ELSEVIER

Net fluxes of pesticides from the Scheldt Estuary into the North Sea: a model approach

R.J.C.A. Steen [a],[*], E.H.G. Evers [b], B. Van Hattum [a], W.P. Cofino [a],[1], U.A.Th. Brinkman [c]

[a]*Institute for Environmental Studies, Vrije Universiteit, de Boelelaan 1115, 1081 HV Amsterdam, The Netherlands*
[b]*National Institute for Coastal and Marine Management/RIKZ, PO Box 20907, 2500 EX The Hague, The Netherlands*
[c]*Department of Analytical Chemistry and Applied Spectroscopy, Vrije Universiteit, de Boelelaan 1083, 1081 HV Amsterdam, The Netherlands*

"Capsule": *Pesticide fluxes are modeled hydrodynamically for a complex estuarine environment.*

Abstract

A hydrological model was constructed with the commercially available modelling environment ECoS for the calculation of mixing plots of dissolved pesticide concentrations in the Scheldt Estuary. The model was based on a one-dimensional advection–dispersion equation and dispersion coefficients were calculated from measured salinity profiles. The model could correctly predict the movement of water masses within the estuary. Nominal flushing times of the estuary were calculated with the fraction-of-freshwater method and ranged between 25 and 95 days, depending on the freshwater discharge. Model calculations demonstrated that the application-related time profiles of pesticide input may well induce curvature in the calculated estuarine mixing plot even if the pesticide behaves conservatively. Calculated mixing plots were compared with experimental data and good agreement was obtained between the measurements and the conservative mixing plot of atrazine. For metolachlor an additional direct emission had to be modelled to explain the differences between the experimental data and the conservative mixing plot. For dichlorvos and simazine, on the other hand, an estuarine loss constant had to be included in the model. Using a least-squares procedure the estuarine loss constants for dichlorvos and simazine were estimated at half-lives of five and 26 days, respectively. Because mixing plots were strongly influenced by the time profiles of pesticide input, standard procedures in which net fluxes are calculated from mixing plots, were not applicable. Therefore, net fluxes were calculated with a newly developed procedure in which the estuarine loss constants and the estuarine flushing time were combined. For the non-conservative compounds dichlorvos and simazine, the net fluxes to the North Sea were found to be 96 and 64%, respectively, lower than the gross fluxes transported by the River Scheldt. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Pesticides; Fluxes; Estuarine losses; Modelling; Scheldt Estuary

1. Introduction

In agriculture a broad range of relatively polar pesticides is used. In recent years, many studies have shown that enhanced concentration levels of these pesticides are frequently encountered in fresh surface water,

drinking water and ground water (Brouwer et al., 1995; Meulenberg and Stoks, 1995; Louter et al., 1996; Planas et al., 1997). Considerably less work has been carried out with respect to the marine environment (Ahel et al., 1992; Readman et al., 1993). For a proper risk assessment of pesticides, information is needed on the fluxes to the marine environment and on their presence in marine ecosystems. In a previous study (Steen et al., 2001), the gross fluxes of some pesticides from the River Scheldt and the Canal Ghent-Terneuzen into the Scheldt Estuary were determined from 1995 to 1997 as part of the EU-Fourth Framework project *Fluxes of Agrochemicals into the Marine Environment* (FAME). A baseline study on the dissolved concentrations of the

---

* Corresponding author. Present address: Duinwaterbedrijf Zuid-Holland, PO Box 34, 2270 AA, Voorburg, The Netherlands. Tel.: +31-70-3577717; fax: +31-70-3577780.

E-mail address: r.steen@dzh.nl (R.J.C.A. Steen).

[1] Present address: Rijksinstituut voor Integraal Zoetwaterbeheer en Afvalwaterbehandeling, PO Box 17, 8200 AA Lelystad, The Netherlands.

herbicides simazine, atrazine, alachlor and metolachlor, and the insecticides dichlorvos and diazinon revealed strong variations in the freshwater sources which discharge into the Scheldt Estuary. The time profiles could often be related to agricultural application patterns (Steen et al., 2001). In order to obtain information on the estuarine behaviour of these pesticides, mixing plots, i.e. the relation between dissolved concentrations and salinity, were determined in April and June 1996 (Steen et al., 2001). It was demonstrated that care has to be taken in interpreting mixing plots of seasonally dependent pesticides in the Scheldt Estuary where the time scale of mixing is relatively large: during dry periods the residence time of fresh water inside the estuary may increase to up to 3 months (Wollast et al., 1988). To quote an example, the time profiles of the riverine concentration of simazine could not exclude that the observed curvature in the mixing plot was solely caused by estuarine losses. It was concluded that for a definite answer on the behaviour of simazine, model calculations had to be performed. In this paper, we present a new procedure to calculate net fluxes of pesticides by using a hydrological model of the Scheldt Estuary. The aims of the model calculations are: (1) to gain insight to which extent the mixing plot is influenced by temporal variations in riverine input; (2) to calculate the time scale of water transport through the estuar; (3) to calculate the estuarine losses of pesticides; and (4) to calculate the net fluxes to the North Sea.

2. Materials and methods

2.1. General

Several modelling environments have been used to simulate the movement of water masses within the Scheldt Estuary (Van Eck and De Rooij, 1990; Soetaert and Herman, 1996; Vuksanovic et al., 1996). These models are of a rather generic nature, i.e. they use long-term averaged data to predict water movement characteristics like, e.g. dispersion coefficients. In the present study, our main objective was to calculate mixing plots of pesticides, specifically for the months April and June 1996. Experimental mixing plots of pesticides were available for these months (Steen et al., 2001), enabling a comparison with the calculated mixing plots. Because of the specific rather than generic nature of the modelling exercise, dispersion coefficients were calculated from salinity profiles that were recorded during the simulation period, i.e. January 1995 through July 1996. Furthermore, actual freshwater loads and pesticide concentrations in the freshwater sources for the simulation period were included in the model. The influence of the temporal variations of pesticide input on the shape of the mixing plots will be studied by initially assuming

conservative behaviour of the pesticides. After comparison with the experimental data a first-order estuarine loss rate constant will be incorporated if estuarine losses are still evidently present. Both the magnitude of this process and the time scale of transport through the estuary, ultimately, determine the amounts of pesticide that reach the North Sea and, consequently, their net fluxes. We decided to construct the model for the Scheldt with the simulation shell EcoS^{TM} (version 3.0, Plymsolve, Plymouth, UK; Corley and Harris, 1997), because it is specifically designed to model the physical, chemical and biological dynamics of estuaries and its user interface allows a flexible definition of inputs of substances. Model calculations will be performed for a selected set of compounds, i.e. dichlorvos, simazine, atrazine and metolachlor. Selection was based on the availability of historical input data, i.e. the availability of concentration data for a period of at least 9 months preceding the sampling date of the mixing plot (Steen et al., 2001).

2.2. Model development

The average discharge of ca. 100 m^3 s^{-1} of the River Scheldt is strongly dominated by the large intertidal exchange volume of ca. 1 billion m^3 (Wollast et al., 1988). That is, the Scheldt Estuary is a well mixed estuary with relatively small vertical and lateral salinity differences compared with the longitudinal gradients (Wollast et al., 1988). Because of the low influence of the river flow on the total volume of the estuary, the tidally averaged cross-sectional area is considered to be constant in time. This allowed the use of tidally averaged simulations. The sectional homogeneity of the estuary allows the distribution of salt to be modelled with a 1-dimensional advection–dispersion equation proposed by Pritchard (1958):

$$\frac{\partial S}{\partial t} = \frac{\partial}{\partial x}(US) - \frac{\partial}{\partial x}\left(K_x \frac{\partial S}{\partial x}\right) \tag{1}$$

where S is the cross-sectional average salinity (g l^{-1}), U the longitudinal velocity (m day^{-1}), K_x the effective longitudinal dispersion coefficient (m^2 day^{-1}), t the time (day) and x the longitudinal distance from the head of the estuary (m).

Although, within ECoS, it is possible to simulate the longitudinal and vertical movement of suspended matter as well as the interaction between particulate matter and dissolved constituents, we decided to focus on the water phase. With the exception of diazinon, the relative contribution of the particulate concentration of the compounds of interest can be taken to be less than 1% of the total, suggesting that adsorption only plays a minor role in the distribution of these compounds in estuaries (Ahel et al., 1992).

2.3. Geometry and segmentation of the Scheldt Estuary

The total length of the estuary is 105 km which is divided by EcoS™ into 21 segments of 5 km each. Data on the geometry of the segments in the Scheldt Estuary (depth, width, cross-sectional area), were interpolated from data from the SAWES model (Van Eck and De Rooij, 1990) provided by the Dutch National Institute for Coastal and Marine Management (RIKZ) (Table 1). Fig. 1 shows a picture of the Scheldt Estuary with the segmentation of the model. Freshwater input is provided at the head of the estuary by the River Scheldt and from three additional tributaries: the Antwerp harbour docks (contains is a mixture of water from Lake Volkerak-Zoom and Canal Albert), the drain-canal at Bath and the Canal Ghent-Terneuzen which have average discharges of 14, 11 and 17 m^3 s^{-1}, respectively. The four freshwater sources constitute approximately 93% of the total freshwater load into the estuary. Discharge data were provided by RIKZ as 10-day-averages for the River Scheldt and as monthly averages for the tributaries.

2.4. Estimation of dispersion coefficients

Use of the advection–dispersion equation (Eq. 1) requires properly assigned values for the dispersion coefficients. There are several methods for predicting the dispersion coefficients in estuaries. In the method described by Deyer (1973), dispersion coefficients are calculated from measured salinity gradients. The method is based on the assumption that the salinity gradients reflect an approximate steady-state balance of flow and dispersion. After integrating once with respect to x and assuming steady state ($\delta S/\delta t = 0$), Eq. 1 reduces to:

$$K_x = \frac{U \cdot S}{(\partial S/\partial x)} \quad (2)$$

Consequently, K_x can be calculated for any position in an estuary if the longitudinal velocity, U, and the salinity gradient along the estuary are known. U can be found by dividing the total freshwater input above the point in question, Q (m^3 day^{-1}), by the cross-sectional area, A (m^2) of the estuary at that point. For the Scheldt, salinity gradients in the period from May 1995 until July 1996 were recorded monthly by RIKZ. The inherent variability in the salinity profiles requires that the data set should be smoothed prior to the calculation of K_x (Soetaert and Herman, 1996). Therefore, the salinity profiles were fitted with a fourth-degree polynome leading to the following expression for K_x:

$$K_x = \frac{Q \cdot (b_4 x^4 + b_3 x^3 + b_2 x^2 + b_1 x + b_0)}{A \cdot (4b_4 x^3 + 3b_3 x^2 + 2b_2 x + b_1)} \quad (3)$$

where b_0–b_4 are the coefficients of the fourth-degree polynome.

2.5. Calculation of flushing times

The flushing time of an estuary is defined as the time required to replace the existing freshwater in the whole estuary or any segment of it, at a rate equal to the river discharge. It determines the time scale of water transport through the estuary and, therefore, the time available for chemical or physical transformations of dissolved compounds. There are several methods to estimate estuarine flushing times (Deyer, 1973; Officer, 1976; Helder and Ruardij, 1982; Takeoka, 1984; Miller and McPherson, 1991; Soetaert and Herman, 1996). The 'fraction-of-freshwater method' requires knowledge of the geometry of the estuary, the freshwater flow, and the salinity distribution within the estuary (Deyer, 1973; Helder and Ruardij, 1982). The latter is provided by the model and the fraction of freshwater in any segment is given by:

$$f_n = \frac{S_{sea} - S_n}{S_{sea}} \quad (4)$$

where S_{sea} is the salinity of the undiluted sea water and S_n the mean salinity in a given segment, n, of the estuary. The flushing time, t_n, of any segment is given by:

$$t_n = \frac{V_n \cdot f_n}{Q} \quad (5)$$

Table 1
Geometry of the Scheldt Estuary

| Segment no.	Distance from head (km)	Depth (m)	Width (m)	Cross-sectional area (m^2)
1	2.5	9.0	380	3400
2	7.5	9.6	390	3690
3	12.5	10.3	400	4160
4	17.5	9.6	520	4970
5	22.5	9.5	620	5890
6	27.5	10.0	710	7070
7	32.5	9.2	950	8780
8	37.5	8.1	1340	10770
9	42.5	8.0	1820	14560
10	47.5	7.1	2480	17620
11	52.5	6.7	2640	17630
12	57.5	8.8	2450	21550
13	62.5	10.6	2880	30470
14	67.5	9.0	5160	46640
15	72.5	9.7	4640	44770
16	77.5	10.5	4310	45350
17	82.5	11.7	4040	47200
18	87.5	12.5	4110	51490
19	92.5	13.2	4310	56670
20	97.5	13.8	4490	61850
21	102.5	14.4	4670	67030
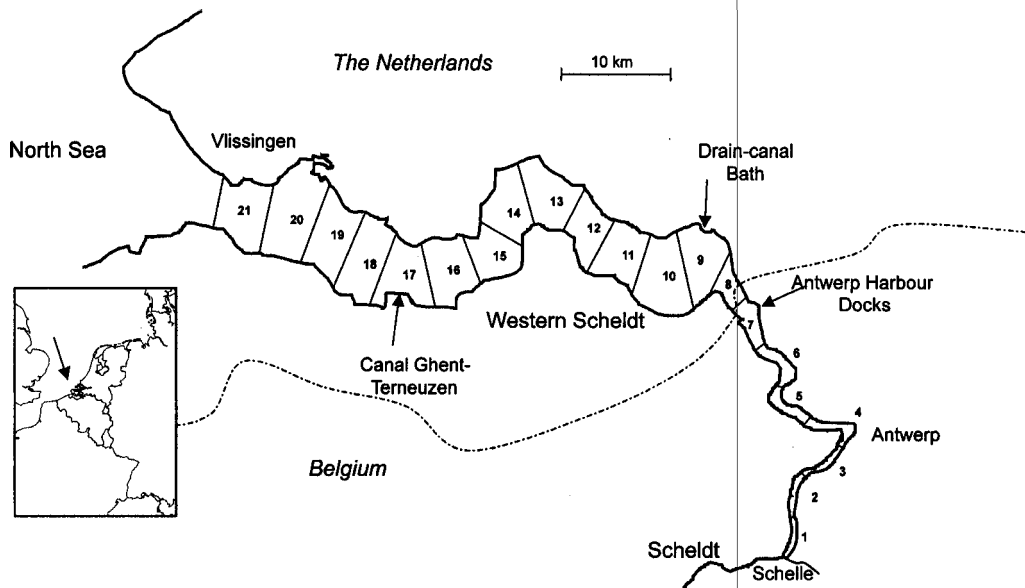
Fig. 1. Map of the Scheldt Estuary with the ECoS division into 21 segments.

where V_n is the volume of the segment and Q the flow rate of the river. The nominal flushing time of the entire estuary, $t_{estuary}$, is calculated by adding up the flushing times of all 21 segments on the same day. $t_{estuary}$ represents the situation on that particular day; due to deviations from steady state, it does not represent the time a freshwater parcel needs to leave the estuary.

2.6. Calculation of net fluxes

In an earlier study, we determined the gross fluxes of pesticides transported by the River Scheldt into the Scheldt Estuary (Steen et al., 2001). The gross flux is defined as the product of the mean river flow, Q, and the flow-weighted mean riverine pesticide concentration. The amount of dissolved pesticides that ultimately reaches the North Sea depends on the rate at which the pesticide is chemically or physically transformed within the estuary and the time which is available for these transformations, i.e. the estuarine flushing time. Estuarine losses can be calculated from the curvature of the mixing plots, as was demonstrated by Boyle et al. (1974). In a simplified approach proposed by Officer (1979), the effective concentration that reaches the sea is calculated through extrapolation to $S = 0$ from a linear regression line that is fitted through data points in the high-salinity region of the estuary. Both authors emphasized that their models and procedures are only valid if the concentration of the compounds of interest and the freshwater flow at the river-end-member remain constant within the time scale of mixing in the estuary (flushing time). In this study, we are faced with relatively strong temporal variations in pesticide input, and relatively long flushing times of the Scheldt. As will be

shown later, both aspects strongly affect the shape of the mixing plots, which means that the above mentioned procedures are less suitable for our task.

In this study, the net fluxes to the sea were calculated by converting the riverine concentrations, C_{river}, to concentrations that effectively reach the sea, $C_{effective}$, by means of the following equation:

$$C_{effective} = C_{river} \cdot e^{-k \cdot t_{estuary}} \qquad (6)$$

where k is the overall first-order estuarine loss constant calculated from by the model (see below). Again, use of the nominal value of $t_{estuary}$, presupposes that the system is in a steady state, which is a requirement that is not often met because fluctuations of freshwater flow occur within the time-span of the flushing time. However, as will be shown later, the imprecision of k is relatively large compared with errors which may be introduced by deviations from the steady state situation.

Finally, k was calculated from the experimental mixing plots by means of a procedure based on minimising the sum of squares. A local estimate of the variance of the calculated value of k is then obtained through the Jacobian matrix (J) which is defined as the derivative of all residuals to k (Eq. 7):

$$\text{Var}(\hat{k}) = \sigma^2 \cdot \left[J(\hat{k})^T \cdot J(\hat{k}) \right]^{-1}$$

with

$$\sigma^2 \approx s^2 = \frac{\sum_{j=1}^{N} \left(C_{measured,\, j} - C_{predicted,\, j} \right)^2}{(N-1)} \qquad (7)$$

Effectively, s^2 is the sum of squares divided by the degrees of freedom (Draper and Smith, 1981).

3. Results and discussion

3.1. Validation of hydrological model

The dispersion coefficients, which were calculated from Eq. 3, are shown in Fig. 2 for river discharges of 40 and 107 m^3 s^{-1}. These values represent low and high freshwater discharge conditions for the simulation period which had an average flow of 70 m^3 s^{-1}. The calculated dispersion coefficients agree with values reported by Soetaert and Herman (1996) who found K_x values ranging from 200 to 300 m^2 s^{-1} close to the Dutch-Belgian border. Good agreement was also found with values reported by Vuksanovic et al. (1996) who based their calculations on a 'physically based formula' rather than experimental salinity profiles. Their values ranged from 150 to 300 m^2 s^{-1} for the Scheldt Estuary. The validity of the calculated dispersion coefficients and the hydrological model as a whole was further evaluated by comparing the predicted salinity profiles and the experimental data from different cruises (Fig. 3). The agreement is seen to be highly satisfactory under both high and low freshwater discharge conditions. Rather distinct differences in salinity profiles were observed during the simulation period. The profiles of May 1995 ($Q = 112$ m^3 s^{-1}) and February 1996 ($Q = 107$ m^3 s^{-1}) demonstrate that the intrusion of salt is reduced under relatively high discharge conditions, as is indicated by the strong curvature in the low salinity zone. At lower flows the curvature of the profiles is reduced and for example, August 1995 ($Q = 40$ m^3 s^{-1}) an almost linear relationship between salinity and distance is found.

3.2. Flushing times

The flushing time of each segment in the model for the period May 1995–June 1996 was calculated according to Eqs. (4) and (5). Fig. 4 shows the results for a low and high freshwater discharge situation. The largest flushing times are found between segments nine and 17 ($x = 40-85$ km) and the dip occurring in segment 11 ($x = 50-55$ km) is caused by its relatively small depth and, consequently, rather small volume (V_n in Eq. 5). As is to be expected on the basis of Eq. 5, the flushing time increases at lower freshwater discharges. Fig. 5 shows that the nominal flushing time of the total estuary varies substantially throughout the year and the insert illustrates that this is due to variations in freshwater discharge. The dependence of flushing time on river discharge was also reported by Helder and Ruardij (1982), viz. for the Ems-Dollard Estuary. In the present instance, the relationship between the reciprocal freshwater discharge and the nominal flushing time is linear. The rather high correlation coefficient, R^2, of 0.93 ($n = 42$) is a further indication that the salinity profiles under different flow conditions are correctly predicted and that the segmentation is sufficiently refined. The flushing times calculated with the fraction-of-freshwater method agree with values reported by Soetaert and Herman (1996) who found flushing times of 50 and 70
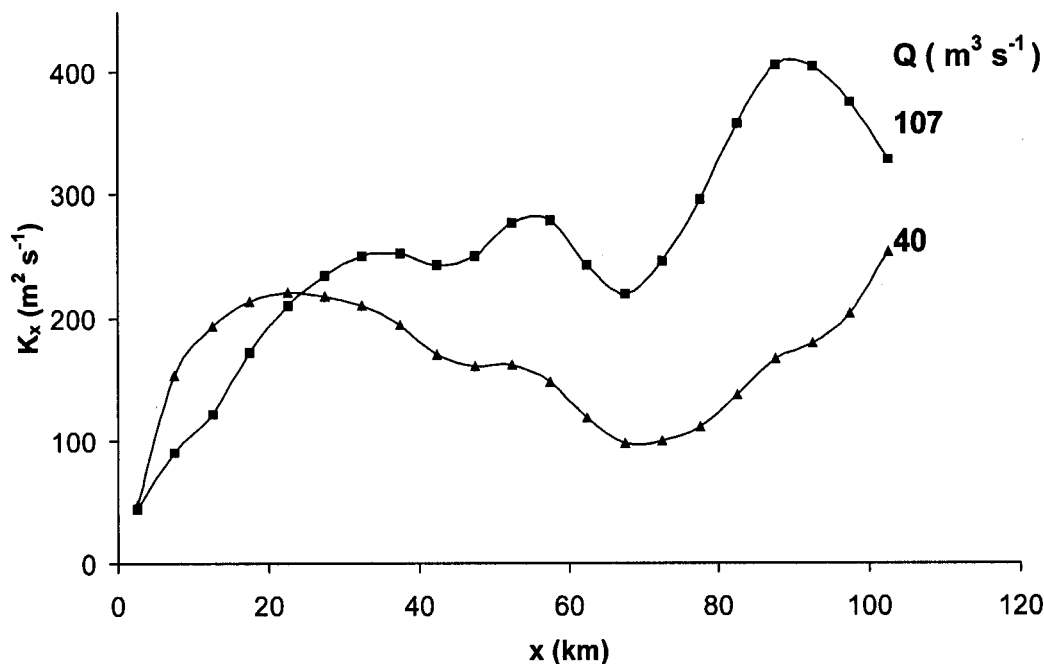

Fig. 2. Dispersion coefficients, K_x, along the Scheldt Estuary for a river discharge of 40 and 107 m^3 s^{-1}; x = distance from Schelle (km).
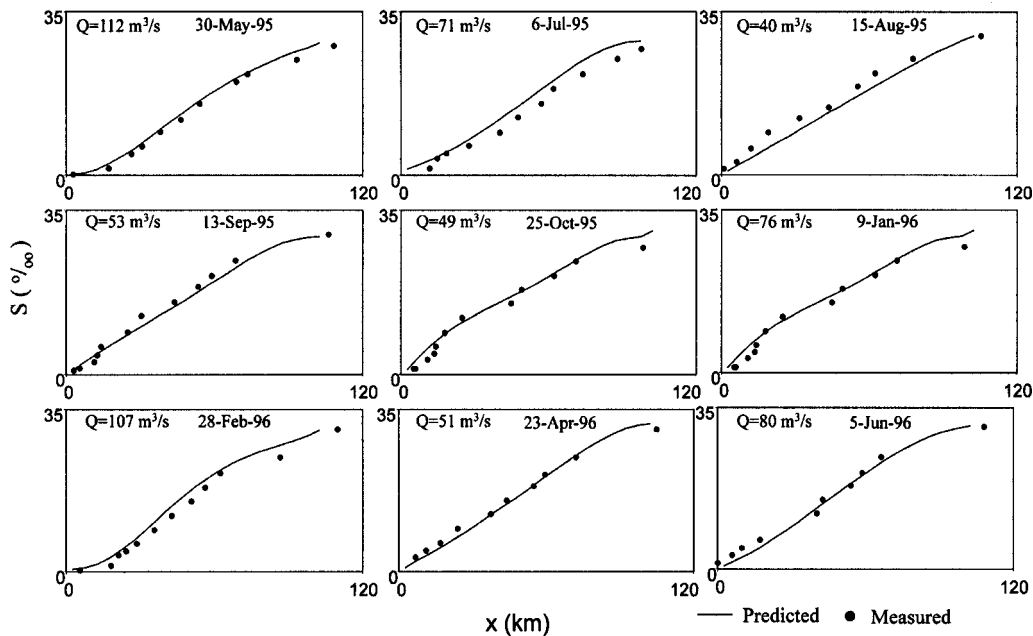
Fig. 3. Predicted and measured salinity profiles for different hydrological conditions during the simulation period in the Scheldt Estuary at nine different days in 1995 and 1996.

days for a winter and summer scenario, respectively, using a generic box model with fixed dispersion coefficients. The values are also in agreement with the general relation between estuarine length and flushing time described by Morris (1990), who estimates that the flushing time of an estuary with a length of 105 km will be between 20 and 100 days.

3.3. Prediction of estuarine loss constant

The agreement between calculated and experimental salinity profiles, calculated dispersion coefficients, and flushing times with values reported in the literature, demonstrate that our model can correctly describe the mixing of water masses in the Scheldt Estuary. Subsequently, the model was used to evaluate the influence of the temporal variations in riverine pesticide input on the shape of the mixing plot of pesticides. Initially, the mixing plots were calculated by assuming conservative behaviour, i.e. no estuarine losses, of the pesticides. Fig. 6 clearly shows that the shape of the mixing plots (solid lines) varies between pesticides and also between dates. The mixing plots of dichlorvos, for example, reveal a slightly convex curve for April 1996 as against a concave curve for June 1996. This demonstrates that, even if a pesticide behaves conservatively, deviations from a linear mixing curve may occur. For dichlorvos and simazine, the experimental data are lower than the predicted conservative mixing plots which indicates that estuarine losses do occur. On the other hand, the measurements and the conservative mixing plot of atrazine show a close agreement.

A convex curve is found for the predicted conservative mixing plot of metolachlor (note the different scale on the X-axis). This is caused by a rather high concentration peak in the River Scheldt in the period preceding the sampling date (Steen et al., 2001). However, the strong concentration increase for the measured data around a salinity of 15‰ cannot be explained; this indicates that there is an additional source of metolachlor. The possibility that metolachlor was released from sediment or suspended matter was rejected because the concentration increase around a salinity of 15‰ was only found in the period from January to September 1996 and desorption processes are not expected to vary substantially throughout the year. To assess the magnitude of the additional source of metolachlor we simulated an additional input from the drain-canal at Bath. The simulated concentration in the canal water was varied from 20 to 40 µg/l in steps of 5 µg/l. A best fit was obtained for a concentration of 25 µg/l (dashed line in Fig. 6). Further evidence that the increase is caused by an incidental additional source rather than desorption was found in a follow-up study in which no convex curvature was found in the mixing plot of metolachlor. (Steen et al., 2000).

To calculate the extent of losses within the estuary, a first-order loss constant, k, was included in the model. The value of k was varied in subsequent model simulations and the 'optimal' value was estimated by a least-squares procedure. The results are summarised in Table 2 and the mixing plots, calculated with the 'optimal' values of k, are included in Fig. 6 (dashed lines). Next to the non-conservative compounds dichlorvos
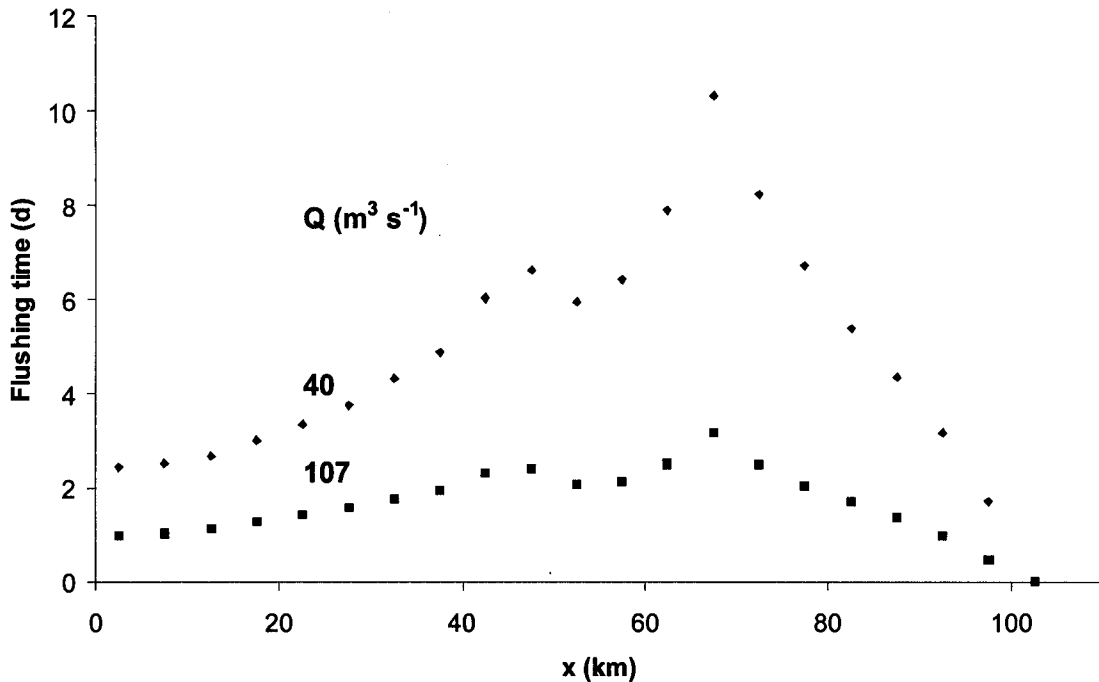
Fig. 4. Flushing time for each model segment along the Scheldt Estuary for a high (107 m³ s⁻¹) and a low (40 m³ s⁻¹) river discharge; x = distance from Schelle (km).

and simazine, atrazine was also assigned a loss constant. One can then evaluate the ability of the model to distinguish between conservative and non-conservative behaviour or, in other words, one can assess which values of k are significantly different from zero.

The standard deviations and, subsequently, the ranges in the calculated values of k were calculated by means of Eq. 7 and the results are shown in Table 2. The relatively large ranges are probably caused by model assumptions (e.g. losses are assumed to be first-order processes) rather than measurement uncertainties, as relative standard deviations of the analytical method are less than 8% (Steen et al., 1997). For dichlorvos, similar estuarine loss constants were found for both sampling dates and for simazine; the overlap in the ranges show that the difference between the loss constants for both dates are not significant. Conservative behaviour is found for atrazine. However, due to model uncertainties, a k value of 0.0014 and, consequently, a half-life of 490 days, still lies within the calculated range.

3.4. Estimation of net fluxes

For each pesticide considered in this study the effective concentration that ultimately reaches the North Sea was calculated from Eq. 6. Next, the net fluxes were calculated by multiplying the flow-weighted mean effective concentrations by the mean annual flow (Walling and Webb, 1985; Steen et al., 2001). In Table 3, the gross fluxes as determined in a previous study (Steen et al., 2001) and the net fluxes for the period March 1996–March 1997 are compared. Using the first-order loss constants and flushing times provided by the model, the corrected gross fluxes, i.e. the gross fluxes at the river-end-member (Schelle) were calculated from the fluxes determined at the Dutch–Belgian border by taking dilution and losses during transport from Schelle to the border (segment eight) into account. As the data of Table 3 show, due to the non-conservative behaviour of dichlorvos and simazine the amounts of those pesticides that reach the North Sea are reduced by 96 and 64%, respectively.

Eq. 6 was used to calculate net fluxes rather than a procedure in which the pesticide concentration at the mouth of the estuary (Vlissingen) is multiplied by the tidally averaged total volume leaving the estuary. With the latter procedure the calculations are based on one model segment only which, moreover, is biased by the boundary conditions chosen for the mouth of the estuary (salinity and pesticide concentration of seawater). Another advantage of using the estuarine flushing time to calculate net fluxes is that $t_{estuary}$ can be derived from readily available river discharge data using the relation presented in Fig. 5. Once the estuarine loss constants have been determined, the net fluxes can be calculated in future studies without the use of a hydrological model.

By using flushing times, a dynamic aspect is included into the calculation of net fluxes. It is, therefore,
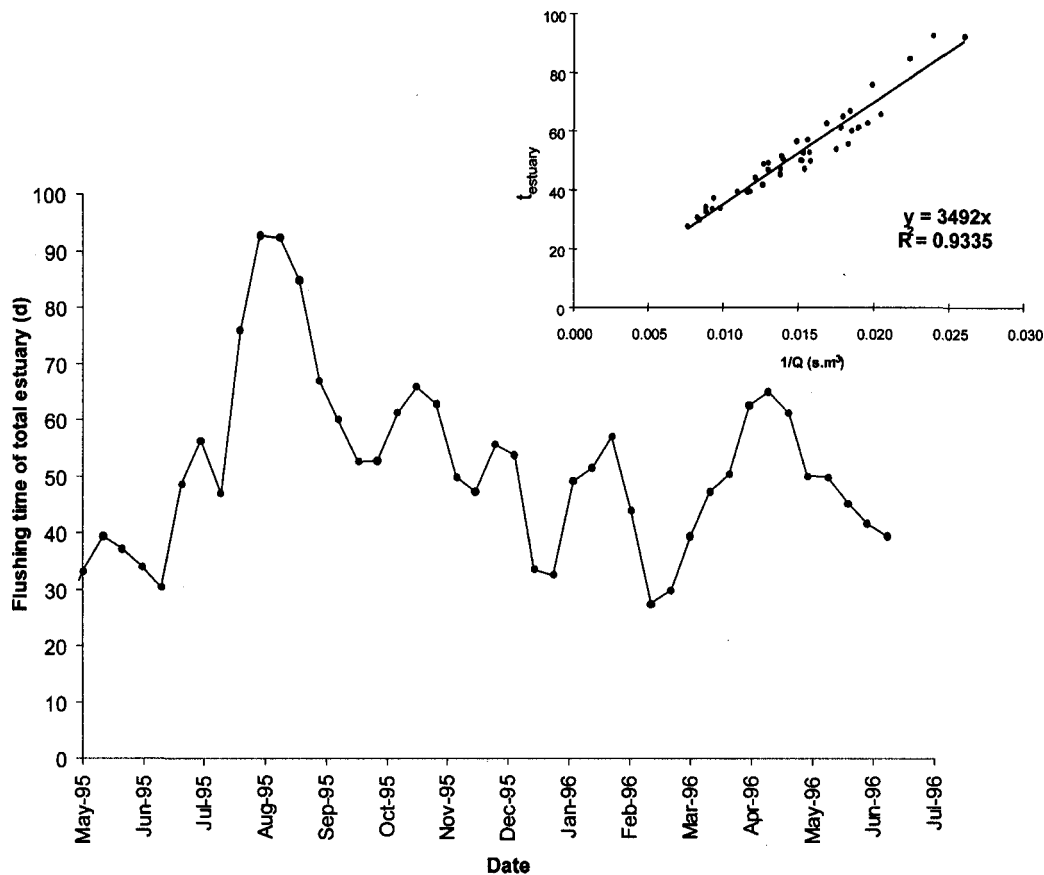
Fig. 5. Nominal flushing time (d) of the entire Scheldt Estuary at different dates during 1995 and 1996. The insert shows the linear relationship between reciprocal river discharge and nominal flushing time in the Scheldt Estuary during 1995 and 1996.

Table 2
First-order estuarine loss constant (k) and half-life ($t_{1/2}$) of three pesticides in the Scheldt Estuary in April and June 1996

Pesticide	Month	Optimal k (day^{-1})	Range[a] (day^{-1})	$t_{1/2}$ (day)	Range* (day)
Dichlorvos	April	0.14	(0.11–0.17)	5	(4.2–6.1)
	June	0.14	(0.10–0.18)	5	(3.9–7.0)
Simazine	April	0.023	(0.014–0.063)	30	(22–49)
	June	0.031	(0.009–0.053)	23	(13–75)
Atrazine	April	0	(0–0.0014)	∞	(490–∞)

[a] Range is defined as k value ± standard deviation.

interesting to briefly consider the relation between flushing time and pesticide concentration. In general, freshwater discharge of the Scheldt decreases during the spring and summer because discharge is controlled by the amount of rainfall in the catchment area. In the same period, pesticide concentrations increase due to agricultural application (Steen et al., 2001). In the case of non-conservative pesticides, the filtering function of the estuary becomes more important in this period, because relatively high riverine concentrations coincide with longer flushing times of the estuary and, consequently, longer periods which are available for estuarine loss processes.

4. Conclusions

A hydrological model of the Scheldt Estuary was constructed based on a one-dimensional advection–dispersion equation with dispersion coefficients calculated from salinity profiles. The model can correctly predict the movement of water masses and the times scales of mixing within the estuary at different river discharges. Model calculations demonstrated that the application-related time profiles of pesticide input may well induce curvature in the estuarine mixing plot even if a pesticide behaves conservatively. Conclusions on the estuarine behaviour of pesticides should, therefore, be
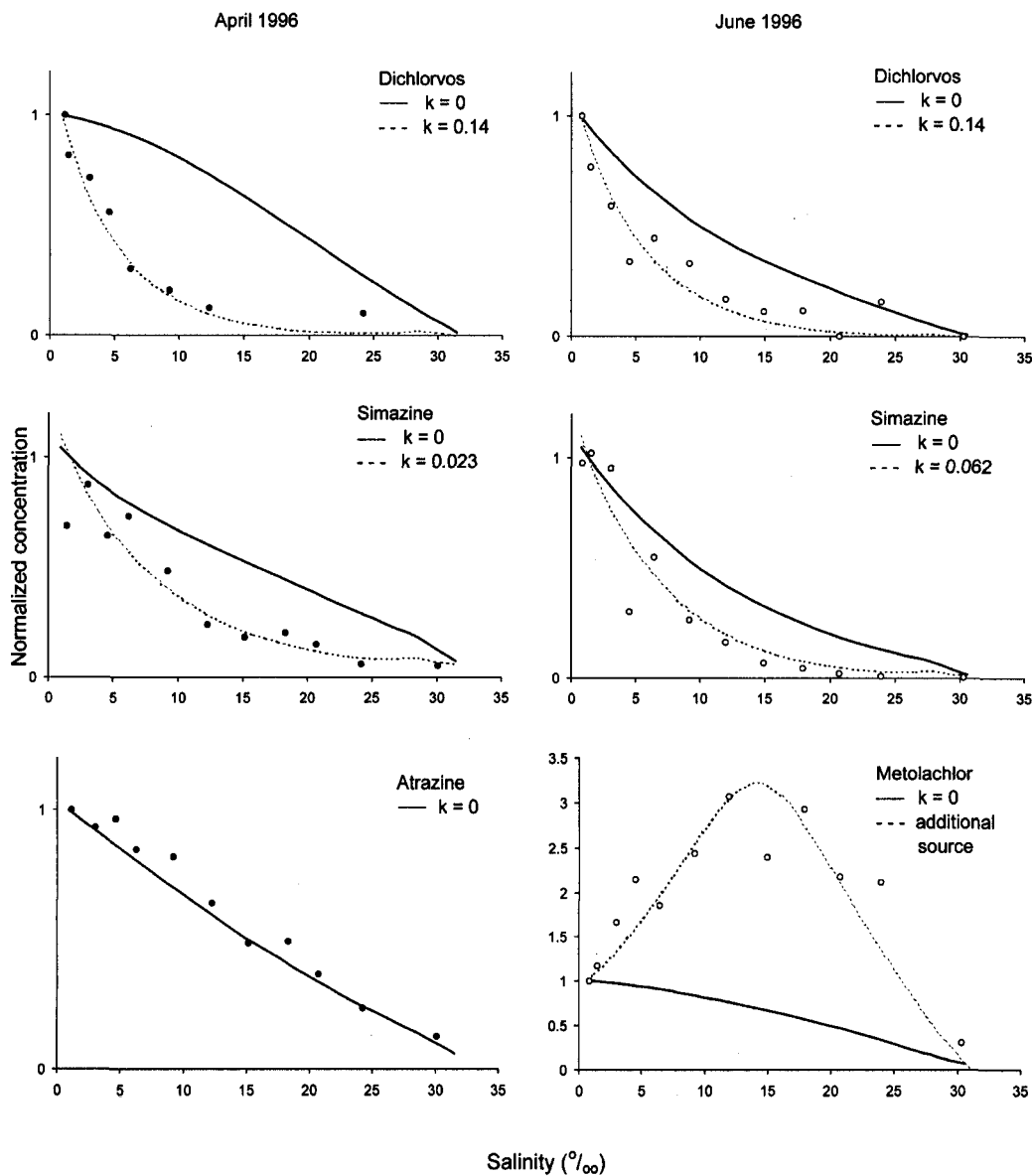
Fig. 6. Experimental (●, April 1996, ○, June 1996) and calculated mixing plots of some pesticides in the Scheldt Estuary. —, conservative behaviour; - - -, calculation with 'optimal' k (see text).

Table 3
Fluxes of four pesticides from the Scheldt to the North Sea in the period March 1996–March 1997

Compound	'Gross' flux[a] (kg year^{-1})	Corrected gross flux[b] (kg year^{-1})	$t_{1/2}$ (day)	Net flux (kg year^{-1})	Percentage of loss in estuary
Dichlorvos	39	150	5	6	96
Simazine	750	1400	26	510	64
Atrazine	803	1090	∞	1090	0
Metolachlor	805	740[c]	∞	1130	0

[a] Fluxes determined for the Scheldt at Dutch–Belgian border in the period March 1996–March 1997 (Steen et al., 2001).

[b] Fluxes estimated for the Scheldt at river-end-member Schelle; fluxes are corrected for dilution and losses during transport from Schelle to Dutch–Belgian border (for details, see Steen et al., 2001).

[c] Flux of metolachlor is also corrected for the additional input at Bath (390 kg), as estimated by the model.

based on the combined interpretation of mixing plots and time profiles of pesticide input. Quantification of any estuarine losses of pesticides should be performed by means of model calculations rather than the more straightforward and frequently used methods reported in the literature (Boyle et al., 1974; Officer, 1979). These methods require that contaminant input remains relatively constant within the time scale of mixing which is, as we have shown, not the case for many pesticides. In this study, net fluxes were calculated using a procedure in which the estuarine loss constants and the estuarine flushing times were combined. As a result, the enhanced filtering function of the estuary during spring and summer is taken into account which is based on the combined phenomena of longer flushing times (i.e. larger estuarine losses) and elevated pesticide concentrations.

References

Ahel, M., Evans, K.M., Fileman, T.W., Mantoura, R.F.C., 1992. Determination of atrazine and simazine in estuarine samples by high-resolution gas chromatography and nitrogen selective detection. Analytica Chimica Acta 268, 195–204.

Boyle, E., Collier, R., Dengler, A.T., Edmond, J.M., Ng, A.C., Stellard, R.F., 1974. On the chemical mass-balance in estuaries. Geochimica et Cosmochica Acta 38, 1719–1728.

Brouwer, E.R., Kofman, S., Brinkman, U.A.Th., 1995. Selected procedures for the monitoring of polar pesticides and related microcontaminants in aquatic samples. Journal of Chromatography A 703, 167–190.

Corley, R.N., Harris, J.R.W., 1997. ECoS 3: User Guide. Natural Environment Council, Plymouth Marine Laboratory, Plymouth, UK.

Deyer, K.R., 1973. Estuaries: A Physical Introduction. John Wiley, London, UK.

Draper, N.R., Smith, H., 1981. Applied Regression Analysis, 2nd Edition. John Wiley, New York, NY, USA.

Helder, W., Ruardij, P., 1982. A one-dimensional mixing and flushing model of the Ems-Dollard Estuary: calculation of time scales at different river discharges. Netherlands Journal of Sea Research 15, 293–312.

Louter, A.J.H., Vanbeekvelt, C.A., Montanes, P.C., Slobodnik, J., Vreuls, J.J., Brinkman, U.A.Th., 1996. Analysis of microcontaminants in aqueous samples by fully automated on-line solid-phase extraction-gas chromatography-mass selective detection. Journal of Chromatography A 725, 67–83.

Meulenberg, E.P., Stoks, P.G., 1995. Water quality control in the production of drinking water from river water — the application of immunological techniques for the detection of chlorophenoxy acid herbicides (2,4-D). Analytica Chimica Acta 311, 407–413.

Miller, R.L., McPherson, B.F., 1991. Estimating estuarine flushing and residence times in Charlotte Harbor, Florida, via salt balance and box model. Limnology and Oceanography 36, 602–612.

Morris, A.W., 1990. Kinetics and equilibrium approaches to estuarine chemistry. Science of the Total Environment 97/98, 253–266.

Officer, C.B., 1976. Physical Oceanography of Estuaries (and Associated Coastal Waters). John Wiley, New York, NY, USA.

Officer, C.B., 1979. Discussion of the behaviour of nonconservatieve dissolved constituents in estuaries. Estuarine and Coastal Marine Science 9, 91–94.

Planas, C., Caixach, J., Santos, F.J., Rivera, J., 1997. Occurrence of pesticides in Spanish surface waters — analysis by high resolution gas chromatography coupled to mass spectrometry. Chemosphere 34, 2393–2406.

Pritchard, D.W., 1958. Salt balance and exchange rate for Chincoteague Bay. Journal of Marine Research 17, 412–423.

Readman, J.W., Albanis, T.A., Barcelo, D., Galassi, S., Tronczynski, J., Gabrielides, G.P., 1993. Herbicide contamination of Mediterranean estuarine waters: results from a MED POL pilot survey. Marine Pollution Bulletin 26, 613–619.

Soetaert, K., Herman, P.M.J., 1996. Estimating estuarine residence times in the Westerschelde (The Netherlands) using a box model with fixed dispersion coefficients. Hydrobiologia 311, 215–224.

Steen, R.J.C.A., Freriks, I.L., Cofino, W.P., Brinkman, U.A.Th., 1997. Large-volume injection in gas chromatography-ion trap tandem mass spectrometry for the determination of pesticides in the marine environment at the low ng/l level. Analytica Chimica Acta 353, 153–163.

Steen, R.J.C.A., Van Hattum, B., Brinkman, U.A.Th., 2000. A study on the estuarine behaviour of pesticides and their transformation products in the Scheldt Estuary using liquid chromatography-electrospray tandem mass spectrometry. J. Environ. Monit 2, 597–602.

Steen, R.J.C.A., Van der Vaart, J., Hiep, M., Van Hattum, B., Cofino, W.P., Brinkman, U.A.Th., 2001. Gross fluxes and estuarine behaviour of pesticides in the Scheldt Estuary (1995–1997). Environmental Pollution, (accepted for publication).

Takeoka, H., 1984. Fundamental concepts of exchange and transport time scales in a coastal sea. Continental Shelf Research 3, 311–326.

Van Eck, G.Th.M., De Rooij, N.M., 1990. Development of a water quality and bio-accumulation model for the Scheldt Estuary. In: Michaelis, W. (Ed.), Coastal and Estuarine Studies. Springer Verlag, Berlin, Germany.

Vuksanovic, V., De Smet, F., Van Meerbeeck, S., 1996. Transport of polychlorinated biphenyls (PCB) in the Scheldt Estuary simulated with the water quality model WASP. Journal of Hydrology 174, 1–18.

Walling, D.E., Webb, B.W., 1985. Estimating the discharge of contaminants to coastal waters by rivers: some cautionary comments. Marine Pollution Bulletin 16, 488–492.

Wollast, R., Salomons, W., Bayne, B.L., Duursma, E.K., Forstner, U. (Eds.), 1988. Pollution of the North Sea. Springer-Verlag, Berlin Heidelberg, Germany.