Diagnosis of the transport of adsorbed material in the Scheldt estuary: A proof of concept
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A B S T R A C T

Many contaminants can attach to suspended particles. Their transport differs therefore from the transport of dissolved substances, especially in highly turbid environment like estuaries. In this paper, we show how the Constituent Age and Residence time Theory (CART – www.climate.be/CART) can be adapted to quantify in a rigorous manner the transport rate of contaminants that are present in both the dissolved and adsorbed phases.

On the basis of numerical experiment using a 1D model of the Scheldt estuary, it is shown that the interaction with suspended particles significantly affects the transport of contaminants with partition coefficients larger than $10^3$ ml/g. The mean transit time from Ghent to Vlissingen of such contaminants can reach 160 days while it is only 60 days for water and dissolved constituents. This increase of the transit time is mainly due to the fact that adsorbed constituents spend long periods of time on the bottom. Surprisingly, the downstream transport of adsorbed constituents in the water column appears more effective than that of dissolved constituents. This transport affects however a small fraction of the adsorbed constituent and is therefore not sufficient to compensate for the long resting phase on the bottom of the bulk of the constituent.

The concept and methodology introduced in this paper are easily applicable to most model studies and provide powerful and flexible tools for the detailed understanding of the transport of contaminants in estuaries. In particular, the concept of age and modified ages taking into account specifically the time spent in the water column or in the bottom provide new diagnostic tools to understand and quantify the dynamics of contaminants.

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1. Introduction

The transport of pollutants in coastal areas and estuaries is a complex process, not only because of the non linear hydrodynamics of such regions, but also because of the variable propensity of many such contaminants to attach to suspended particles.

Heavy metals are known to associate easily with particulates. Baeyens et al. (1998b) report for instance that, because of the high turbidity in the Scheldt estuary, less than 3% of the total Pb burden is present in the dissolved phase. The interaction with suspended particles is also known to play a major part in the regulation of the transport of heavy metals, like zinc, that have a large partition coefficient in the Scheldt estuary, less than 3% of the total Pb burden.

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The transport of many other contaminants, like many polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), is also linked to the dynamics of sediments (e.g. Smith et al., 2009).

The dynamics of some nutrients depends also on that of suspended particles. Many ecosystem models take therefore into account the adsorption of ammonium and phosphate on suspended solids. In addition, detrital particulate organic material is produced that tends to sink through the water column and is transported in much the same way as sediments and contaminants adsorbed on suspended particles (e.g. Arndt et al., 2011; Gregoire and Beckers, 2004; Lancelot et al., 1998).

Consequently, the transport rates and even the transport routes of many contaminants are likely to differ significantly from the general movement of the water masses. A strong and complex control by the processes responsible for the dynamics of sediments (tidal variations, sedimentation/erosion, river flow, waves, stratiﬁcation,...) is therefore expected, in addition to the many environmental and chemical parameters (pH, temperature, salinity, composition of suspended matter,...) influencing the process of adsorption/desorption (e.g. Gao et al., 2009; Liu and Lee, 2007; Tappin et al., 2010; Tremblay et al., 2005; Xu and Li, 2009).

Obviously, the settling of suspended particles is the main physical mechanism at the origin of the difference between the transport rates
of the tracers in dissolved and particulate forms. If turbulence is not strong enough to mix the water column, suspended particles tend to accumulate in the bottom layer and their transport depends therefore mainly on bottom currents (and the interaction with waves). In tidal estuaries, the dynamics is dominated by strong variations of turbulence, oscillating currents and recurrent episodes of settling on the bottom and resuspension. The net movement of adsorbed contaminants depends therefore on the particular sampling of the oscillating velocity field experienced by suspended particles during their vertical movements in the water column, taking into account a possible resting phase on the bottom. Tidal asymmetry (Son and Hsu, 2011; Uncles, 1981; Uncles and Jordan, 1980) and the time-lag effect, associated with the competitive effects of settling and mixing (Christie et al., 1999; de Swart and Zimmerman, 2009), influence therefore the net transport in a complex manner.

The resulting delay of the transport of adsorbed constituents was demonstrated in previous studies on the dynamics of radioactive pollutants in the English Channel. Boust (1999) estimated a transport timescale of particle-bound radionuclides by comparing the isotopic ratio of artificial radionuclides collected in the bottom sediments to the time evolution of the isotopic ratio of the release at the nuclear fuel reprocessing plant of La Hague. They reported apparent transit times of 10–30 years for the Western Channel and of 10–15 years for the Eastern Channel, which are much larger than the correspond timescales for the dissolved constituents estimated to a few months only by Salomon et al. (1995). Similar results are obtained by Perianez and Miro (2009) using a numerical model of the English Channel. These authors demonstrate that the transport time scales increase when the interaction with the solid phase is taken into account; while the transit time from La Hague to Dover is about 70 days for a conservative radionuclide, the transit time of $^{137}$Cs is about 2.7 years while that of $^{239,240}$Pu requires 65 years.

The previous studies aiming at the quantification of the transport rate of adsorbed constituents rely on the analysis of the correlation between the time series of the concentration of the target pollutant at the source and at the observation point where the transit time is estimated. The method basically ignores the diffusion process and introduces a systematic bias (Delhez and Deleersnijder, 2008). It is also not appropriate to capture temporal variations of the transit time. In the following, we show how the concept of age can be used to diagnose and quantify in a rigorous way the transport rate of such contaminants.

The age of a particle is defined as the time elapsed since a given origin that can be regarded as the ‘birth’ of the particle (Bolin and Rhode, 1973; Delhez et al., 1999; Monsen et al., 2002; Takeoka, 1984; Zimmerman, 1976). With an appropriate definition of this time origin, the age can be used to quantify the ventilation rate of the ocean (e.g. Bendtsen et al., 2009; England, 1995; Holzer and Hall, 2000), the transport in the atmosphere (e.g. Hall and Plumb, 1994), the horizontal transport of dissolved contaminants (Deleersnijder et al., 2001; Delhez and Deleersnijder, 2002; Orre et al., 2008; Shen and Lin, 2006), the renewal rate of water masses (e.g. de Brye et al., this issue; Gourgue et al., 2007), the fluxes of nutrients in an ecosystem model (Delhez et al., 2004b). The age of a dissolved constituent can be easily computed using the Constituent Age and Residence time Theory (CART — www.climate.be/CART), which is well suited to mathematical or numerical models (Deleersnijder et al., 2001; Delhez and Deleersnijder, 2002; Delhez et al., 1999, 2004a). The approach requires only the resolution of an evolution equation for the so-called ‘age concentration’. Since the equation for the age concentration is basically an advection–diffusion equation with a source term introducing a coupling with the concentration of the tracer and accounting for its aging, it is easily implemented in existing numerical models.

As a first extension to CART, Mercier and Delhez (2007) computed different characteristic timescales associated with the dynamics of suspended matter in the Belgian coastal zone. They quantified the horizontal transport of suspended matter using a ‘transport age’. Complementarily, they also defined a ‘resuspension age’ to assess the time spent by particles in the water column after their erosion from the bottom. Similar transport ages were also computed by Gong and Shen (2010).

In this paper, we propose a further extension of CART in order to quantify the transport rate of contaminants that are adsorbed on suspended particles. While results of the application of the method to Scheldt estuary are presented, the main objective of this manuscript is to demonstrate the feasibility of the approach and its applicability to more realistic models and case studies.

This paper is organized as follows. Section 2 is devoted to the description of the Scheldt estuary and its hydrodynamic modeling. The modules for the dynamics of suspended particulate matter (SPM) and contaminants are described in Section 3. The developments of CART are explained in Section 4. The information obtained by application of CART is discussed in Section 5. Some concluding remarks are then elaborated.

2. Hydrodynamics of the Scheldt estuary and its 1D modeling

The Scheldt estuary is located at the border between Belgium and The Netherlands (Fig. 1). The Scheldt river has a catchment basin of 22 $10^3$ km$^2$ and flows through highly industrialized and densely populated areas. As a result, the estuary receives large inputs of contaminants.

The Scheldt estuary is macrotidal with a tidal range of about 3.8 m at its mouth (Vlissingen). The tidal range remains large up to Ghent (2 m), some 160 km upstream. A system of locks in the vicinity of Ghent stops the propagation of the tidal signal upstream. Thanks to the strong tidal currents and its mean depth of about 10 m, the estuary is well mixed with a small vertical stratification appearing only occasionally in the neighborhood of Antwerp. Taking into account the lateral input from tributaries (Dender, Durme and Ruppel, including Nete, Zenne and Dijle), the total mean fresh-water discharge in the estuary is of the order of 100 m$^3$/s but with marked seasonal variations (Fig. 2); the average fresh-water input reaches 200 m$^3$/s in winter but decreases to 70 m$^3$/s or less in summer. Together with the strong tidal signal, these variations form the predominant factors determining the hydrodynamics of the Scheldt estuary (Baeyens et al., 1998a).

For the purpose of this study, we use a one-dimensional model of the tidal part of the Scheldt river and of its main tributaries with a spatial resolution of 2 km. The cross-section and wetted perimeter of each river segment are interpolated from tabulated data as a function of the water level (Laforce et al., 1977).

The hydrodynamic model is based on the continuity and momentum equations integrated over the cross-section of the river. In this approach, baroclinic processes are neglected as well as the curvature of the river channels. These parameters have however only a small influence in the Scheldt, as suggested by the results obtained in previous studies using the same model approach (De Smelt et al., 1998; Regnier et al., 1997).

The hydrodynamic model is forced at Vlissingen with observed water surface elevation extracted from the DONAR database maintained by the Dutch Ministry of Infrastructure and the Environment (Rijkswaterstaat — Ministerie van Infrastructuur en Milieu) and made available through the WATERBASE online application (http://live.waterbase.nl). At the upstream boundaries, where tidal effects are negligible, the model uses daily mean river discharges obtained from Flanders Hydraulics Research.

The hydrodynamic model has been validated against observed water surface elevations at various stations along the estuary. It provides a reliable description of the propagation and dissipation of the tidal signal in the estuary (Gypens et al., this issue).
3. SPM and contaminant transport modules

In the 1D set-up of the model, the evolution of the concentration in the water column $C_i$ of suspended matter or of dissolved or suspended contaminants can be described by means of differential equations of the generic form

$$\frac{\partial AC_i}{\partial t} + \frac{\partial QC_i}{\partial x} = A \frac{\partial (KA \frac{\partial Ci}{\partial x})}{\partial x} + A R_i + L J_i$$

where $t$ is the time, $x$ is the longitudinal coordinate, $A$ and $L$ are, respectively, the local cross-section and wetted perimeter of the river segment, $Q$ is the flow rate, $K$ is the longitudinal dispersion coefficient, $R_i$ is the production/destruction term of the constituent and $J_i$ is the net flux from the bottom.

The cross-section, the wetted perimeter and the flow rate are provided as functions of space and time by the hydrodynamic module. The longitudinal dispersion coefficient depends only on the spatial coordinate. It varies between 75 m$^2$/s and 450 m$^2$/s. The transport module has been validated against observed salinity distribution (Gypens et al., this issue).

To compute the distribution of salinity or of passive tracers that are not subject to biological or chemical transformations nor sedimentation or lateral exchanges, the above Eq. (1) is solved with $R_i=J_i=0$.

For those substances that are exchanged between the water column and the bottom, a budget equation for the bottom concentration must be considered. Here, the bottom is described by means of two layers, on top of each other. The top layer is made of freshly deposited material and is therefore assumed to be easily eroded. In the following, we refer to this layer as the ‘soft layer’. The thickness and composition of this soft layer depend on recent deposition events explicitly described by the model simulation. Underneath this layer, we consider a ‘parent layer’ made of consolidated material. This layer has prescribed composition and properties and acts as a potentially infinite source of material during episodes of strong erosion. Erosion of the parent layer occurs only when all the sediments of the soft layer have been removed.

With this description of the bottom, the bottom flux $J_i$ appearing in (1) can be decomposed as

$$J_i = E_i + E_i^p - D_i$$

where $E_i$ and $E_i^p$ are the fluxes associated with the erosion of, respectively, the soft and the parent layers and where $D_i$ denotes the flux associated with the deposition of material on the bottom. The budget equation for the soft layer can then be written as

$$\frac{\partial LS_i}{\partial t} = L(-E_i + D_i)$$

where $S_i$ is the concentration of the considered material in the soft layer. Note that bed transport of the material in the soft layer is not taken into account.

In order to take into account, yet in a very simplified manner, the variety of the properties and origins of the particles forming the suspended matter, two sediment classes are considered. These two classes are characterized by different settling velocities and can therefore be regarded as representative of the fractions of fine
(1–15 μm) and coarse (15–63 μm) sediments. The corresponding concentrations in the water column and in the soft layer are denoted by the subscript f for the fine fraction and by the subscript c for the coarse fraction. In addition, while a constant value \( w_c \) of the settling velocity is used for the coarser sediment particles, the settling velocity \( w_f \) of the finer fraction depends on its concentration in the water column through

\[
w_f = w_f^0 \left( \frac{C_f}{C_f^0} \right)^n \tag{4}
\]

where \( w_f^0, C_f^0 \) and \( n \) are appropriate constants. This formulation takes into account the effect of flocculation (e.g. Winterwerp, 2002).

Specific forms of Eqs. (1) and (3) are solved for the concentrations of the two sediments classes with specific forms for the erosion and deposition fluxes. The deposition flux is parameterized as

\[
D_i = \tau^D w_i C_i, \quad i \in \{f, c\}
\]

where \( \tau^D \) denotes the probability of deposition. When resuspension takes place, the fraction of fine and coarse sediment in the erosion flux reflects the composition of the eroded layer. Therefore, for \( i \in \{f, c\} \), one has

\[
E_i = \begin{cases} \tau^M M_i C_i & \text{if } S_f + S_c \neq 0 \\ 0 & \text{if } S_f + S_c = 0 \end{cases}
\]

and

\[
E_i^f = \begin{cases} \tau^{P_f} M_c \chi_i & \text{if } S_f + S_c \neq 0 \\ 0 & \text{if } S_f + S_c = 0 \end{cases}
\]

where \( M \) and \( M^p \) are erosion constants and \( \chi \) characterizes the prescribed composition of the parent layer. The coefficients \( \tau^D \) and \( \tau^{P_f} \) describe the influence of the bottom stress on the rate of erosion. According to the classical paradigm for cohesive sediments, it is assumed that erosion and deposition do not happen simultaneously (e.g. Parchure and Mehta, 1985; Partheniades, 1965) and that the rate of deposition and erosion are related to the critical shear stress for erosion \( \tau^{crit} \) using the classical formulation

\[
\tau^D = \begin{cases} 1 - \frac{\tau}{\tau^{crit}_f} & \text{if } \tau < \tau^{crit}_f \\ 0 & \text{if } \tau \geq \tau^{crit}_f \end{cases}
\]

\[
\tau^D = \begin{cases} 0 & \text{if } \tau < \tau^{crit}_c \\ \frac{\tau}{\tau^{crit}_c} - 1 & \text{if } \tau \geq \tau^{crit}_c \end{cases}
\]

and

\[
\tau^{P_f} = \begin{cases} 0 & \text{if } \tau < \tau^{crit,p,f} \\ \frac{\tau}{\tau^{crit,p,f}} - 1 & \text{if } \tau \geq \tau^{crit,p,f} \end{cases}
\]

The parameters used in the SPM module are listed in Table 1. These parameters were obtained from previous model studies of the dynamics of SPM in the Scheldt estuary and adjacent coastal regions (De Smedt et al., 1998; Mercier and Delhez, 2007; Van den Eynde and Fettweis, 2006; Villars and Vos, 2000) or calibrated against observed longitudinal distributions and time series of SPM (Figs. 3 and 4). Note that, in order to keep the model as simple as possible, the same rate of erosion is used for both sediment types, which is consistent with the hypothesis that bottom sediments of different sizes are packed together on the bottom and are resuspended simultaneously when a critical value of the shear stress is exceeded. The critical stress for erosion of the soft layer is also used as critical stress for deposition. A different (larger) critical stress \( \tau^{crit,p} \) controls the erosion of the parent layer. Obviously, more detailed parameterisations of the erosion process could be developed by, for instance, using different critical shear stress for the different sediment types or by introducing a functional dependency of the critical shear stress on the bottom composition.

The concentrations of the sediments at the upstream boundary are prescribed as monthly mean values extracted from the database maintained by the Flemish Environment Agency (VMM – http://www.vmm.be). At the downstream boundary, the concentration of the two sediments is relaxed towards constant values that are representative of the concentration of marine sediments (Villars and Vos, 2000).

We turn now to constituents, like trace metals or inorganic phosphorus, that can be adsorbed on SPM. Such constituents are present in the water column in both dissolved and particulate forms. While more detailed parameterizations taking into account the adsorption–desorption kinetic are used in some advanced models of the dynamics of heavy metals (e.g. Perianez, 2009) and are known be preferable in the immediate vicinity of the sources of such contaminants (Perianez, 2003), we describe here the sorption on SPM by means of two partition coefficients

\[
K_{D,i} = \frac{C_d}{C_i}, \quad i \in \{f, c\}
\]

relating the concentration \( C_d \) (μg/l) in dissolved form to the concentration \( C_i \) of the contaminant adsorbed on the two types of sediments, expressed as per unit mass of these suspended particles (μg/g). The concept of partition coefficient, which assumes an immediate and reversible equilibrium between the adsorption and desorption processes, is indeed widely used in estuaries and applies to various kinds of contaminants (e.g. Balls, 1989; Gao et al., 2011; Li et al.,

| Table 1
<table>
<thead>
<tr>
<th>List of parameters of the SPM module.</th>
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<tr>
<td>Reference settling velocity of fine sediment ( w_f^0 )</td>
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<tr>
<td>Reference concentration of fine sediment ( C_f^0 )</td>
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<tr>
<td>Parameter of the flocculation law ( n )</td>
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<tr>
<td>Critical stress for erosion of the soft layer ( \tau^{crit}_f )</td>
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<tr>
<td>Erosion constant of the soft layer ( M )</td>
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<tr>
<td>Critical stress for erosion of the parent layer ( \tau^{crit,p} )</td>
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<tr>
<td>Erosion constant of the parent layer ( M^p )</td>
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</table>

Fig. 3. Annual mean longitudinal profile of the total concentration of suspended matter plus and minus one standard deviation. Model results and observations for 2000.
Accordingly, the total concentration in the water column is given by
\[ C_t = C_d + C_{pf}C_f + C_{pc}C_c. \]  
(12)

This relation can be used to relate the concentrations of the particulate forms to the total concentration \( C_t \), i.e.
\[ C_{pi} = \frac{K_{pi}C_t}{1 + K_{pf}C_f + K_{pc}C_c}. \]  
(13)

Note that the direct adsorption of the constituent on the bottom sediments could also be taken into account in shallow regions with small concentrations of suspended sediments. In such a highly turbid environment as the Scheldt estuary, with large amounts of energy available for erosion, the mass exchanges between the water column and the bottom are dominated by the erosion/sedimentation fluxes. The direct adsorption on bottom sediments is therefore usually neglected in similar estuarine models (e.g. Gao et al., 2011; Li et al., 2010; Thouvenin et al., 2007).

Using Eq. (13), evolution equations of the general forms Eqs. (1) and (3) can be derived for the total concentration \( C_t \) in the water column and the total concentration in the soft layer \( S_t \). Ignoring the biological and chemical transformation, one takes \( R_i = 0 \) and only the mass exchange with the bottom must be parameterized. Since the deposition and erosion fluxes of the contaminant are controlled by the deposition and erosion fluxes of sediments, the parameterizations are easily adapted from Eqs. (5)-(6). The deposition flux can be expressed as
\[ D_t = \sum_{j \in \{ f \}} w_{ij}C_{pi} = \sum_{j \in \{ f \}} K_{pi}C_i, \]  
(14)

where
\[ w^* = \sum_{j \in \{ f \}} w_{i} \frac{K_{pi}C_i}{1 + K_{pf}C_f + K_{pc}C_c} \]  
(15)
is the effective settling velocity. The erosion fluxes can be written as
\[ E_i = \begin{cases} \tau_{i}M \frac{S_i}{S_i + S_j} & \text{if } S_i + S_j \neq 0, \\ 0 & \text{if } S_i + S_j = 0 \end{cases} \]  
(16)

and
\[ E_i^f = \begin{cases} 0 & \text{if } S_i + S_j \neq 0, \\ \tau_{i}M \chi_i & \text{if } S_i + S_j = 0 \end{cases} \]  
(17)

where \( \chi_i \) is the mass ratio of the studied constituent in the sediment of the parent layer.

4. Age of adsorbed contaminant

The concept of age is very flexible and can be used to study various aspects of the dynamics. To fix the ideas and clarify the presentation, consider the particular procedure required to assess the time taken by a tracer to travel from Ghent, the upstream limit of the tidal part of the river and of the computational domain, to some point downstream in the estuary, say Antwerp. Experimentally, be it in the field or numerically, one should release some tracer at Ghent and follow this tracer as it travels downstream. If one considers that a clock is attached to every tracer parcel and that the time starts to run when the parcel is released in Ghent, the time shown by the clock when the parcel reaches Antwerp is the age of this tracer parcel. Because of diffusion, the tracer parcels present at Antwerp at a given time are however a mixture of parcels with various ages, i.e. there is a distribution of ages. Here is where the basic assumptions of CART comes to play: the mean age of a set of particles must be understood as the mass-weighted, arithmetic average of the ages of the particles considered. This is the so-called age-averaging hypothesis (Deleersnijder et al., 2001; Delhez et al., 1999).

Basically, the age is a property attached to each parcel, i.e. it is a Lagrangian concept. In order to be able to compute the mean age in an Eulerian framework, CART relies on the introduction of the age concentration, which can be roughly considered as a weighted sum of the times shown by the different clocks attached to the tracer parcels present at a given location at a given time (more precisely, it is the first order moment of the distribution of the concentration in the age space). The mean age can then be evaluated as the ratio of the age concentration to the tracer concentration. The crux of the procedure is that the age concentration can be obtained as the solution of an advection–diffusion problem with a source term that couples this equation to the dynamics of the considered tracer and accounts for the aging of the tracer (Deleersnijder et al., 2001; Delhez et al., 1999).

The approach can be easily applied to diagnose the transport of the adsorbed contaminant for which a model has been derived in the previous section. Using the procedure described in (Deleersnijder et al., 2001) the evolution equations for the age concentration in the water column \( \alpha_t \) and the age concentration in the soft layer \( \alpha_c \) can be expressed as, ignoring lateral inputs,
\[ \frac{\partial \alpha_t}{\partial t} + \frac{\partial Q_{\alpha_t}}{\partial x} = A C_t \frac{\partial}{\partial x} (K_{A} \frac{\partial \alpha_t}{\partial x}) + L(E_{\alpha_t} - D_{\alpha_t}) \]  
(18)

\[ \frac{\partial \alpha_c}{\partial t} = L S_t + L(-E_{\alpha_t} + D_{\alpha_t}) \]  
(19)

where \( E_{\alpha_t} \) and \( D_{\alpha_t} \) take into account the erosion and deposition fluxes in the budget equations for the age concentration. Since the contaminant adsorbed on the suspended particulate matter settles on the bottom and is resuspended ’with its age’, one has
\[ D_{\alpha_t} = \tau_{\alpha_t} w^* \alpha_t \]  
(20)
\[ E_{a,t} = \begin{cases} \frac{\alpha_i S_c + \alpha_f}{S_c + S_f} & \text{if } S_c + S_f \neq 0 \\ 0 & \text{if } S_c + S_f = 0 \end{cases} \] (21)

Using the solutions of the above equations, the mean age of the adsorbed constituent in the water column \( a_i \) and in the soft layer \( a_s \) can be obtained from

\[ a_i = \frac{\alpha_i}{C_i} \] (22)

and

\[ a_s = \frac{\alpha_s}{S_i} \] (23)

Note that we do not consider any flux of the contaminant associated with the erosion from the parent layer since the aim is to diagnose the transport of the contaminant from Ghent to Vlissingen. Because the equations are linear with respect to total concentration of the contaminant, lateral inputs and inputs from the parent layer do not modify the dynamics of the material entering the model domain through the upstream boundaries and can therefore be ignored when diagnosing the downstream transport of the contaminant from upstream sources.

Also, since sorption is considered as an instantaneous and reversible mechanism, the age distributions of the particles of the contaminant that are present in the dissolved phase and of those that are adsorbed on the sediment are also assumed to achieve an immediate equilibrium. There is therefore no reason to consider different mean ages for the contaminant present in the different phases or adsorbed on different types of particles in the water column.

5. Results and discussion

The dynamics of suspended matter is very complex in a tidal estuary like the Scheldt. A zone of pronounced maximum turbidity is often reported at the Belgian–Dutch border, downstream Antwerp (e.g. Baeyens et al., 1998a; Muylaert et al., 2000) and is associated by Regnier et al. (1997) to the dissipation of large amounts of tidal energy in this area. This feature is well reproduced by the SPM module (Fig. 3) with a mean increase of the mean concentration from below 100 mg/l to more than 150 mg/l in a few kilometers. The peak values of the concentration of SPM computed with the model are however much higher than this and can often exceed 300 mg/l. The exact location of this maximum turbidity zone varies slightly during the year and with the spring–neap tidal cycle, which explains why the maximum is not very sharp on average.

The detailed validation of the SPM model is difficult because of the scarcity of the available data (especially in the upper estuary). In addition, one has to cope with the high variability of the concentration of suspended matter, as demonstrated by the high resolution time series of observation at Baalhoek (km 45, see Fig. 1 for a precise location) plotted in Fig. 4. Oscillations of about 100 mg/l take place at the semi-diurnal and quart-diurnal frequencies and also at the spring–neap tide frequency which reduce the significance of instantaneous measurements, as reported in Fig. 3. These oscillations are clearly associated with both the advection of spatial gradients of SPM concentrations by the tidal currents and with the succession of local deposition/resuspension events induced by the varying bottom stress. In spite of these difficulties, the model results agree reasonably well with the observations: the mean level and the timing and amplitude of the oscillations are comparable with the measurements, except at neap tide when the variability is somewhat underestimated.

In order to diagnose the downstream transport of adsorbed material, an artificial tracer is introduced in the freshwater input at the upstream boundary of the model (Upper Scheldt and Tijarm) with a constant unit concentration. At the downstream boundary, the tracer can leave the computational domain at ebb tide while the concentration of this tracer in the incoming water from the coastal zone is prescribed to be zero. Different values of the partition coefficient \( K_D \) ranging from 0 to \( 10^6 \) ml/g are considered. To simplify the discussion the same value of the partition coefficient is used for both types of sediments. For \( K_D = 0 \), the tracer cannot attach to suspended particles and the artificial tracer just tags the freshwater discharged at Ghent. The result for \( K_D = 0 \) is also representative of the dynamics of dissolved constituents.

The mean longitudinal profile of the total concentration of the artificial tracer in the water column (in dissolved and adsorbed phases) is shown in Fig. 5. The full simulation covers the whole year of 2000 but the mean profile is computed as an average over the last 6 months of the year in order to get rid of transient effects associated with the spin-up of the model. As expected, the concentration decreases steadily from Ghent to the downstream boundary of the estuary with clear dilution effects by the lateral tributaries.

Adsorption on suspended sediments has nearly no noticeable effect on the distribution of the concentration for partition coefficients smaller than \( 10^2 \) ml/g. The concentration of such tracers closely follows the dilution curve of the water itself. Note that the concentration of the water plotted in Fig. 5 only reflects the influence of the freshwater discharged at Ghent and its dilution by lateral inputs; the concentration of this artificial tracer at the sources of the other tributaries is prescribed to zero. As a result, the concentration of the water shown in Fig. 5 is not directly related to the salinity gradient in the estuary since the Zeeschelde discharge at Ghent only contributes to about 40% of the total freshwater discharge.

For partition coefficients larger than \( 10^3 \) ml/g, a clear reduction of the total concentration is observed at all locations. This is associated with the retention of the tracer in the upper estuary as a result of its adsorption on suspended particles and its deposition on the bottom. The maximum effect is observed for a partition coefficient of the order of \( 10^5 \) ml/g. Any further increase of the partition coefficient has very little influence on the total concentration in the water column.

In order to quantify this retention effect, the age of the tracer is computed according to the procedure described in Section 4, i.e., by solving the Eqs. (18)–(19). The age of the tracer is defined here as the time elapsed since its discharge at the upstream boundary (Upper Scheldt and Tijarm). The age concentration is therefore

\begin{align*}
\text{Normalized concentration [day]} &= \frac{C_t(t) - C_t(0)}{C_t(0)} \\
\text{Distance to the mouth [km]} &= 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160
\end{align*}

![Fig. 5](https://example.com/fig5.png) Mean longitudinal profile of the total concentration in the water column of the artificial tracer introduced at Ghent. The average is computed over the last six months of 2000.
prescribed to be zero at Ghent, so that the ratio of the age concentration to the concentration, i.e. the mean age, equals zero. At the outflow boundary, the tracer is allowed to leave the domain with its age and the age concentration is therefore advected seawards when the current is directed from the estuary towards the coastal zone. When the current flows into the estuary, the concentration of the tracer in the incoming water mass is assumed to be zero and, therefore, the age concentration must also vanish. This assumption introduces a systematic bias in the mean age since older particles returning into the estuary are not taken into account in the computation of the mean age. The resulting underestimation of the mean age is inherent to the limited regional coverage of the model; it is not a shortcoming of the method itself.

Fig. 6 shows the mean longitudinal profile of the age of the tracer in the water column. By definition, the age is zero at the upstream boundary. As expected, the age increases downstream and reaches its maximum value at the mouth. The local maximum at km 150 corresponds to the input of slightly older material from the Tijaraam.

It takes on average about 60 days for the freshwater to travel from Ghent to Vlissingen. This transit time is comparable to the value of the age of the freshwater computed by de Brye et al. (this issue) with their high resolution two-dimensional model in their winter scenario. The set-up used by these authors is however slightly different since they put the geographical origin for the computation of the age at the limit of the salinity intrusion, i.e. around kilometer 90, and consider only average conditions (constant discharge and tidal forcing only) while the current simulations are carried out with actual forcing data for 2000.

The mean age of tracers that can adsorb on sediments is similar to the mean age of the water itself if the partition coefficient does not exceed $10^2$ ml/g. This confirms the conclusion obtained from the analysis of the mean concentration profile (Fig. 5). For larger values of the partition coefficient, however, the transit time, i.e., the age at the downstream boundary, increases by as much as 100 days and reaches 160 days for $K_d$ values above $10^3$ ml/g! This demonstrates and helps to quantify the dramatic effect of the interaction with sediments of those contaminants that can attach to suspended matter. The effect becomes particularly significant downstream the zone of maximum turbidity, where the estuary widens. It can however also be observed in the upper estuary.

To be more realistic, Fig. 6 also shows the result obtained with the salinity dependent partition coefficient

$$K_d = 185765.29 - 15291.96 \times 333.28 \times S^2$$  \hspace{1cm} (24)

where $S$ is the salinity, derived from the analysis of the cadmium data gathered by Baeyens et al. (1999b). Cadmium is known to adsorb easily on suspended matter and this result in its efficient retention in the estuary and a mean age of more than 150 days at Vlissingen.

The mean picture does however not tell all the story, for the age also varies with time. As an example, Fig. 7 shows the variations of the age at Baalhoek during the last four months of 2000. The age of the water and of tracers with low $K_d$ values reaches a maximum value of about 60 days in October. During winter, it decreases sharply to a minimum value of 25 days, only. This is clearly induced by the variations of the freshwater discharge (Fig. 2). The maximum value of the age is obtained after a period of low discharge during the summer months. With the increase of the discharge during the winter months the age of the water decreases significantly.

The same seasonal trend is observed for the age of the tracers with larger partition coefficients. For these tracers, an additional process must however also be taken into account; the storage of the tracer in the bottom (soft) layer. During summer, less energy is available to mix the estuary and erode the bottom layer. The sediments, and the contaminants attached to them, can therefore settle and rest on the bottom for longer periods of time. This results in a less efficient downstream transport of the contaminants and relatively large value of their age. In winter, erosion events occur more regularly. The sediments do not spend much time on the bottom and are thus younger.

The age of the contaminants exhibits also large variations at the tidal frequency. For water itself and for those contaminants with a low partition coefficient, the tidal excursion is responsible for oscillations of about 10–15 days at the semi-diurnal frequency (Fig. 7). Such oscillations of the residence time and exposure time of the water are also computed by de Brye et al. (this issue) with their high resolution two-dimensional model of the Scheldt estuary. The age of contaminants with a stronger affinity for SPM exhibits much stronger oscillations reaching 50 days. These are associated with marked erosion and deposition cycles which are apparent in both observations and model results (Fig. 4). Resuspension events bring older material from the bottom layer into the water column, which increases the mean age. In addition, the erosion/deposition dynamics also reinforces spatial gradients that can be advected by the tidal currents.

The age of the contaminants with a high $K_d$ varies also significantly along the spring–neap tidal cycle. These oscillations superpose on the seasonal variability and the semi-diurnal oscillations. Their amplitude reaches about 20 days at Baalhoek. Since the SPM concentration shows large variations associated with the spring–neap cycle (Fig. 4), it is not surprising to see significant oscillations of the age at this...
frequency. In their study of the transport timescales in James River, Shen and Lin (2006) report age differences of about 10 days related to the spring–neap variations. James River is a partially mixed estuary and the regulation of the regulation of the stratification/mixing by the spring–neap tidal cycles influences the age of the water itself. In the well-mixed Scheldt estuary, the spring–neap cycle has a negligible effect on the age of the water itself but a significant one on SPM dynamics and the transport of contaminants that can adsorb on it.

To get further insight into the dynamics of the contaminants, the concept of age can be adapted to quantify specifically the time spent in the water column or the time spent in the resting phase on the bottom. Remember that the age of a particle can be understood as the time shown by a clock attached to it that starts running when the particle enters the estuary through the upstream boundary. In order to quantify the time spent by that particle in the bottom layer, one has just to start the clock each time it settles on the bottom and stop the clock when the particle is resuspended. Conversely, the time spent in the water column, disregarding the resting phases on the bottom, can be quantified using a modified age according to which the clock stops when the particle settles on the bottom and runs only when in suspension. This is easily incorporated in the Eulerian framework leading to Eqs. (18)–(19). The first terms on the right-hand-sides of these equations account indeed for the aging of the tracer, respectively, when in suspension in the water column and when resting in the bottom layer. Therefore, the modified ages that we have just introduced can be computed by dropping one of these two terms. For instance, the mean time spent in the water column is given by

$$q_i^{wc} = \frac{\alpha_i^{wc}}{\Gamma}$$

(25)

for the particles present in the water column and

$$q_i^{wc} = \frac{\alpha_i^{wc}}{S_i}$$

(26)

for the tracer in the soft layer where

$$\frac{\partial \alpha_i^{wc}}{\partial t} + \frac{\partial Q \alpha_i^{wc}}{\partial x} = A \ C_i + \frac{\partial}{\partial x} \left( K_d \frac{\partial \alpha_i^{wc}}{\partial x} \right) + L \left( E_{wc} - D_{wc} \right)$$

(27)

and

$$\frac{\partial \alpha_i^{wc}}{\partial t} = L \left( E_{wc} + D_{wc} \right)$$

(28)

where the parameterizations of the deposition and erosion fluxes $D_{wc}$ and $E_{wc}$ are easily adapted from Eqs. (20)–(21). The equations for the age $\alpha_i^{wc}$ corresponding to the resting phase are derived in a similar way by keeping the aging term in Eq. (19) and dropping it in Eq. (18).

Fig. 8 shows the mean longitudinal profile of these modified ages for $K_d = 10^4$ m$^2$/g. These modified ages are consistent with the original age computed before in that

$$\alpha_i = \alpha_i^{wc} + \alpha_i^{bot}$$

(29)

i.e., the time elapsed since the tracer entered the estuary is the sum of the time spent in the water column and the time spent in the bottom layer during the resting phases. The time spent in the bottom layer is dominant in the total age: the large values of the age of the tracer are mainly due to long resting phases on the bottom. On average, the particles leaving the estuary with a mean age of 140 days spent about 110 days in the bottom and only 30 days in the water column.

Surprisingly, the modified age $\alpha_i^{wc}$ measuring the time spent in the water column is much smaller than the age of the water itself; the latter reaches about 60 days at Vlissingen (Fig. 6) while the former does not exceed 30 days at the same location. The time series of the modified age $\alpha_i^{wc}$ at Baalhoeck for various partition coefficients confirms this observation (Fig. 9). The time spent in the water column even appears as a decreasing function of the partition coefficient. Since the horizontal transport takes place in the water column only, this means that the transport is more efficient, in terms of rapidity, as $K_d$ increases, albeit affecting only a decreasing proportion of the tracer.

To understand this paradox, one must consider that the downstream transport of contaminants does not only depend on the time spent in the water column but also on the correlation between the concentration in the water column and the horizontal current. For a tracer with a small partition coefficient that remains in suspension during the whole tidal cycle, the actual transport depends mainly on the net downstream residual current, which is directly related to the freshwater discharge. For tracers that are subject to sedimentation and resuspension, the net movement at the end of a tidal cycle depends on the sampling of the tidal currents corresponding to its intermittent presence in the water column. With asymmetric tidal currents that are one or two order of magnitude larger than mean Eulerian current the resulting net movement can be significantly

![Fig. 8. Mean longitudinal profile of the age (total) for $K_d = 10^4$ m$^2$/g, the modified age accounting only for the time spent in the water column and the modified age associated with the time spent on the bottom. The average is computed over the last six months of 2000.](image)

![Fig. 9. Time series of the modified age $\alpha_i^{wc}$ accounting only for the time spent in the water column. Data are from Baalhoeck (km 45) for various partition coefficients.](image)
larger than the downstream transport corresponding to the mean current. To demonstrate this effect, the annual mean Eulerian residual velocity is shown in Fig. 10 together with the modified Eulerian residual velocity computed by sampling the velocity field only at those times when the critical stress for erosion of the soft layer is exceeded (dashed curve).

The Eulerian residual velocity is positive in the whole estuary, which corresponds to the mean downstream transport associated with the freshwater discharge. Because of the downstream increase of the cross-section, the residual velocity is much smaller at the mouth of the estuary than in upstream sections. In all the sections, the statistical distribution of the velocity is also negatively skewed (not shown), which means that flood currents tend to be larger than ebb currents, with shorter flood phases and longer ebb phases. Between km 50 and km 120, the modified residual velocity is significantly larger than the true Eulerian residual velocity (Fig. 10). The opposite effect is observed only in small regions. A rigorous description of the transport at the residual level should rely on the analysis of the Lagrangian residual. Still, the difference between the two Eulerian residual fields provides a first explanation for the more efficient downstream transport of adsorbed contaminants when these are in suspension in the water column, as is observed in Fig. 9.

6. Conclusion

The Constituent-Oriented Age and Residence Time Theory (CART) provides a well suited formalism for the quantification of transport rates in marine systems. Previous applications of CART mainly considered water itself, dissolved constituents or suspended matter. In this paper, the concepts and tools have been extended to diagnose the transport of the contaminants that can also adsorb on sediments, which enlarges significantly the scope of CART to a wider class of environmental problems (heavy metals, PCBs, ...). In order to demonstrate the applicability of the concepts and method, the transport rate of an hypothetical contaminant along the Scheldt estuary has been quantified using CART for a wide range of values of the partition coefficient.

For adsorbed contaminants with partition coefficients of $10^2$ ml/g or smaller, the numerical experiments show that the downstream transport is not significantly affected by the interaction with suspended matter. Both the concentration profiles and age are close to the results obtained for dissolved constituents.

For larger values of the partition coefficient, adsorption on suspended matter and sedimentation are responsible for a significant retention effect affecting both the concentration profile and the age. The mean transit time from Ghent to Vlissingen can reach up to 160 days, which is about 100 days more than the transit time of water and purely dissolved substances. The large increase of the age is mainly due to long resting phases on the bottom which is only weakly compensated by a more surprisingly efficient downstream transport in the water column.

The age and transit time of dissolved and adsorbed constituents show also large seasonal variations in response to the variability of the freshwater discharge and energy available for mixing and erosion. Obviously, the results presented here form only a first estimate of the actual values for the Scheldt estuary, since a simplified 1D model is used. Further investigations are required with more realistic models taking into account the three-dimensional and baroclinic effects as well as more detailed parameterisations of the SPM dynamics. The adsorption/desorption kinetics could also be modeled explicitly. The concept and methodology introduced in this paper are however equally applicable to such model studies and provide a powerful and flexible tool for the detailed understanding of the transport of contaminants in estuaries.

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