
</tr>
<tr>
<td>ZL0105</td>
<td>May 2001</td>
<td>14.2–28.2</td>
<td>3.88±0.12</td>
<td>404.8</td>
<td>0.0025</td>
<td>47±5</td>
</tr>
<tr>
<td>ZL0107</td>
<td>Jul 2001</td>
<td>16.9–30.1</td>
<td>5.57±0.27</td>
<td>121.3</td>
<td>0.0081</td>
<td>52±6</td>
</tr>
</tbody>
</table>

The uncertainty on the fluxes was calculated from the uncertainties on regression and freshwater flow. The latter was estimated at 10%.
tions matched observations that were made in the Scheldt itself (De Gieter, unpublished) and these concentrations varied only slightly from one season to another.

4.3. Comparison in- and output fluxes

The resulting input fluxes varied from 18 to 51 kg day\(^{-1}\) As\(_d\). The highest input flux coincided with the

Table 3
Statistical parameters of polynomial (over the entire range) and linear (salinity<10) trendlines of dissolved As in function of salinity and corresponding input fluxes

<table>
<thead>
<tr>
<th>Cruise</th>
<th>Date</th>
<th>Polynomacl</th>
<th>Linear</th>
<th>Daily input flux (kg day(^{-1}) As)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_{As,0}) (µg l(^{-1}))</td>
<td>St. dev.</td>
<td>F</td>
<td>P [≤(F_{crit}), 95%]</td>
<td>C(_{As,0}) (µg l(^{-1}))</td>
</tr>
<tr>
<td>B9716</td>
<td>Jul 1997</td>
<td>2.38</td>
<td>0.099</td>
<td>267.7</td>
</tr>
<tr>
<td>B9809</td>
<td>Apr 1998</td>
<td>2.08</td>
<td>0.025</td>
<td>657.8</td>
</tr>
<tr>
<td>B9820</td>
<td>Sep 1998</td>
<td>2.76</td>
<td>0.096</td>
<td>76.4</td>
</tr>
<tr>
<td>B9905</td>
<td>Feb 1999</td>
<td>1.92</td>
<td>0.050</td>
<td>41.4</td>
</tr>
<tr>
<td>B9910</td>
<td>Apr 1999</td>
<td>1.94</td>
<td>0.10</td>
<td>10.0</td>
</tr>
<tr>
<td>ZL0105</td>
<td>May/01</td>
<td>2.09</td>
<td>0.042</td>
<td>110.0</td>
</tr>
<tr>
<td>ZL0107</td>
<td>Jul 2001</td>
<td>2.19</td>
<td>0.11</td>
<td>56.2</td>
</tr>
</tbody>
</table>

The uncertainty on the fluxes was calculated from the uncertainties on regression and freshwater flow.

Fig. 3. Fitted trends for calculation of C\(_{As,0}\), the riverine As\(_d\) concentrations (µg l\(^{-1}\)) versus salinity. (@ points that were included in the linear relationship).
high freshwater flow observed in winter (307 m$^3$ s$^{-1}$, cruise B9905), while the lowest was observed in the period with the lowest freshwater flow (88 m$^3$ s$^{-1}$ in summer, cruise B9716). The fact that the size of the input As flux changed equally to the freshwater flow was not surprising, since the variations on the estimated riverine As concentrations were relatively small, average (2.2±0.3) µg l$^{-1}$ As$_{d}$. It could therefore be stated that the most important factor controlling the input flux of As$_{d}$ in the estuary was the prevailing flow of the river.

For the output fluxes, this was not the case; the maximum As flux was also found for the winter campaign, but it was followed by the late summer campaign (cruise B9820) when the river flow was not exceptionally high; it was actually even lower than in the period in which minimum output was found. This indicated that estuarine processes—and very likely seasonally influenced ones—could not be ruled out. Moreover, the output flux’s variability was large, from 37 to 99 kg day$^{-1}$ As$_{d}$, as was the variability of the $C_{e semen}$’s, from 2.92 to 8.70 µg l$^{-1}$.

Three possible explanations could be premised for the large discrepancy between input and output fluxes: (1) the existence of anthropogenic sources in-between the riverine and marine end-members on the one hand, and the sampling point from where conservative behaviour was observed on the other hand; (2) the Scheldt estuary is characterised by relatively long flushing times, between 1 and 3 months (Soetaert and Herman, 1995; Steen et al., 2002) and thus time for chemical and physical transformations such as release of As from spm or diffusion from porewaters is abundant; (3) arsenic accumulated in sediments could be released over a period much longer than the period that it is brought into the estuary, as is the case for a lot of other metals (Baeyens et al., 1998c; Van Eck and De Rooij, 1993). Such diffusion from sediment is moreover reported to be of large importance to the As cycling in the Thames and Humber estuaries (Kitts, 1991; Millward et al., 1997).

### 4.4. Seasonal and yearly dissolved fluxes

From the large differences between input and output fluxes, or between $C_{As,0}$ and $C_{e semen}$, it could be deduced that deviations from conservative behaviour, despite their omnipresence in all periods, varied largely in extent over the seasons. Summer and early autumn output fluxes had tripled compared to their input fluxes, while the increases in As$_{d}$ along the estuary were less marked in spring and in winter; in these latter seasons, the output fluxes were barely twice the amount of the input fluxes. By rearranging the fluxes according to season, we noticed large comparabilities between the separate observations within a single season. This again strengthened the assumption of significant importance of seasonal effects. It also allowed us to estimate the yearly As$_{d}$ fluxes by averaging over the seasons (Table 4), instead of averaging over the separate flux values (no equal number of observations was made in low discharge, mean flow and flood conditions). On a yearly basis, the amount of dissolved As that is introduced into the estuary by the river was estimated at 11.6×10$^{3}$ kg year$^{-1}$; the annual output to the sea at around 26.3×10$^{3}$ kg year$^{-1}$. In other words, the Scheldt estuary is an annual source of no less than 26 tons of dissolved As to the North Sea.

#### 4.5. Spatial quantification of the additions in dissolved As

The observation described above of seasonal variations in dissolved As in- and output fluxes induced the question of whether (a) the larger increases in As$_{d}$ in summer and in autumn were due to a more pronounced mobilisation of As than in spring and winter (e.g., through reduction/dissolution of Fe- and Mn oxyhydroxides); or whether (b) rather the other way around, the smaller increases in spring and in winter were due to larger counteraction of the mobilisation process by scavenging processes (e.g., adsorption onto organic matter or clay). The primary

<table>
<thead>
<tr>
<th>Season</th>
<th>In kg day$^{-1}$ As</th>
<th>Out kg year$^{-1}$</th>
<th>kg day$^{-1}$ As</th>
<th>kg year$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Summer</td>
<td>(19.5±2.1)</td>
<td>11.6×10$^{3}$</td>
<td>(59±10)</td>
<td>26.3×10$^{3}$</td>
</tr>
<tr>
<td>Autumn</td>
<td>33.0</td>
<td></td>
<td>85</td>
<td></td>
</tr>
<tr>
<td>Winter</td>
<td>51.0</td>
<td></td>
<td>99</td>
<td></td>
</tr>
<tr>
<td>Spring</td>
<td>(24.0±1.7)</td>
<td></td>
<td>(45.7±8.1)</td>
<td></td>
</tr>
</tbody>
</table>

Table 4 Seasonal (± standard deviation) and annual As$_{d}$ transport in and out of the estuary
The key to solving this question is to have a thorough understanding of the existence and extent of the specific processes that affect As in the Scheldt estuary. Although such information is scarce at present, we believed that some features could be deduced from the patterns of As mobilisation versus geographical/morphological/hydrological area in the estuary. We therefore aimed at spatially quantifying the additions in dissolved As throughout the estuary by applying a simple estuarine analogue, similar to the one described by Steen et al. (2002). The 105 km of estuary between Schelle and Vlissingen were divided into a sequence of 21 tanks, each 5 km in length and regarded upon as homogeneous. Salinity and As$_d$ concentrations in each tank were predicted: the latter by applying the polynomial function described above, salinity S from a function between experimental salinity observations, and distance D from the mouth of the estuary. This function was of the sigmoidal kind with the form

$$S = \frac{a}{1 + \exp \left( -\frac{(D - D_0)}{b} \right)}$$

(3)

where $D_0$ is the intercept with the y-axis and $a$ and $b$ are coefficients. The experimental and predicted salinity profiles are compared in Fig. 4. From this salinity information, a representation of the theoretical dilution concentrations in each box could be drawn up: the fraction of freshwater ($\Phi_n$) in each segment $n$ was calculated as

$$\Phi_n = \frac{S_{\text{sea}} - S_n}{S_{\text{sea}} - S_{\text{fresh}}}$$

(4)

where $S_{\text{sea}}$ was the salinity of the marine end-member, $S_n$ the salinity of segment $n$ and $S_{\text{fresh}}$ that of the freshwater end-member. When only consider-

Fig. 4. Predicted (--) versus experimental (●) profiles of salinity in function of distance from the mouth of the estuary (km).
ing the mixing of the two waterbodies, the theoretical As concentrations in the segments would then equal the fraction of freshwater times the riverine end-member concentration \( C_{As,0} \) plus the fraction of seawater \((1-f_n)\) times the marine end-member concentration (we considered station 150 as the marine end-member). However, considering the difference between the measured and this theoretically diluted concentration in a segment \( n \) would have overestimated the addition in that segment, since an addition in segment \( n \) results in a large deviation from the theoretical dilution from the river to the sea, already from segment \( n+1 \) onward. Conversely, only considering the increase in effective concentration from segment \( n \) to the next, \( n+1 \) would have underestimated the addition, since then dilution from \( n \) to \( n+1 \) would not have been taken into account. Therefore, we regarded the previous segment \( (n-1) \) as a new ‘freshwater’ end-member for each segment \( n \). An equation similar to Eq. (4), then gave us the fraction of water, present in \( n \), originating from \( n-1 \)

\[
f(n-1)_n = \frac{S_{sea} - S_n}{S_{sea} - S_{n-1}}
\]

This fraction \( f(n-1)_n \) multiplied by the measured As\(_{sd}\) concentration in \( n-1 \), plus \([1-f(n-1)_n]\) times the marine end-member concentration, then yielded the As\(_{sd}\) concentration that would prevail if there would only have been dilution from \( n-1 \) onward. The realistic additions estimated in each segment were then equal to the differences between the measured and the thus calculated/theoretically diluted concentrations. The result of this approach is depicted in Fig. 5 (a—summer, high addition situation, and b—winter, low addition situation). These graphical representations indicated that the addition remained low to non-existing in the first 6–

---

\[\text{Fig. 5. (a) Estimate of dissolved As additions per segment in a period of high addition (summer—B9716); measured concentrations (●); theoretical dilution curves in each segment (−); mobilised As amounts (⋯). (b) Estimate of dissolved As additions per segment in a period of low addition (winter—B9905); measured concentrations (●); theoretical dilution curves in each segment (−); mobilised As amounts (⋯).}\]
9 segments of the model, then increased to maximum values in the segments 12 and 13, or occasionally in 10 and 11, and decreased again towards the point where conservative mixing took over. Translated to salinities, the most significant additions (i.e., additions of 0.11–0.45 $\mu$g $\text{l}^{-1}$ As$_d$) occurred between salinity 6 and 11.

4.6. Particulate As fluxes

Fig. 6 shows the longitudinal profiles of suspended particulate matter and particulate As (As$_p$) versus salinity. The trend in these profiles appeared to be more straightforward than the one for dissolved As, in the sense that the As$_p$ profiles seemed to be much more dominated by dilution of the riverine As. Nevertheless, all of these profiles were marked by an As$_p$ maximum in the low salinity region. Geographically, this maximum largely coincided with the turbidity maximum by which a substantial number of estuaries are characterised, including the Scheldt estuary.

The rather irregular shape of the particulate profiles made it hard to deal with the experimental data in an analogous way like we did for the dissolved phase. However, the As$_p$ amounts did not differ notably over the seasons; the variability in concentrations observed for the dissolved phase was quasi non-existing for the particulate phase. Therefore, in order to obtain information on the As$_p$ fluxes through the estuary, we calculated the average experimental As$_p$ concentrations within each box and over the entire dataset, and fitted them readily into the box-model of Baeyens et al. (1998b) described previously. This procedure yielded the As$_p$ concentrations summarised in Table 5 and the fluxes in Fig. 7. As could be expected from

![Fig. 6. Longitudinal profiles of turbidity in mg $\text{l}^{-1}$ (grey) and As$_p$ in mg $\text{kg}^{-1}$ (black) versus salinity.](image)

<table>
<thead>
<tr>
<th>Salinity range</th>
<th>Particulate As $\text{(mg kg}^{-1}\text{)}$</th>
<th>Sediment As $\text{a}^\text{(mg kg}^{-1}\text{)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zone I 0–2</td>
<td>40.8</td>
<td>80.2</td>
</tr>
<tr>
<td>Zone II 2–10</td>
<td>34.2</td>
<td>18.1</td>
</tr>
<tr>
<td>Zone II 10–20</td>
<td>20.6</td>
<td>6.0</td>
</tr>
<tr>
<td>Zone IV 20–27.5</td>
<td>17.8</td>
<td>11.0</td>
</tr>
<tr>
<td>Sea &gt;27.5</td>
<td>16.6</td>
<td></td>
</tr>
<tr>
<td>River$^b$</td>
<td>34.0</td>
<td></td>
</tr>
<tr>
<td>Lateral$^a$</td>
<td></td>
<td>36.0</td>
</tr>
</tbody>
</table>

$^a$ From Zwolsman et al. (1996).

$^b$ From observations in the Scheldt river (De Gieter, unpublished).
the patterns in ssm transport, the major Asp fluxes appeared to be the longitudinal fluxes in downstream direction, and the sedimentation fluxes of continental material in zone II. Indeed, this zone is known to be an exclusive site in the estuary, in the sense that the initial rise in salinity leads to the neutralisation of the mainly anionic continental particles and thus allows them to flocculate and become amenable to sedimentation (Paucot and Wollast, 1997). Plus, the net current near the bottom in this area is zero, strongly enhancing the residence time and the possibility of the flocculates to sedimentate. This sedimentation of river-borne particles greatly reduced the fluxes of Asp to the coastal zone. When comparing the Asp input flux in box I with the flux from box IV to the sea, we found an output of only 16% of the initial Asp. This finding contrasted greatly with Asd, where the flux out of the estuary had at least doubled compared to the influx.

4.7. Additional fluxes

Since they were based on sediment mass balances, the particulate As mass balances in each box added up relatively well. However, little or nothing was known on lateral inputs and so this value was represented by a rough estimate only, derived from sedimentary As concentrations. Additionally, also the probability of additional fluxes in each box should be taken into account. Several possibilities of transport not associated to ssm transport exist (e.g., adsorption of As onto or release from ssm, and diffusion from porewaters and sediment). Although at present not much is known on the processes that dominate As behaviour in the Scheldt estuary, some conclusions on this matter could be drawn from the combined findings of this study and from literature on As behaviour in other study areas. Without going into details on the individual properties of As biogeochemical processes (such explanations can be found elsewhere, e.g., in Millward et al. (1997) or Waslenchuk and Wisdom (1978)), plausible explanations for the (seasonal) changes in this study could be formulated as follows:

4.7.1. Zones III and IV

In the dissolved profiles, As exhibited conservative behaviour from salinities 14 to 22 onward, depending on the season. We could therefore deduce that chemical and physical processes which were likely to cause As to change phase were non-existing or negligible in the entire zone IV and in a part of zone III. Indeed, also the partitioning coefficient $K_{dp}$, defined as $As_p$ concentration (in $\mu$g kg$^{-1}$) over $As_d$ concentration (in $\mu$g l$^{-1}$), remained constant over these zones (average 7.8 $10^3$ l kg$^{-1}$).
Fig. 8. (a) Proposed cycling of As through Box II. (Full arrows represent As transport associated to water or spm transport; dotted arrows are associated to chemical or physical processes and indicate their importance.) (b) Proposed As cycling through Box I. (Full arrows represent As transport associated to water or spm transport; dotted arrows are associated to chemical or physical processes and indicate their importance.)
4.7.2. Zone II

The quantifications of additions in As_d indicated that the most pronounced additions occurred between the salinities 6 and 11, i.e., in the zone of the Scheldt estuary defined as zone II. K_d values throughout this zone gradually decreased by 30–40% (average from 15.4 to 10.5×10^3 kg^1/C0 1), while percentages As_d of the total As increased by 46% on average (from 14% to 60%). Both observations provided strong indications for an increased affinity of As for the dissolved phase. When looking for an explanation for the average increase of 0.20 μg l^1 As_d in this region of the estuary, processes such as changes in phase due to chemical and physical transformations, or diffusion of As from sediment came to mind. Both explanations could to some extent be backed up by additional findings, but neither of them could be proposed as the only/dominating process in this region of the estuary, nor could they explain the large seasonal differences in As_d additions. Since additions in As_d were observed in every season (despite changes in extent), we could assume that mobilisation was the dominating process throughout the year, yet that it was counteracted, to some extent at least, by the removal processes that have been identified in estuaries. The situation was even more complicated by the fact that several of these processes (e.g., the influence of Fe- and Mn oxyhydroxides) are redox bound and that redox conditions in this zone tend to change from oxygenated in winter to oxygen depleted in summer. Logically, the extent of the occurring processes could be expected to change accordingly. A plausible explanation for the seasonal changes observed in this study would be that mobilisation (from change in phase or diffusion from sediment), was counteracted by uptake of As by microorganisms in spring and by the formation of As adsorbing Fe and Mn oxyhydroxides in winter, when oxygen levels were restored. Inversely, in summer the mobilisation was likely to be enhanced by reduction and dissolution of Fe and Mn oxyhydroxides, with subsequent release of As. Summarised, this reasoning adds three fluxes additional to the ones induced by spm transport in this box (Fig. 8a).

4.7.3. Zone I

Several findings pointed towards an increased accumulation of As_p in this region: (1) a maximum in As_p at the transition of box 1 and 2, (2) maximum in turbidity (the number of available sites for adsorption increased equally), (3) higher K_d values in zone I than in zone II and (4) low to non-existing additions in As_d in this low saline zone. Several explanations for such increased affinity of As for the particulate phase could be found; river-borne particles imported in this zone are largely organically enriched through human activities (Wollast, 1988) and organoarsenic complexes are reported to exist (Ferguson and Gavis, 1972; Jenner and Browner, 1990). The sediments of zone I are characterised by high contents of clay and are capable of adsorbing both cations and anions (Lin and Puls, 2000). Nevertheless, removal of As from the dissolved phase was not observed either and therefore it seemed unlikely that the increase in As_p resulted from a change in phase, but rather from extra estuarine inputs or from early diagenesis of sediments. The small reactivity of metals bound to the sediments in this region, however contradicts the idea of diagenesis. Redox conditions here are unchanging throughout the year and render the sediments highly anoxic, creating a more ideal site for accumulation than for release. At the same time, this finding offers a plausible explanation for the extremely high sedimentary As concentrations encountered in the study of Zwolsman et al. (1996) (Table 5). Also, in this case, the influence of Fe and Mn redox chemistry should not be excluded. Contrary to the sulphide cycling, reducing conditions in the sediments of the low saline region could have caused the sediments to be an important source of reduced, dissolved Fe and Mn—and its associated dissolved As—to the water column. This reasoning equally adds several transport directions other than those associated to spm transport to the box-model (Fig. 8b).

5. Conclusions and recommendations

We calculated that on a yearly basis, the Scheldt river caused an As presence in the estuary of 22.5 ton year^1, of which 48% in the form of associated to suspended particulate matter, and 52% in dissolved forms. However, by the time this introduced As had reached the other end of the estuary, several
biogeochemical processes had taken their toll on both As’s quantity and forms. Only 8.1% remained in the particulate phase. This large affinity of As to be transported through a waterbody as a dissolved substance showed its mobility, and consequently also its bioavailability, to be very large. Knowledge of processes that tend to change the element’s distribution between the dissolved and particulate phase is therefore of great importance. The reasonings in this study on arsenic’s distribution and fluxes suggested several of such potential biogeochemical contributions in different parts of the Scheldt estuary. However, these interpretations partially relied on literature data. ‘Real-time’ data on for instance spm composition, sulphur and dissolved Fe and Mn concentrations could allow extra insights on the prevailing processes and their extents. Also, arsenic speciation data would yield such valuable information. Additionally, as a close linking was observed with the As cycle at the sediment–water interface determinations of the As content of underlying sediment would contribute to the understanding of the cycling. From the point of view of environmental quality and short time-scale geochemical cycling, however, concentrations in unstable phases would be of even greater importance. Progress in this direction is currently being made by the application of sampling techniques such as diffusive equilibrium techniques (DET) and diffusion gradient techniques (DGT).

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